Lithium Resources and Requirements by the Year 2000

GEOLOGICAL SURVEY PROFESSIONAL PAPER 1005

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JAMES D. VINE, Editor

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INTRODUCTION

By James D. Vine,
U.S. Geological Survey, Denver, CO

An assessment of the mineral resources within our nation's borders is a continuing responsibility of the U.S. Geological Survey; it is continuing because there is never a final answer. While mineral resources are not renewable, neither are they static. An assessment of a mineral commodity is a function of the adequacy of the data base, economic factors that influence demand, technologic changes, and ingenuity applied to the discovery and definition of commercially extractable material, as well as, the accuracy of measurements applied to the dimensions and grade of material to be extracted. When a recent reassessment of United States lithium resources and a comparison with potential demand suggested a possible depletion of known resources much sooner than previously indicated, the decision was made to sponsor a symposium which would bring these facts to light. Possible participants were contacted from Foote Mineral Company, Gulf Resources and its subsidiary, Lithium Corporation of America, Kerr-McGee Chemical Corporation, the U.S. Geological Survey, several state geologists, U.S. Bureau of Mines, U.S. Energy Research and Development Administration, Lawrence Livermore Laboratory, Argonne National Laboratory, and Brookhaven National Laboratory. The participants represented the lithium producing industry, government specialists on the reserves, resources, and geologic occurrence of lithium, and the sponsors and contractors involved in the design and testing of new energy-related applications for lithium in batteries and in thermonuclear power. When it became apparent that there were enough potential participants to address the problem of resources and requirements, a tentative program was formulated and a date set for the symposium. It became apparent that interest was not limited to those who had been asked to participate, and invitations were extended to many others who expressed interest in attending the symposium. Although not widely advertised because of the time limitation, the symposium attracted nearly 150 participants and observers from the United States, Canada, Great Britain, and Rhodesia.

A noteworthy difference of opinion between the participants from industry and the government specialists regarding the gravity of the impending shortage of lithium forecast by representatives from the U.S. Geological Survey developed. Representatives from industry were united in their opinion that the potential increased demand for lithium suggested by the engineers working on the development of batteries suitable for electric vehicles could be met. This difference of opinion is emphasized because only the prepared papers are contained here, and there is no record of the ensuing discussions that are an essential part of a symposium. (See Hammond, 1976.)

This symposium was the first of its kind for lithium and unique in having brought together specialists from such diverse points of view. The benefits far outweighed the concern of a few participants who felt that too much emphasis and publicity were placed on the forecast of a shortage of lithium. The forecast itself can best be judged from hindsight, a task for some future symposium.

The arrangement of the papers in this volume is similar to the order of presentation at the symposium, beginning with papers dealing with potential new energy-related uses for lithium in batteries and fusion power. These are followed by papers dealing with the lithium industry, lithium resources, and finally the geology and geochemistry of lithium, geophysical exploration techniques, computer applications of resource data, and chemical analytical technique.

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BATTERY RESEARCH SPONSORED BY THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION[1]

ALBERT A. LANDGREBE, ENERGY RESEARCH and DEVELOPMENT ADMINISTRATION,
WASHINGTON, DC, and PAUL A. NELSON, ARGONNE NATIONAL LABORATORY, ARGONNE, IL

ABSTRACT

An important part of the Energy Storage Program of the U.S. Energy Research and Development Administration is the development of storage batteries for loadleveling on electric utilities and automotive propulsion, and for application to new energy generating systems. The successful development of batteries for these purposes will provide significant savings of oil resources and will also have beneficial environmental effects. A very high manufacturing volume may be required for these batteries, and the availability of the required raw materials is an important consideration. Lithium-aluminum/iron sulfide batteries show promise both for utility energy storage batteries and electric vehicle batteries, and serious consideration should be given by the lithium industry to the availability of lithium resources.

INTRODUCTION

The primary goal of the Energy Storage Program of the U.S. Energy Research and Development Administration (ERDA) is to develop energy storage techniques that will have the most favorable impact on U.S. energy systems, in terms of resources, environment, and economics. Investigations are being directed toward developing safe and economical storage devices for storing heat or electrical energy generated from nuclear fuel, coal, or solar energy, which are plentiful sources. Such storage devices are needed for electric utilities, advanced automotive systems, and other residential, commercial, and industrial applications. The storage devices developed for these applications would replace systems that now use petroleum or natural gas, which are in short supply. For many of these applications energy is stored most conveniently as electric energy in storage batteries. This paper describes the programs now in progress on developing these batteries and the justification for these programs. Some of these programs are a continuation of work started by the Division of Applied Technology of the U.S. Atomic Energy Commission. However, most of the programs are new, and a considerable increase has been made in funding over the levels of fiscal years 1974 and 1975.

ENERGY CONSUMPTION IN THE UNITED STATES

Within the past quarter of a century, significant changes have occurred in the mix of fuels in the U.S. The fraction of total fuel supplied by coal has decreased from 38 percent in 1950 to a level of 18 percent in 1974, in spite of the fact that the coal input to the rapidly growing electrical sector has tripled during this interval. To some extent, coal has been displaced by a cheaper, cleaner, and far more convenient-to-use form of energy, namely, natural gas, which has experienced a fivefold increase in usage during the last 25 years. In this interval, the fraction of the total national fuel mix supplied by natural gas has increased from 18 to 33 percent. At the same time, reliance on oil in the U.S. has generally grown at about the same rate as the total energy demand. Within the past few years, oil consumption has grown at an average rate of 6 percent per year. The changing pattern of consumption of energy resources in the recent past is shown in table 1.

The energy consumption in the U.S. in 1972 was 72×10^{15} Btu. The forecast for energy consumption in 1985 is 105×10^{15} Btu, and that for longer-term consumption (for the year 2000) is 162×10^{15} Btu. The values in table 2 show the domestic supply for each major energy source in selected years, along with the total energy consumption for those same years, and by difference the energy shortfall. The latter values represent the amounts that will have to be satisfied by imported fuels or by some method of rationing if energy conservation measures are not adopted.

OIL SAVINGS BY MEANS OF ENERGY STORAGE

At the present time, most utilities use gas turbines as the major source of peaking power. These devices are low in capital cost, but they are expensive to operate;

TABLE 1.—*United States consumption of energy resources by major sources*[1]

	10^{15} Btu		
	1950	1960	1970
Petroleum	13.489	20.067	29.614
Natural gas	6.150	12.699	22.029
Coal	12.913	10.140	12.922
Hydro	1.440	1.657	2.650
Nuclear	--	.006	.229
Total primary energy	33.992	44.569	67.444

[1] Dupree and West, 1972.

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[1] Work performed under the auspices of the Assistant Administrator for Conservation Energy Research and Development Administration.

TABLE 2.—*United States energy shortfall*[1]

	10^{15}Btu				
	1971	1975	1980	1985	2000
Domestic supply:					
Natural gas	21.810	22.640	22.960	22.510	22.850
Petroleum	22.569	22.130	23.770	23.600	21.220
Coal	12.560	13.825	16.140	21.470	31.360
Hydro	2.833	3.570	3.990	4.320	5.950
Nuclear	.391	2.560	6.720	11.750	49.230
Total	60.163	64.725	73.580	83.650	130.610
Domestic consumption	68.728	80.265	90.075	105.300	162.450
Shortfall to be satisfied by imports	8.656	15.540	16.495	21.650	31.840
(10^6 bbl oil)	(1,546)	(2,775)	(2,946)	(3,866)	(5,686)

[1] Dupree and West, 1972; Hoffman, Beller and Doernberg, 1975.

TABLE 3.—*Energy storage research and development program.*

Program	Program goals	Projected annual savings of imported oil, 10^6 bbl/yr 1985	2000	Total research, costs, $$10^6$
1. Energy storage for electric utilities	Reduce oil consumption in gas turbines by 80 percent in the year 2000,[a] reduce requirements for new transmission facilities by 10 percent.	39[b]	681	300
2. Advanced energy storage for automotive applications.	Introduce 22.5 million electric and hybrid vehicles into the transportation sector by 2000.	3	120	45[c]
3 Industrial applications.	Reduce fossil fuel (oil and gas) consumption in industry by 10 percent in the year 2000.	3	212	40[c]
4. Commercial and residential.	Reduce fossil fuel (gas and oil) consumption in space heat applications by 12 percent in the year 2000.	nil	123	8[c]
5. Applications to solar energy.	Allow practical implementation of solar energy to save 2 percent of the total oil in the year 2000.	26	215	30[c]
Total		71[d]	1,351[e]	

[a] Assumed 6 percent of electricity generated by the utilities was produced by gas turbines with an efficiency of 40 percent.

[b] Assumed that all of the new gas turbine capacity installed between 1977 and 1985 and 12 percent of the capacity existing in 1977 were replaced by energy storage devices.

[c] It is assumed that the costs required for the other storage programs are incremental cost to the utility storage program. The utility need is current and these energy storage systems can be implemented in the near term.

[d] Approximately 2 percent savings of projected oil imports in year 1985; about 1 percent of total oil demand in 1985.

[e] About 24 percent savings of projected oil imports in year 2000; about 13 percent of total oil demand in the year 2000.

moreover, they produce significant quantities of nitrogen oxides and are noisy. Development of alternative electrical-storage technology would reduce the need by the utilities for the high-grade fossil fuels and natural gas that are required to operate peaking turbines. With the increasing introduction of nuclear central electric generation, electric energy storage becomes an increasingly important consideration because safety and economics dictate that reactor systems operate at base load.

The transportation sector of the energy economy is presently almost totally dependent on the use of gasoline and distillate oils. Thus, the development of energy storage for transportation systems by means of batteries or of the use of hydrogen as an automotive fuel is potentially of great value. The energy supplied to charge batteries or to produce hydrogen would be off-peak power and thus would serve to level the load, in a manner analogous to load leveling at a utility substation or central station.

Petroleum and natural gas savings would also result if economical systems can be devised to utilize replenishable energy sources such as solar energy and wind energy. Because the availability of these sources is intermittent, economical storage devices are needed. For heating homes with solar energy, thermal storage appears to be the most appropriate. If solar or wind energy are to be used to generate electricity, however, the use of storage batteries is appropriate. The requirements for such batteries would be similar to those for utility storage batteries except that units of smaller capacity would be needed.

A summary of the goals of the energy storage programs, expected oil savings, and the research costs are shown in table 3. It is estimated that these programs will save 24 percent of the imported oil projected for the year 2000; this is approximately 13 percent of the total oil demand in the year 2000.

The electric utility industry has estimated that 15 to 25 percent of the daytime generating capacity of future utility systems could be supplied by batteries that are charged during off-peak periods. Unfortunately, a suitable battery does not yet exist for this application. The introduction of bulk energy storage batteries on utility networks would eliminate the need for gas turbines which are presently used to generate power during peak periods. If 80 percent of the gas turbine units could be replaced by battery units, the oil savings would be approximately 450 million bbl/year by the year 2000. Plants employing these batteries are expected to be compact, efficient, quiet, and nonpolluting. Consequently, siting problems should be minimal, and battery plants could be located near load centers to achieve maximum savings in transmission costs. Also, the batteries could be supplied in modular form, which would allow the storage capacity to be easily altered as the electric utility requirements change.

The advanced battery systems currently under development for use in utility networks after 1985 include sodium/sulfur, lithium/metal sulfide, and zinc/chlorine, as well as several other systems which are presently in an earlier stage of development. The sodium/sulfur, lithium/metal sulfide, and zinc/chlorine systems are approaching the battery hardware stage, but will require additional research and development to improve electrical performance and lifetime and to reduce costs. None of these battery systems have advanced to the point where successful development has become certain; however, it appears very likely that at least one of these advanced batteries will be successfully developed, thereby resulting in the major petroleum savings described above. Present plans call for the sodium/sulfur, lithium/metal sulfide, and zinc/chlorine batteries to become operational in 1980, 1981, and 1983, respectively. (The other electrochemical systems appear to require major technical advances before the hardware stage is reached.) The ERDA program provides for research and development on the most promising alternative battery systems. If major technical advances are made in one or more of these systems, the level of funding will be increased, and the more promising systems will be brought to the demonstration and commercial development stage, if warranted. The total cost of the ERDA program for research and development of advanced batteries is projected at $200 million through the year 2000. It is anticipated that industry will participate on a cost sharing basis and that some of the demonstration projects may be funded as loans.

A Battery Energy Storage Test (BEST) Facility will be constructed for the testing of advanced batteries and power-conditioning equipment. The electrical performance and lifetime capabilities of the batteries will be determined under standardized conditions to allow direct comparisons to be made among the various systems. The test results will be used to determine what improvements are necessary for each system and to aid in determining which systems should receive additional support. The BEST Facility will become operational in 1979 and will be used first for testing advanced lead-acid batteries. Large-scale testing of lithium-aluminum/metal sulfide, sodium/sulfur, and zinc/chlorine batteries should be under way in the BEST Facility in the period from 1980 to 1985.

BATTERIES FOR ELECTRIC VEHICLES

Existing electric vehicles for highway use are severely limited in their range and performance because of the low specific energy and low specific power of the batteries that are available. Such vehicles normally have a range of 20 to 50 miles and a top speed of 30 to 50 mph, depending on the driving conditions. This lack of performance not only discourages consumer acceptance, but also creates safety problems. Vehicles of this type may be suitable for certain interim, limited applications; however for the long range, electric vehicles of acceptable performance will require new types of batteries of high specific energy (120 to 150 W-hr/kg) and high peak specific power 150 to 200 W/kg). It appears that these long-range requirements can be met only by new advanced battery systems—very likely some of the systems are currently under development.

For near-term application, the battery systems being investigated include lead-acid, nickel/iron, and nickel/zinc. Improvements in these systems will make it possible to attain interim goals that will aid in assessing the long-range viability of electric vehicles. Among the systems that are under consideration for the longer range application are sodium/sulfur, lithium-aluminum/FeS_2, zinc/chlorine, zinc/bromine, zinc/air, iron/air, lithium/air, and aluminum/air. The sodium/sulfur and lithium-aluminum/iron sulfide systems are both well advanced into the cell hardware stage and will soon be tested in battery configurations. Both systems have achieved cycle lives of several hundred charge-discharge cycles and lifetimes of several thousand hours. (The minimum requirements for an electric vehicle battery are about 1000 cycles and 25,000 to 50,000 hr.) Both systems also show promise for meeting the long-term specific energy and specific power goals. A zinc/chlorine battery has been demonstrated in a test vehicle and a rechargeable zinc/chlorine battery has attained about 100 cycles in the laboratory. The zinc/air and iron/air systems are under development by industry and are now capable of about 150 cycles. However, both these systems have low specific powers (20 to 40 W/kg) and low overall energy efficiencies of only about 30 percent. The zinc/bromine, lithium/air and aluminum/air systems are under consideration for development, but little or no work is currently in progress.

Only a few thousand electric vehicles are on the road today in the U.S. However, the development of high-performance batteries is expected to increase their acceptability to the public, and the number of electric vehicles on the road is expected to increase from 10,000 in 1978 to 18 million by the year 2000. The corresponding annual production of electric vehicle batteries would increase from 7,000 in 1978 to 10 million in the year 2000. On the basis of a battery capacity of 35 kW-hr per vehicle, the cumulative battery capacity produced over this period would be about 2 million MW-hr. The total value of all of the batteries produced during this period at a price of $30/kW-hr would amount to approximately 60 billion dollars. On this same basis, the annual value of batteries produced would increase from 8.5 million dollars in 1978 to about 12 billion dollars in 2000.

The widespread use of electric vehicles will affect several areas of our society. The overall environmental impact of electric vehicles should be favorable. Although the level of pollution will not be decreased, the pollution problem will be transferred from the highways to the electric generating plant, where it can be coped with more easily. The use of electric vehicles will also have a significant economic impact on the automotive, petroleum, battery manufacturing, and electric utility industries. However, the changeover from gasoline-powered to electric-powered vehicles is expected to be gradual, and no major disruptions are anticipated.

MATERIAL SUPPLIER FOR ADVANCED BATTERIES

The manufacture of batteries for storing energy on electric utilities and for propulsion of electric vehicles will be a multibillion-dollar business by the year 2000, if any of several battery programs now under development are successful. The manufacturers of these batteries will require huge quantities of strategic materials. Of particular interest here is that one of the most promising systems—the lithium/metal sulfide system—utilizes lithium, not only as one of the active materials, but also as a constituent of the LiCl-KCl molten salt electrolyte. If the performance goals for the lithium/metal sulfide battery are achieved, the demand for these batteries will, in turn, create a greatly increased demand for lithium. Accordingly, serious consideration should be given by the lithium industry to possible problems related to the availability of lithium resources and to greatly increased production rates. However, the problem of lithium availability may not continue for the long term if other molten-salt systems can be developed that have performance capabilities similar to that of the lithium/iron sulfide systems. Work on molten-salt systems not containing lithium is in the early development stage at Argonne National Laboratory.

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BATTERY SYSTEMS FOR LOAD-LEVELING AND ELECTRIC-VEHICLE APPLICATION, NEAR-TERM AND ADVANCED TECHNOLOGY[1]

By N. P. YAO and W. J. WALSH,
ARGONNE NATIONAL LABORATORY, ARGONNE, IL

ABSTRACT

Intensive efforts are underway in the United States and elsewhere to develop secondary batteries for utility load-leveling systems and electric vehicles. The lead-acid battery is the only candidate system that can meet the performance requirements using presently available technology, but it has the drawbacks of higher-than-desired battery cost and marginal energy-storage capacity for the vehicle application. The Zn/Ni system appears to have a good chance of capturing the near-term electric-vehicle market, provided that advances can be made in reducing costs and increasing battery lifetime. Advanced secondary battery systems that may come into commercial use by 1985 include Li-Al-FeS$_x$, Na/S, and Zn/Cl$_2$. These advanced systems are expected to possess superior performance characteristics and economic prospects compared to lead-acid and Zn/Ni batteries.

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[1] Work supported by the Conservation Division of the Energy Research and Development Administration

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LITHIUM REQUIREMENTS FOR HIGH-ENERGY LITHIUM-ALUMINUM/IRON-SULFIDE BATTERIES FOR LOAD-LEVELING AND ELECTRIC-VEHICLE APPLICATIONS[1]

By A. A. CHILENSKAS, G. J. BERNSTEIN, and R. O. IVINS,
ARGONNE NATIONAL LABORATORY, ARGONNE, IL

ABSTRACT

Lithium-aluminum/iron-sulfide batteries are being developed at Argonne National Laboratory for use as energy-storage devices on electric utilities and as power sources for electric vehicles. These batteries are expected to come into commercial use around 1985 and to achieve rapid market penetration thereafter. By the end of the year

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[1] Work performed under the auspices of the Assistant Administrator for Conservation, Energy Research and Development Administration.

2000, as much as 3 percent (3×10^8 kW-hr) of the projected total U.S. energy consumption could be supplied by lithium-aluminum/iron-sulfide off-peak energy-storage batteries. At the same time 18 million electric vehicles or more may be powered by lithium-aluminum/iron-sulfide batteries.

Projections have been made of the quantity of lithium required for lithium-aluminum/iron-sulfide batteries produced from 1985 to 2000. The projected lithium requirement in the year 2000 represents a substantial fraction of the present estimate of world lithium resources and is nearly equal to the estimated economically recoverable lithium resources in the U.S. In addition, the potential market for primary batteries using lithium will add to these requirements. Expansion of exploration for new sources and increases in production capacity will be needed to meet the projected lithium requirements for the introduction of these batteries in sufficient quantities to produce the desired impact upon petroleum-conservation goals in the U.S. transportation sector and electrical-power generation.

INTRODUCTION

The Chemical Engineering Division of Argonne National Laboratory is engaged in a research and development program on high-performance lithium-aluminum/iron-sulfide batteries suitable for powering electric automobiles and for storing off-peak energy to level the loads on generating equipment in electric utility systems. At the present time, commercially available batteries are limited in their ability to meet the stringent performance, cost, and lifetime requirements for these applications. The successful development of more economic, high-specific-energy batteries for either application would provide a means of using energy produced from nonpetroleum sources (for example, nuclear, coal) and reduce our dependence on foreign oil sources.

The current effort in the battery program consists of about 65 engineers, chemists, metallurgists, and other technical personnel, including temporary industrial participants, postdoctoral appointees, students, and faculty members, and is funded chiefly through the Division of Conservation Research and Technology in the Energy Research and Development Administration (ERDA) (Nelson and Webster, 1974; Nelson and others, 1974).

The batteries consist of cells containing a lithium-aluminum alloy in the negative electrode and a metal sulfide such as FeS or FeS_2 in the positive electrode. The electrolyte is the LiCl–KC1 eutectic, which has a melting point of 352°C. For this reason the cells are operated at temperatures between 380° and 450°C. A drawing showing a full-scale cell designed for a utility load-leveling battery is shown in figure 1.

To provide an opportunity for industry to develop manufacturing techniques and expertise in the fabrication of lithium-aluminum/metal-sulfide cells, commercial development contracts have been let with Gould, Inc.; Eagle-Picher Industries, Inc.; and Catalyst Research Corp. to develop, fabricate, and deliver cells to Argonne for testing and evaluation. Argonne has also contracted with Atomics International for a supporting development program; at the present time their approach incorporates a lithium-silicon-alloy negative electrode of their own development.

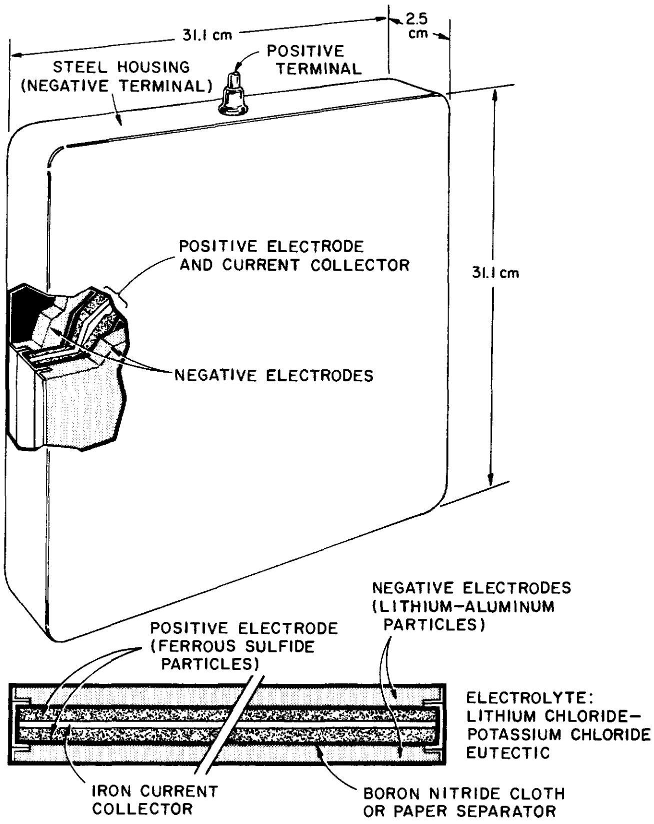

FIGURE 1.—Design of prismatic cell for Argonne National Laboratory lithium/aluminum/iron sulfide battery.

Test cells and electrodes have been fabricated by both Gould and Eagle-Picher and are now being tested. During 1976 the industrial-cell-fabrication development will be extended to the fabrication of battery systems. Current plans include large-scale battery tests both in the laboratory and in a test automobile early in 1978.

The cells currently being tested are square in shape, 13 cm on a side, and 2 to 3.8 cm thick. Both FeS and FeS_2 positive electrodes are being evaluated. The former appear attractive for electric-utility-storage application owing to potentially lower cost, whereas the latter appear more suitable for automobiles owing to their higher power capability. Cells containing FeS electrodes have achieved a capacity of about 90 A-hr at 1.2 V, and cells with FeS_2 electrodes have demonstrated a capacity of about 120 A-hr at 1.5 V. These values, which correspond to specific-energy values of about 100 W-hr/kg for FeS cells and 150 W-hr/kg for FeS_2 cells, are about three to five times that obtainable from a lead-acid battery. With further improvements in cell design, the specific energy is expected to increase by at least 25 percent and possibly as high as 50 percent.

LITHIUM REQUIREMENTS

Because of the potential demand for large quantities of lithium for fabrication of lithium-aluminum/iron-sulfide batteries, we have attempted to forecast the need for lithium in the time period 1985–2000. In this regard, not only the total amount of lithium contained in the batteries, but the production rate necessary for meeting annual needs is of importance.

The projected lithium requirement for off-peak energy-storage batteries is based upon a total U.S. electrical-energy consumption of 4×10^9 MW-hr in 1985, 6×10^9 in 1990, and 10×10^9 in the year 2000 (Electric Research Council, 1971). The fraction of this energy supplied from lithium-aluminum/iron-sulfide batteries was estimated to be minimal in 1985, about 1 percent in 1990, and about 3 percent in 2000. Based upon these assumptions, the projected energy supplied from battery storage plants in the year 2000 is 3×10^8 MW-hr. Laboratory test cells have achieved 150 W-hr/kg. These cells have a lithium content of 6.5 weight percent. About 4 percent of this is in the electrodes, and the remaining amount is contained as lithium chloride in the molten salt electrolyte. Assuming 250 charge-discharge cycles per year and the above values, the lithium content in battery systems on utility networks would be about 5×10^8 kg in the year 2000.

In table 4, we estimate the annual requirement for lithium based upon our projected rate of growth of utility storage facilities and assuming 10-yr life-time for the batteries. We have also indicated the production rate of new lithium if the lithium in used batteries can be recycled with a 90 percent recovery. Recycling of lithium has the advantage of reducing the amount of new lithium that has to be extracted from available lithium resources. Because of the relatively small use of these batteries prior to 1990, recycling of utility storage batteries does not become important until after 1995.

A projection was also made of the number of electric vehicles in operation in the U.S. until the year 2000. These vehicles are expected to be introduced in significant numbers around 1985, with annual production rising to about 2.7 million in the year 2000. Based upon an expected average lifetime of these vehicles of at least 10 years, about 18 million electric vehicles would be on the road in the year 2000. Figure 2 shows the growth rate of electric vehicles starting with modest production in 1982.

TABLE 4.—*Projected requirements for lithium in lithium-aluminum/iron-sulfide batteries for utility energy storage*

	1985	1990	2000
Total U.S. electrical-energy consumption, MW-hr	4×10^9	6×10^9	10×10^9
Electrical energy supplied by batteries, MW-hr	5×10^5	6×10^7	3×10^8
Lithium in utility batteries, kg	1×10^6	1×10^8	5.2×10^8
Annual new lithium production; no lithium recycle, kg	1×10^6	2.8×10^7	8×10^7
Annual new lithium production; 90 percent lithium recycle, kg	1×10^6	2.8×10^7	5.3×10^7

A typical vehicle would be equipped with a 42 kW-hr lithium-aluminum/iron-sulfide battery weighing about 350 kg and would be capable of driving the vehicle more than 240 km per charge. The electric-vehicle cells would contain about 7.2 weight percent elemental lithium as metal and salt. Thus, each vehicle battery would hold about 15 kg of lithium; this value represents a total of 2.7×10^8 kg in vehicle batteries in the year 2000.

During the period between 1985 and 2000, about 20×10^6 vehicles would have been built and about 2×10^6 would have been scrapped, based upon an average lifetime of 10 years. Consideration was also given to the effect upon annual demand for new lithium if the vehicle batteries had lifetimes of 5 years instead of 10 years and if the lithium in used batteries could be recycled with 90 percent recovery. (see fig. 3.) Table 5 shows the annual demand for new lithium for 5– and 10–year battery lifetimes and under the conditions noted above.

Table 6 summarizes the total annual requirements for lithium and the total lithium in battery use for both

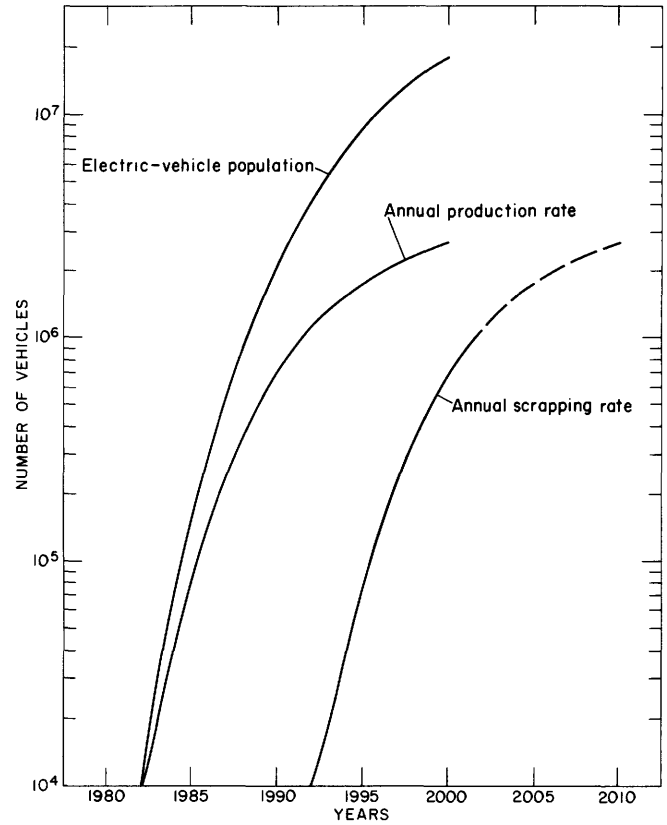

FIGURE 2.—Electric-vehicle production.

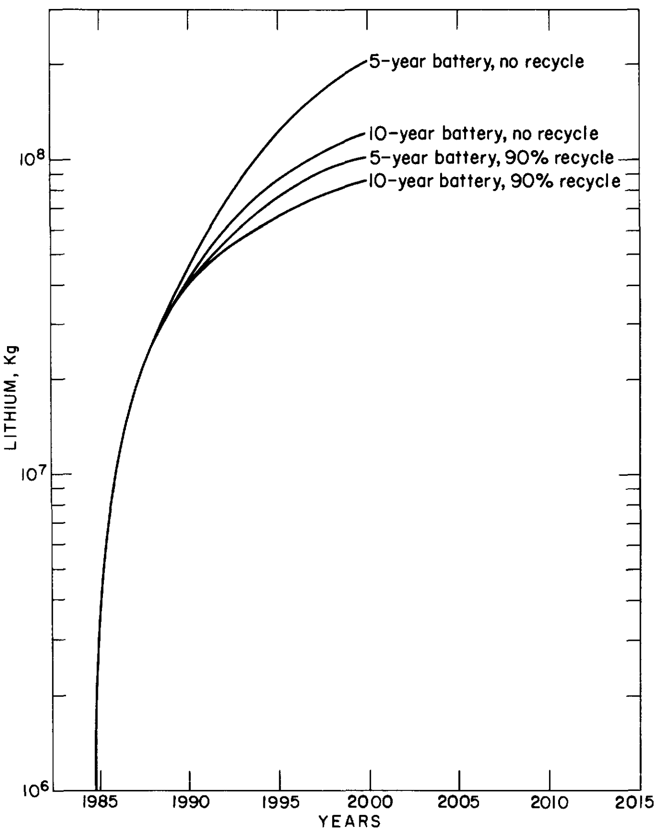

FIGURE 3.—Annual lithium requirements for electric-vehicle batteries.

TABLE 5.—*Projected requirements for lithium in lithium-aluminum/iron-sulfide batteries for electric-vehicle propulsion*

	1985	1990	2000
Annual electric vehicle production	8.0×10^{4}	7.0×10^{5}	2.7×10^{6}
Total electric vehicles in operation	1.5×10^{5}	2.1×10^{6}	1.8×10^{7}
Lithium in operating electric vehicles, kg	2.3×10^{6}	3.2×10^{7}	2.7×10^{8}
Annual new lithium production: 5-yr battery life, no recycle, kg	1.2×10^{6}	1.2×10^{7}	7.7×10^{7}
Annual new lithium production: 5-yr battery life, 90 percent recycle, kg	1.2×10^{6}	1.1×10^{7}	4.4×10^{7}
Annual new lithium production: 10-yr battery life, no recycle, kg	1.2×10^{6}	1.1×10^{7}	4.1×10^{7}
Annual new lithium production: 10-yr battery life, 90 percent recycle, kg	1.2×10^{6}	1.1×10^{7}	3.1×10^{7}

TABLE 6.—*Projected requirements for lithium in lithium-aluminum/iron-sulfide batteries for utility energy storage and electric vehicles*

	1985	1990	2000
Lithium in utility facilities, kg	1.0×10^{6}	1.0×10^{8}	5.2×10^{8}
Lithium in electric vehicles, kg	2.3×10^{6}	3.2×10^{7}	2.7×10^{8}
Total lithium in use, kg	3.3×10^{6}	1.3×10^{8}	7.9×10^{8}
Total annual new lithium production: 10-yr battery life, no recycle, kg	2.2×10^{6}	3.9×10^{7}	1.2×10^{8}
Total annual new lithium production: 10-yr battery life, 90 percent recycle, kg	2.2×10^{6}	3.9×10^{7}	8.4×10^{7}
Cumulative production of lithium: no recycle, kg	3.3×10^{6}	1.3×10^{8}	9.3×10^{8}
Cumulative production of lithium: 90 percent recycle, kg	3.3×10^{6}	1.3×10^{8}	8.1×10^{8}

electric vehicles and energy storage under the conditions noted above. The requirements shown in this table must be compared with estimated lithium resources and the required rates of production. In addition, some allowance must be made for lithium requirements for other battery applications, such as primary batteries for military and civilian use.

Considerable uncertainty surrounds estimates of lithium resources. World lithium resources have been estimated as high as 2×10^{10} kg (H. R. Grady, written commun. 1974). Other estimates suggest that economically recoverable U.S. resources might be less than 1×10^{9} kg (J. D. Vine, written commun. 1975). Table 6 shows that the cumulative production of lithium by the year 2000 could equal the presently identified, economically recoverable U.S. resources.

Consideration must be given to lithium production rates. The U.S. Bureau of Mines (J. D. Vine, written commun., 1975) estimates that lithium production was about 2.6×10^{6} kg in 1968. On the basis of an estimated annual growth rate of 10 percent, the production in 1974 would have been about 4.5×10^{6} kg. If a 10 percent annual growth rate is maintained until 1985, annual production would be 1.2×10^{7} kg. This would be about 10 times the projected requirements for lithium-aluminum/iron-sulfide batteries in that year. If the same growth rate continued until 1990, annual production would reach 2×10^{7} kg. This is less than the annual battery-production requirements under the conditions of 10-yr battery life and 90 percent recycle (3.9×10^{7} kg). The requirements for the year 2000 (8.4×10^{7} kg) would also exceed projected capacity at 10 percent growth (5.2×10^{7} kg). In addition to expansion of capacity for producing new lithium from ores, it will be necessary to establish a lithium-recovery technology to permit recycling of the increasing amounts of lithium in used batteries. It should be noted that the chemical form of lithium that will be used in commercial cells will very likely be Li_2S, as suggested by recent results of the cell-fabrication development effort. The commercial production of Li_2S will be based upon the chemical conversion of lithium ores to Li_2S rather than the current practice of producing the sulfide from lithium metal.

The availability of lithium clearly constitutes a major supply problem for the period 1985–2000, and accelerated efforts at discovery of new resources and expansion of production facilities will be needed if lithium-aluminum/iron-sulfide batteries are to be introduced into the economy at rates sufficient to produce the desired impact upon petroleum conservation goals in the U.S. transportation sector and in electrical power generation.

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LITHIUM REQUIREMENTS FOR ELECTRIC VEHICLES USING LITHIUM-WATER-AIR BATTERIES[1]

By J. F. Cooper, I. Y. Borg, L. G. O'Connell, E. Behrin, B. Rubin, and H. J. Wiesner,
Lawrence Livermore Laboratory, University of California,
Livermore, CA

ABSTRACT

The lithium-water-air battery is a new primary battery of such exceptional power and energy that it is a candidate to provide propulsion for electric automobiles of the future. In the electrochemical reaction involved, lithium, oxygen, and CO_2 are combined, leaving Li_2CO_3 as a by-product to be removed from the battery and recycled. A subcompact car weighing 910 kg would transform 7.2 kg of lithium in traveling 320 km at 97 km/hr. At least an equal amount of lithium per car would be unavailable because of the need to recycle the by-product (Li_2CO_3). Thus, a minimum of 14.4 kg of lithium per car is required to support a transportation system based upon this power source. Assuming that in the year 2000, 12 to 16 percent of all vehicles are powered by lithium-water-air batteries, we will need 234,000 to 425,000 metric tons of lithium. This amount is somewhat less than the total known U.S. lithium reserves, but if the current rate of consumption of lithium for other purposes continues, the supply of lithium will have to be increased.

INTRODUCTION

The 1973 petroleum embargo by major Arab petroleum exporters and the subsequent price increases by OPEC (Organization of Petroleum Exporting Countries) focused attention on oil-consuming technologies and industries. Because the passenger automobile consumes about 4.8 million bbl/day (approximately 28 percent of the nation's total oil consumption), the automotive industry has been pressured to modify existing vehicles so that gasoline economy is increased. There is an urgent need to develop vehicles that use alternate fuels or propulsion systems.

One alternative to the gasoline automobile is an all-electric vehicle. However, the most advanced batteries available today have power and energy capacities per unit weight that are too low to provide performance and range comparable to conventional automobiles. The lithium-water-air battery, which is closely related to the lithium-water battery developed for marine use by the Lockheed Missile & Space Company (Halberstadt, 1973), offers apparent high-performance potential. Further development could provide the basis for an all-electric vehicle with the range, speed, acceleration, and rapid refueling capabilities of current automobiles.

CHARACTERISTICS OF THE LITHIUM-WATER-AIR BATTERY

The projected performance of the lithium-water and lithium-water-air batteries approaches that of the internal combustion engine. We have compared the performance of various power sources on a graph of specific power against specific energy in the manner of Ragone (1968) (see fig. 4). For fixed battery and vehicle weights, top speed and acceleration are determined by specific power, whereas the vehicle range for a given speed is proportional to specific energy. On the basis of demonstrated cell performance data, a lithium-water battery weighing 230 kg could be built to deliver an energy density of 225 to 300 Wh/kg at a specific power of over 100 W/kg. This would suffice to power a vehicle weighing about one tonne for 300 to 400 km at about 100 km/h. Modification of the lithium-water battery to include an air cathode has been shown to increase cell

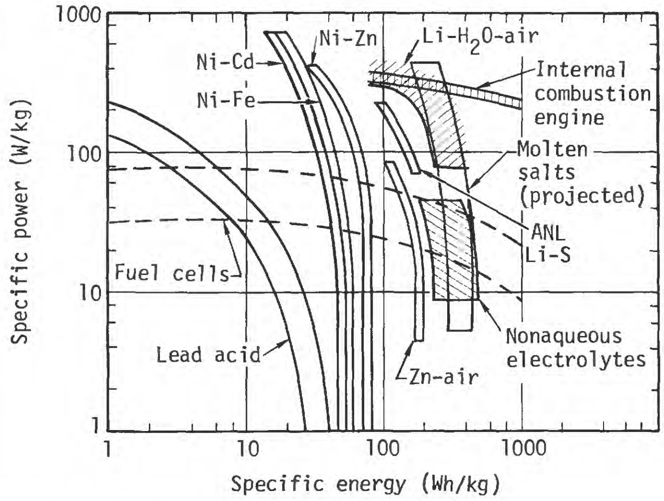

FIGURE 4.—Performance characteristics of vehicle power sources.

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[1] This work was performed under the auspices of the U.S. Energy Research and Development Administration under contract No. W–7405–Eng–48.

voltage. A specific energy of 350 to 400 Wh/kg at 110 W/kg has been projected, based on specific cell data and a preliminary battery design.

PRINCIPLES OF OPERATION OF BATTERIES OF THE LITHIUM-WATER TYPE

The lithium-water battery utilizes the electrochemical reaction of lithium and water:

$$\mathrm{Li} = \mathrm{Li}^+ + 1e^- \qquad \text{(anode)} \quad E^O_O = -3.05\,\mathrm{V};$$

$$\mathrm{H_2O} + 1e^- = \mathrm{OH}^- + \tfrac{1}{2}\mathrm{H_2} \qquad \text{(cathode)} \quad E^O_O = -0.83\,\mathrm{V};$$

$$\mathrm{Li} + \mathrm{H_2O} = \mathrm{LiOH(aq)} + \tfrac{1}{2}\mathrm{H_2} \qquad \text{(net)} \quad \Delta E^O_O = 2.22\,\mathrm{V}.$$

In a simple version of the cell, an iron wire mesh cathode current collector is pressed against the lithium anode and the leads are connected through a load. When this electrode assembly is immersed in an aqueous solution of lithium hydroxide, a thin film of reaction products forms on the lithium surface and separates the two electrodes. The film inhibits corrosion of the lithium metal and prevents internal shorting of the cell. Practical cell voltages of 1.6 V are obtainable at current densities of 10^3 A/m^2.

The lithium-water-air battery is considered to be the most energetic of the batteries of the lithium-water type, although other cathodes and electrolytes are under investigation (O'Connell and others, 1974). In the lithium-water-air battery, the iron mesh is placed in contact with a catalyzed, porous graphite electrode doped with an appropriate catalyst such as platinum (fig. 5). The battery utilizes atmospheric oxygen with the net cell reaction,

$$\mathrm{Li} + \tfrac{1}{4}\mathrm{O_2} + \tfrac{1}{2}\,\mathrm{H_2O} = \mathrm{LiOH(aq)}\,\Delta E^O_O = 3.45\ \mathrm{V}.$$

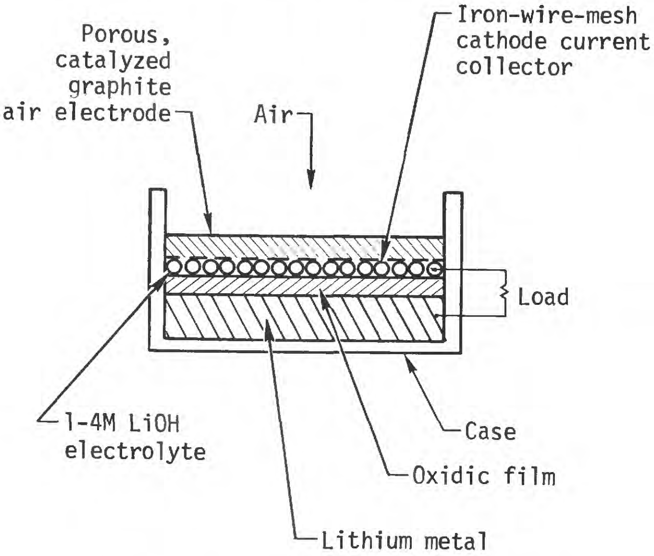


FIGURE 5.—A simple lithium-water-air cell.

Protective properties of the anode surface film are retained, and cell voltages of 2.6 to 2.7 V at 10^3 A/m^2 are practical, depending on the choice of air cathode.

Stable cell discharge requires maintenance of electrolyte temperature and concentration within certain bounds. Precipitation of lithium as $\mathrm{LiOH \cdot H_2O}$ upon electrolyte cooling is one means of concentration control. Concentration might also be controlled by precipitation of lithium hydroxide with carbon dioxide. The overall reaction for the lithium-water-air battery would then become

$$\mathrm{Li} + \tfrac{1}{4}\mathrm{O_2} + \tfrac{1}{2}\mathrm{CO_2(g)} = \tfrac{1}{2}\mathrm{Li_2CO_3}.$$

The energy losses and hazards associated with hydrogen evolution in the lithium-water-air battery are thus avoided, and a 50 percent increase in cell power is obtained.

ANODE REPLACEMENT AND LITHIUM RECYCLING

The lithium-water-air battery is a primary battery. Recharging is accomplished by removing the reaction product (a slurry of lithium carbonate) and replacing the battery's supply of lithium and carbon dioxide. For a 910 kg vehicle, 7.2 kg of lithium and 23 kg of carbon dioxide suffice for a 320-km range at 97 km/h. For this range, the present distribution of gasoline service stations is adequate. One attractive option, depicted in figure 6, is to remove the lithium carbonate and replace the carbon dioxide every 320 km, while replenishing the supply of lithium only at intervals of 1,600 km. This would raise the necessary initial inventory of lithium from 7 to 36 kg, making the average amount carried 21 kg. Such an option would reduce the frequency of the most difficult phase of refueling and reduce the number

FIGURE 6.—The lithium-water-air battery concept for electric vehicles.

of service stations required for handling lithium metal. The mechanics of refueling the battery pose no serious problems, and details will be determined by consideration of economics and convenience.

The lithium carbonate reaction product would be transported to a recycling plant for reduction to lithium metal and carbon dioxide, as shown schematically in figure 7. Such a distribution system involving reprocessing and service centers does not currently exist. The cost of reprocessing lithium carbonate to lithium metal in large quantities is largely conjectural, but Foote Mineral Company (written commun., March 1975) stated that it may be in the range of $3.30/kg. If the cost of recycling lithium could be reduced to $1.30/kg, the fuel costs for the vehicle would be roughly $0.05/mile. This rate corresponds to a gasoline cost of $1.50/gal for an internal combustion engine vehicle achieving 30 miles/gal.

HYBRID BATTERY SYSTEMS

The lithium-water-air battery can be employed in several different configurations. Thus far, it has only been considered as a primary battery system. However, dual battery hybrid systems could allow more economical operation without a sacrifice of performance. A secondary battery (for example, Ni-Zn) would provide propulsion energy for all short trips (that is, under 32 km), which constitutes 55 percent of total vehicle travel (Motor Vehicle Manufacturers Association, 1973–74, p. 37). The primary battery would be activated when needed for greater range or rapid refueling. Hybrid systems would thus serve to reduce operating costs and make the vehicle competitive with internal combustion engines. A dual-battery hybrid system is an attractive means of combining the high performance of the lithium-water-air primary battery with the economical operation of the secondary (table 7).

ELECTRICAL CARS IN THE FUTURE

We do not know with certainty what percentage of automobiles used in the U.S. will have electrical propulsion systems. Table 8 includes estimates from several sources (Kalhammer, 1974; Nelson and others, 1974; Harvey and Menchen, 1974). These suggest that the penetration of the conventional automobile market by such vehicles will be gradual. By the year 2000, electric vehicles are expected to comprise 12 to 16 percent of all automobiles.

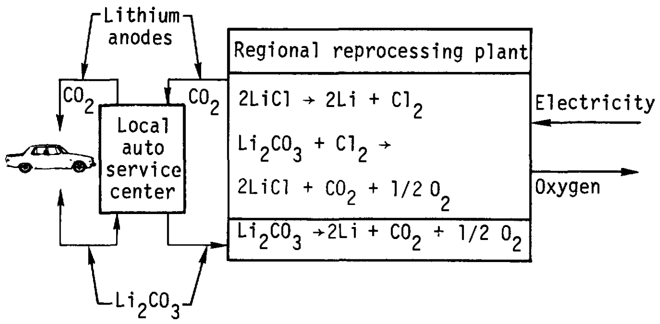


FIGURE 7.—An automotive system involves recycling of Li_2CO_3 (O'Connell and others, 1974).

Electric vehicles require considerable design study in addition to development of an adequate battery. Lower cost electric motors are necessary, lighter weight vehicles are desirable, and reliable and inexpensive electronic controls must be devised. Much new servicing equipment must be introduced also. These problems are not major ones, however. Vehicle design will vary in detail and complexity depending on the type of battery.

TABLE 8.—*Projected effect of electric vehicles on the automotive industry*

	1975	1985	1990	2000
Auto population (millions)	92	126	134	151
Estimated electric vehicle population (millions)	0	0.2–1	1.8–5	18–25
Percent of electric vehicles	0	0.1–.8	1.3–3.7	12–16

TABLE 7.—*Performance specifications for dual battery hybrids*

[Assumptions: Propulsion energy and power requirements for 97 km/h cruise: 169 Wh/km and 40 kW for 0–97 km/h acceleration in 25 sec. Propulsion requirements based on the representative vehicle: curb weight, 910 kg; battery weight, one-quarter of vehicle weight; aerodynamic drag coefficient, 0.4; rolling resistance (constant), 137 nt; frontal area, 1.86m^2; drive train efficiency, 75 percent]

Vehicle power	Battery weight (kg)	Specific energy (Wh/kg)	Specific power (average) (W/kg)	Power (peak) (kW)	Range—at 97 km/h (km)	Mileage use (percent)
Hybrid (secondary with 32-km range):						
Primary battery[1]	146	370	110	16	320	45
Secondary battery[1]	81	67	200	24	32	55
Effective total	227	262	70	40	350	100
Hybrid (secondary with 80-km range)						
Primary battery[1]	146	370	110	16	320	25
Secondary battery[1]	81	167	200	24	80	75
Effective total	227	297	70	40	400	100

[1] Alone.

LITHIUM REQUIREMENTS OF ELECTRICAL VEHICLES POWERED WITH LITHIUM-WATER-AIR BATTERIES

A total of 7.2 kg of lithium is required for a subcompact vehicle with a range of 320 km. For every battery in use, an equivalent amount of lithium will be in process. Thus, for each vehicle in use, about 14.4 kg of lithium are needed. A better estimate of the requiremet would be 13 to 17 kg per vehicle, because the actual designs may cause the requirements to change. Taking all vehicles into account and using the projections from table 8, we can arrive at the following estimate:

Year	*Number of electric vehicles (million)*	*Lithium required (tonnes)*
1985	0.2–1	2,600– 17,000
2000	18 –25	234,000–425,000

It is estimated that by the year 2000, 36,000 tonnes of lithium will be produced annually. Estimates of anticipated cumulative production of lithium in the U.S. to the year 2000 are on the order of 400,000 tonnes (Vine, written commun. Feb. 1975; Borg and O'Connell, 1976). This supply is adequate to meet the demand for lithium in glass, ceramics, aluminum, fluxes, greases, etc., but clearly, any additional demand, such as extensive use of lithium in automotive batteries or in a fledgling controlled thermonuclear reactor industry, will tax existing reserves and resources which are on the order of 320,000 and 830,000 tonnes respectively (Vine, written commun., July 1, 1975). The supply of lithium would have to be increased to accommodate these newly emerging technologies.

FEASIBILITY OF THE LITHIUM-WATER-AIR BATTERY

At this point, the lithium-water-air battery, as part of an automobile propulsion system, is in a developmental stage. The exact nature of the air cathode is still open, and the required utilization of lithium might be reduced to about 5 kg per 320 km. Alternate electrolytes may prove more advantageous. Alternative ways of controlling lithium hydroxide concentration may be feasible. The behavior of lithium anodes in the aqueous electrolyte batteries must be explored. In addition, vehicle design options must be investigated so as best to accommodate the specific features of the battery, and the required servicing and fuel distribution system must be investigated. The economical reprocessing of the lithium carbonate is also crucial to successful employment of the battery. The total cost per vehicular kilometre must be assessed carefully and compared to the systems involving other battery types or types of fuel. Lastly, the availability of lithium must be critically examined. We do not want to create in the year 2000 an analogue to the present oil crisis. Much remains to be done, but it is clear that the lithium-water-air battery shows great promise as part of the transportation system of the future.

FUSION POWER AND THE POTENTIAL LITHIUM REQUIREMENT

By S. Locke Bogart,
U.S. Energy Research and Development Administration, Washington, DC

INTRODUCTION

Thermonuclear fusion is regarded by most people as one of the attractive long-range solutions for the Nation's and the world's energy supply problem because of its major advantages:

1. Effectively infinite fuel supply at low cost (<<1 mill/kwhr)
2. Inherent safety, no runaway
3. No chemical combustion products
4. Relatively low radioactivity and attendant hazards
5. No emergency core-cooling problem
6. No use of weapons grade materials so no diversion possibility
7. Flexibility to site plants near load centers, possibly even in urban areas

Fusion is the process by which the nuclei of light elements are forced to combine and form new light elements with a net yield of significant quantities of energy per reaction. Fusion compares with fission in the sense that the fission process is the conversion of heavy nuclei to nuclei of intermediate weights with comparable releases of energy. Thus, the fundamental distinctions between fusion and fission are the nature of the fuels, the nature of the reaction products, and the mechanisms by which the two processes are made to occur. In this paper, I will restrict the scope to the fusion process and one of the basic fuels for first generation reactors.

The first generation fusion reactors will be based on the deuterium-tritium (D–T) reaction, within the deuterium-lithium fuel cycle. This choice results simply from the fact that the D-T reaction will be easiest to achieve given what is felt as achievable physics and engineering in the next three to four decades. The deuterium resource is affectively infinite, being found in one part in 6,500 in water. Commercial lithium is obtained from pegmatite ore and specific brines in large but not unlimited quantities. Lithium also is found in seawater, but present availability of this element has not required utilization of this source.

The lithium requirement for different fusion reactor concepts is strongly design dependent. When lithium is used both as a breeder and a coolant in either the metallic or the salt form, the inventories are very high. In alternative solid breeder concepts the lithium requirements is much smaller, but this lithium must be enriched in the isotope lithium-6, and a neutron multiplying element also must be used. Because of the high burnup rate in solid breeder concepts, periodic refueling must be performed which will affect the annual net lithium requirement. This is not the case in liquid lithium breeder/coolant concepts which have such a high initial inventory of lithium-6 that the small fractional burnup per year does not mandate periodic refueling.

In the balance of this paper, these concepts will be developed more fully. The basic properties of the fusion process will be described, and the requirements for this process will be related to the potential lithium demand. An energy supply scenario will be developed which includes fusion as part of the mix. The lithium requirement for a developing fusion reactor economy will be presented.

THE CONTROLLED THERMONUCLEAR FUSION PROCESS

The fusion of light nuclei (deuterium and tritium) with the subsequent release of energy results from forcing the nuclei together, thus overcoming the coulombic barrier, to form a compound nucleus which spontaneously decays to stable products. The energy released is simply the energy equivalence of the difference between the mass of the fuels and the mass of the products, a fundamental result of the expression $E = mc^2$. To achieve significant reaction rates, the temperature of the reactants must be very high (about 100 million degrees Kelvin) and they must be confined away from surfaces which would cool them. The last restriction basically defines the two types of confinement methods presently being investigated.

The Division of Controlled Thermonuclear Research focuses on magnetic confinement. In this method, the reactants which are highly ionized are confined by magnetic fields which are kept away from the walls of the reactor vessel. This satisfies two conditions: reducing the energy flow from the fuels to the wall and confining the fuels for a sufficiently long time to allow a significant number of energy releasing reactions to occur. The technical definition of this condition is called the Lawson criterion, which prescribes the plasma requirements for net energy release from the reaction. Figure 8 illustrates the Lawson operating regime. An alternative to fusion by magnetic confinement is fusion by inertial confinement, which is a process being sponsored by the Division of Military Applications in the U.S. Energy and Research Development Administration. In this concept, a small particle of fusionable fuel is imploded by the irradiation of either laser light or relativistic electron or proton beams. The Lawson criterion also must be obeyed in this concept, but energy loss to the reactor vessel is not as important.

Fundamental to either approach using deuterium and tritium as the basic fuel is the necessity to breed the tritium in a lithium blanket surrounding the reactor vessel. First, however, some background information of the basic fuel cycle must be presented. The fusion of a deuterium and tritium atom results in a helium nucleus and a neutron as the products (see fig. 9). The energy release from this reaction is 17.6 MeV with 3.5 MeV being carried away by the helium nucleus and 14.1 MeV being carried away by the neutron. The helium nucleus, being charged, is confined by the magnetic field and subsequently heats incoming fuel to keep the reaction going. The neutron, however, is not charged, and it rapidly escapes the magnetic field and enters the blanket region. Inelastic scattering with blanket material converts the kinetic energy of the neutron to thermal

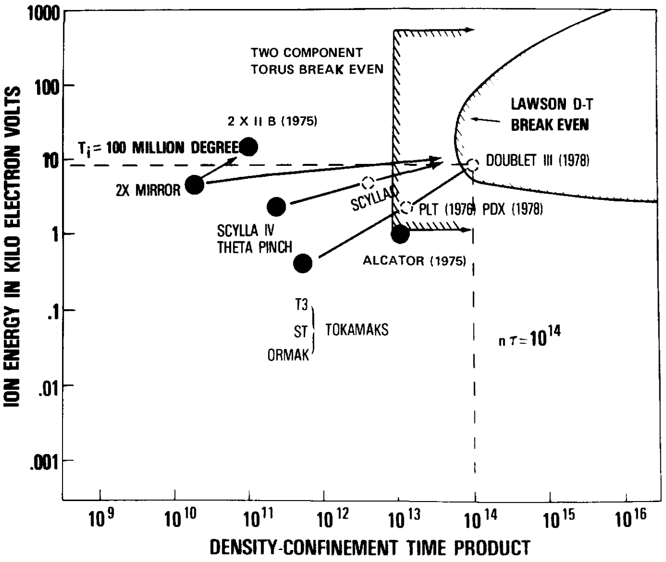


FIGURE 8.—"Break even" plasma conditions for fusion power.

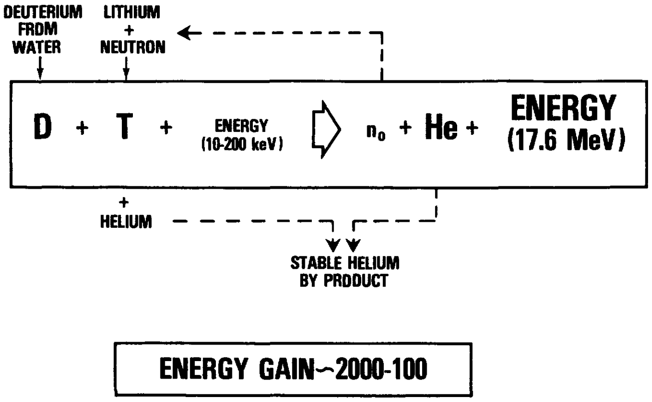


FIGURE 9.—Deuterium-tritium reaction.

energy which is removed by the coolant for the conversion to electricity.

Now comes the part critical to the deuterium-tritium fusion reaction concept. To regenerate sufficient amounts of tritium to maintain the fuel cycle, the neutron must be absorbed by either a lithium-6 or a lithium-7 atom. By proper blanket design, the sum of these reactions will result in the net production of more than one tritium atom per fusion event. As it turns out, the lithium-6 reaction predominates in all concepts, and it is this reaction that provides the bulk of the tritium fuel. However, the lithium-7 reaction is required to achieve a breeding ratio of greater than 1 providing other neutron multipliers such as beryllium are not used. To avoid this increase in blanket design complexity, very thick liquid lithium blankets have been proposed (fig. 10). Unfortunately, large quantities of natural lithium must be provided for this concept. If one is willing to accept the complexities introduced by neutron multipliers in the blanket, then lithium in the enriched form of lithium-6 can be used which significantly reduces the quantity of lithium required (fig. 11). The choice of either of these two concepts cannot be made at this time simply because the basis for such a decision is not yet developed. However as we shall see, the choice of either blanket concept strongly effects the quantities of lithium required in given fusion reactor design.

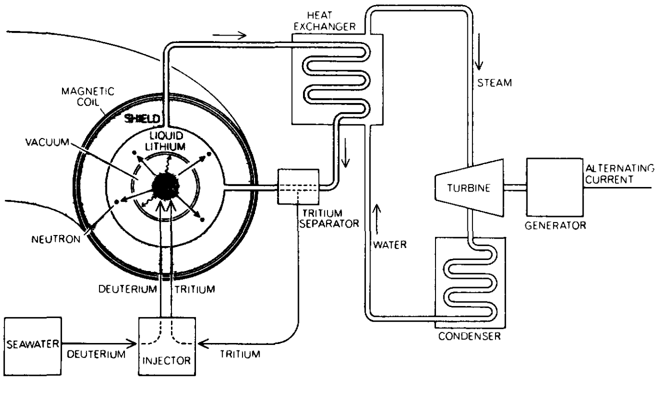


FIGURE 10.—Liquid lithium blanket design for a fusion reactor.

FUSION POWER DEVELOPMENT PLAN

Let us look at the four basic approaches to fusion power reactors. The Division of Controlled Thermonuclear Research presently studies the theta-pinch, the mirror, and the tokamak concepts (fig. 12). Both the theta-pinch and the mirror approaches are regarded as backup to the tokamak approach, so I will focus on the latter as being typical of what might be a commercial fusion power reactor after the turn of the century. Figure 13 is an artist's rendering of such a plant. Since the inertial confinement concept is not part of my program I will not discuss it at all, but mention that the laser fusion reactor is equally as probable as a tokamak fusion reactor.

The development of tokamak fusion reactors is planned such that a demonstration commercial fusion power plant will be built before the turn of the century. Figure 14 presents the current plan to achieve this goal. The first major fusion facility designed to burn deuterium and tritium will be the Tokamak Fusion Test Reactor presently planned to operate in the 1980–1981 time frame. This is a plasma physics experiment which will release significant quantities of thermonuclear power but will be incapable of producing any net electrical power. The subsequent experiment is called the first Experimental Power Reactor. This machine will operate in the 1986–1988 interval and probably will be capable of producing net electric power from the fusion process. It probably will not be a complete fusion power reactor in the sense that it is not likely that tritium will be bred in sufficient quantities to maintain the fuel cycle equilibrium. The provision for fuel-cycle equilibrium may add unnecessary complexity which could compromise the design goal for the machine. However, the second experimental power reactor, presently planned for operation in the 1990–1991 time frame, would be a miniature fusion power electric plant. This machine would demonstrate the technologies of all future fusion power reactors but would not provide the basis from which vendors and utilities could assess the economic viability of the concept. The last experimental power reactor, the Demonstration Fusion Power Plant (DEMO), would operate before the end of the century and would provide the basis for an economic assessment of the viability of fusion power as an alternative to other energy supply options that may exist at that time. The DEMO will be a small scale commercial fusion power plant.

Of course the development schedule presented above depends upon the solution to a number of significant technical problems that have been identified at this time.

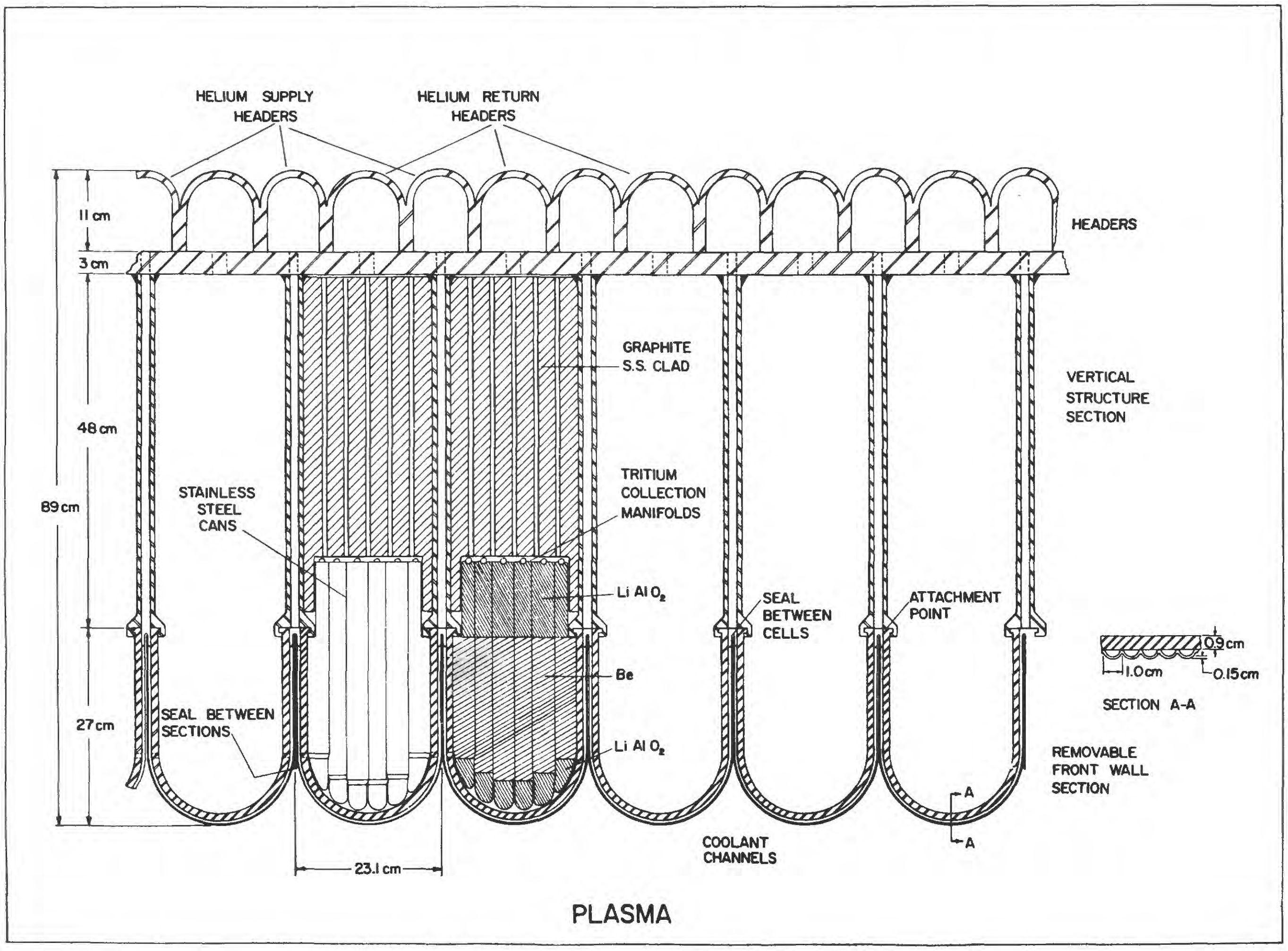


FIGURE 11.—Blanket design using enriched lithium-6 and neutron multipliers.

Perhaps foremost among these is the development of materials which are highly resistant to the energetic reaction products that result from the fusion process. These materials will be exposed to neutron and charged particle flux and will experience the potential for damage not yet observed in reactor engineering. This problem was early recognized and an intensive program is underway to test selected materials in a simulated fusion radiation environment and to develop new materials which are resistant to fusion radiation. The prognosis is optimistic because of the experience in fission technology and the lead time intrinsic to the program. However, the effect of materials problems on economics has yet to be demonstrated.

The second major problem (characteristic) of the fusion process is recirculating power and the need for energy storage and transfer. With all known controlled fusion concepts, a significant amount of power will be required to bring the fuels to reaction conditions and temperatures. For example, although the tokamak seems least demanding in this respect, calculations indicate that perhaps 500 MW(e) over 10 seconds may be required for reactor start-up. In principal, the energy produced by the fusion reactions will be significantly larger than the invested energy providing that the burn time is reasonably long. However, for shorter burn times or lower duty cycles, there may be strong economic incentives to recover the invested energy at a high efficiency at the end of the burn. Answers to this problem are now significantly inconclusive because it is not yet clear what the duty cycle of a tokamak reactor may be.

A third problem facing fusion by magnetic confinement is the development and construction of superconducting magnets which are more than several times larger than the present state-of-the-art of this technology. Superconducting magnets are necessary because the energy balance of the facility cannot tolerate the use of normal conducting copper or aluminum magnets. Large superconducting magnets have been built for physics facilities such as the Brookhaven National Laboratory and the Argonne National Laboratory bubble

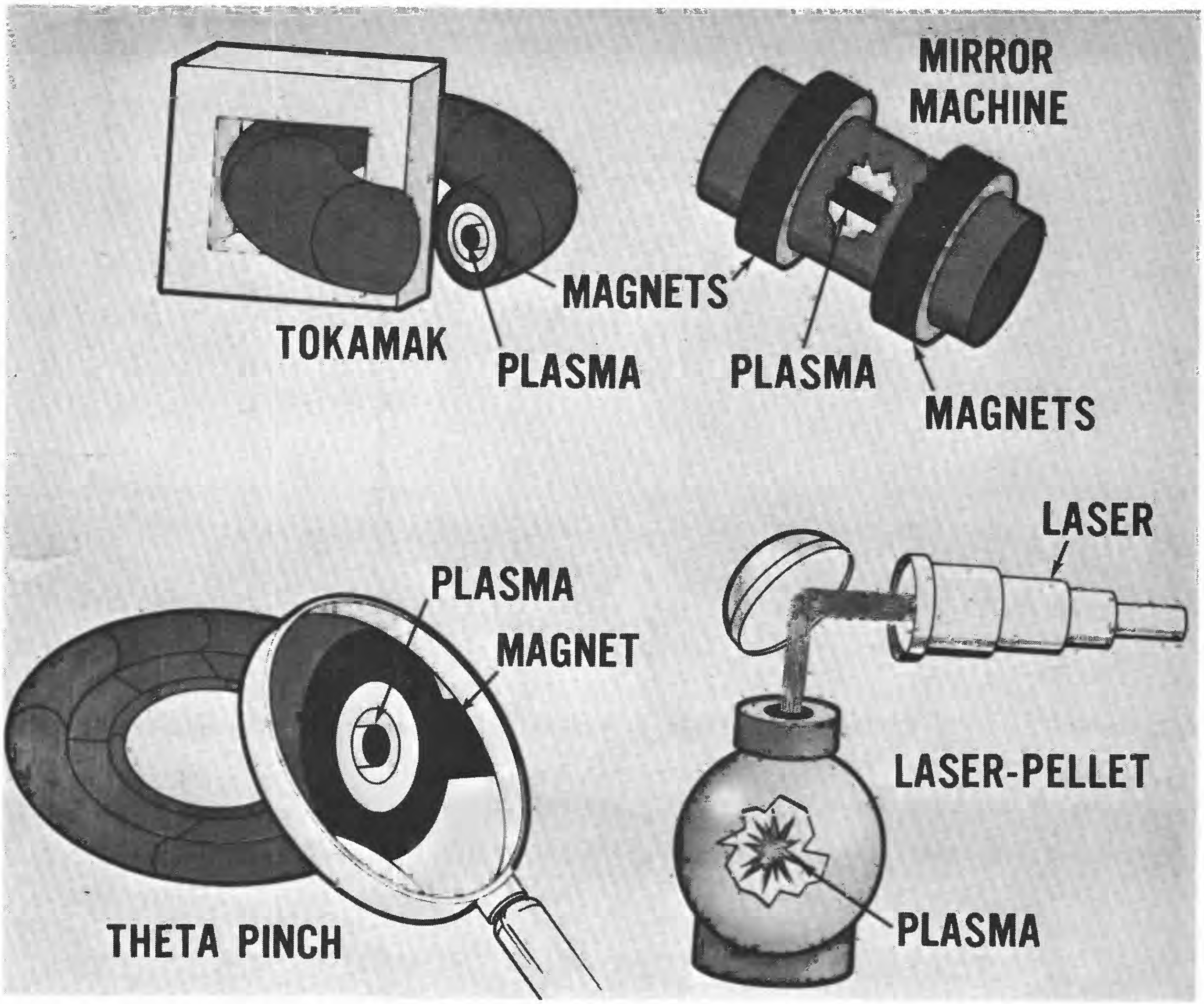
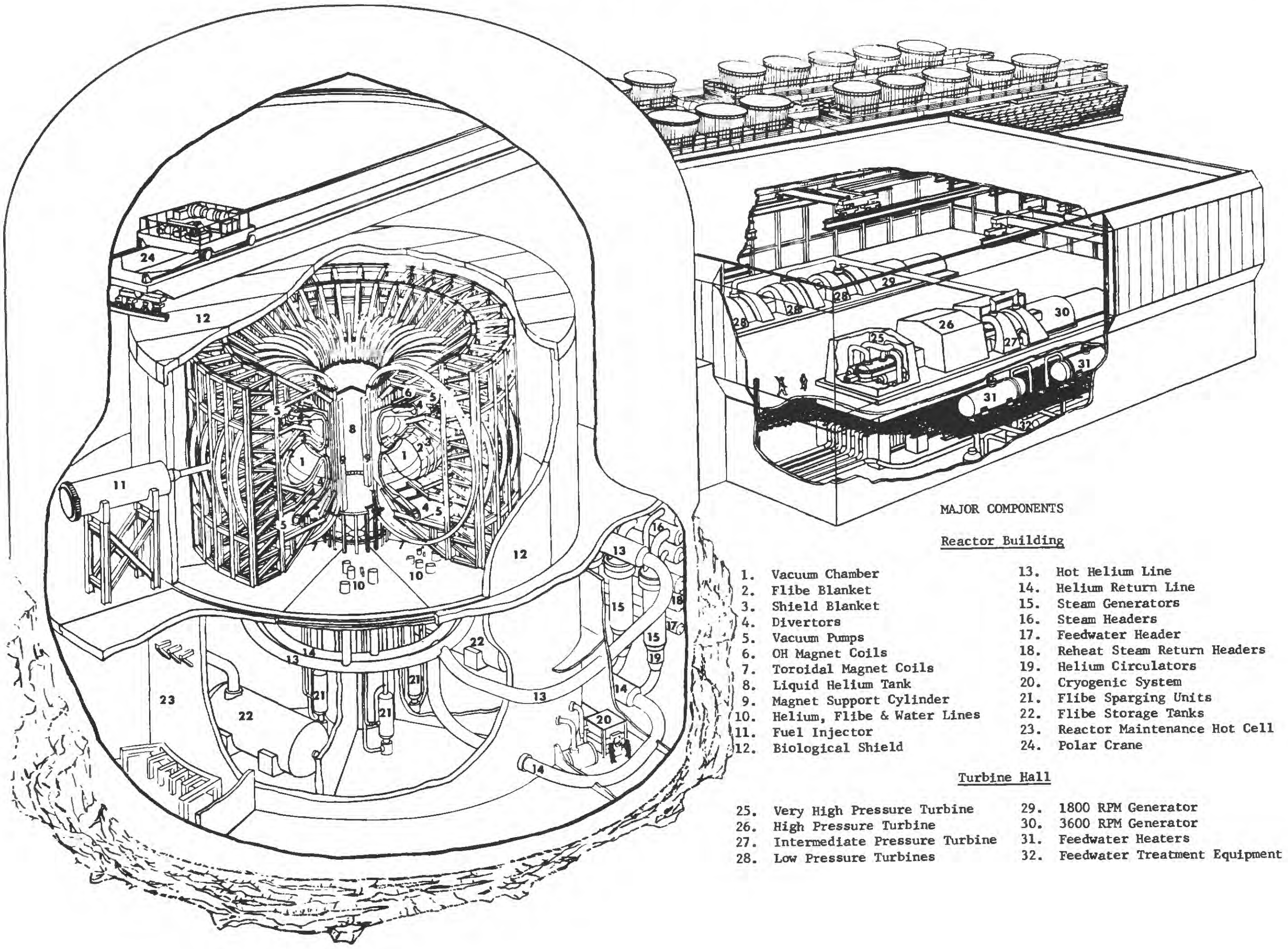


FIGURE 12.—Comparison of four basic designs for fusion power reactors.

chambers, but these are of a very simple solenoidal design. Further, these are by a factor of two or more smaller than those which will be required in a tokamak fusion power reactor. But size is not the most important criterion; for toroidal systems, the superconducting magnet set must be built in the shape of a doughnut. is is not clear how the complex magnetic field and force structure will affect the stability of such magnet sets and especially how these forces may prescribe the structural material necessary to make the device rigid. A major part of the Development and Technology Program of the Division of Controlled Thermonuclear Research is the design and construction of large toroidal superconducting magnet sets.

Another potential problem area arises from the fundamental properties of one of the basic fuels, tritium. Since tritium is mildly radioactive, there are prescribed certain maximum allowable releases either in normal operation or in accident situations. Tritium is an isotope of hydrogen and, consequently, has similar diffusive properties of that element through hot metallic surfaces. The diffusivity of tritium affects the normal release characteristics of a fusion power plant whereas the inventory of tritium in a state which possibly could become volatile affects the accidental release characteristics. In either case it is felt that adequate tritium confinement will be achieved, but with a nontrivial effect on the economic parameters of the fusion power plant.

It is evident that the fusion power development schedule can be affected strongly by the degree of difficulty of these and other problems. Also becoming evident as inhibiting the development of pure fusion



MAJOR COMPONENTS

Reactor Building

1. Vacuum Chamber
2. Flibe Blanket
3. Shield Blanket
4. Divertors
5. Vacuum Pumps
6. OH Magnet Coils
7. Toroidal Magnet Coils
8. Liquid Helium Tank
9. Magnet Support Cylinder
10. Helium, Flibe & Water Lines
11. Fuel Injector
12. Biological Shield
13. Hot Helium Line
14. Helium Return Line
15. Steam Generators
16. Steam Headers
17. Feedwater Header
18. Reheat Steam Return Headers
19. Helium Circulators
20. Cryogenic System
21. Flibe Sparging Units
22. Flibe Storage Tanks
23. Reactor Maintenance Hot Cell
24. Polar Crane

Turbine Hall

25. Very High Pressure Turbine
26. High Pressure Turbine
27. Intermediate Pressure Turbine
28. Low Pressure Turbines
29. 1800 RPM Generator
30. 3600 RPM Generator
31. Feedwater Heaters
32. Feedwater Treatment Equipment

FIGURE 13.—Artist's conception of a tokamak fusion power reactor plant.

power is the inadequate commitment of both public and private sector funds necessary for the prerequisite research to enable commercial fusion to be demonstrated in this century. This is an institutional problem arising from the reluctance to commit near term funds for long term benefits and seems to be endemic to all long term energy supply options. For the sake of argument, the balance of the analysis presented in this paper will assume that adequate funding is provided for the fusion power research and development program.

ASSUMPTIONS AND ANALYTICAL TECHNIQUE

Fundamental to this analysis as well as any other resource demand projection is how the ultimate demand is expected to grow in future years. For pure fusion reactors, the basic product will be electric power for which there now exist a number of projections, many of which have electric power growing at the near historical or historical rate. However, recent estimates are not as generous with electric power production growth, and I will use these as they represent a fairly realistic scenario. Two cases are extrapolated from data in the Project Independence Report which was published little more than one year ago (fig. 15). The first scenario is defined as the Base Case which is the continuation of present electric energy growth trends with a smaller growth rate after the year 1990 as a result of conservation. The Base Case assumes no significant change in energy use patterns with the growth of electrical energy demand principally based upon population expansion. The second case is called the Massive Shift which assumes essentially the same total energy use as the base case but that many energy uses now satisfied by conventional fuels will be satisfied by electricity. This projection could come about if nuclear energy thrives and is competitive in historical nonelectric final use categories or if coal cannot be converted competitively to nonelectric energy products.

The selected implementation schedule for fusion power reactors as presented in figure 16 follows trends exhibited by other high technology programs (for

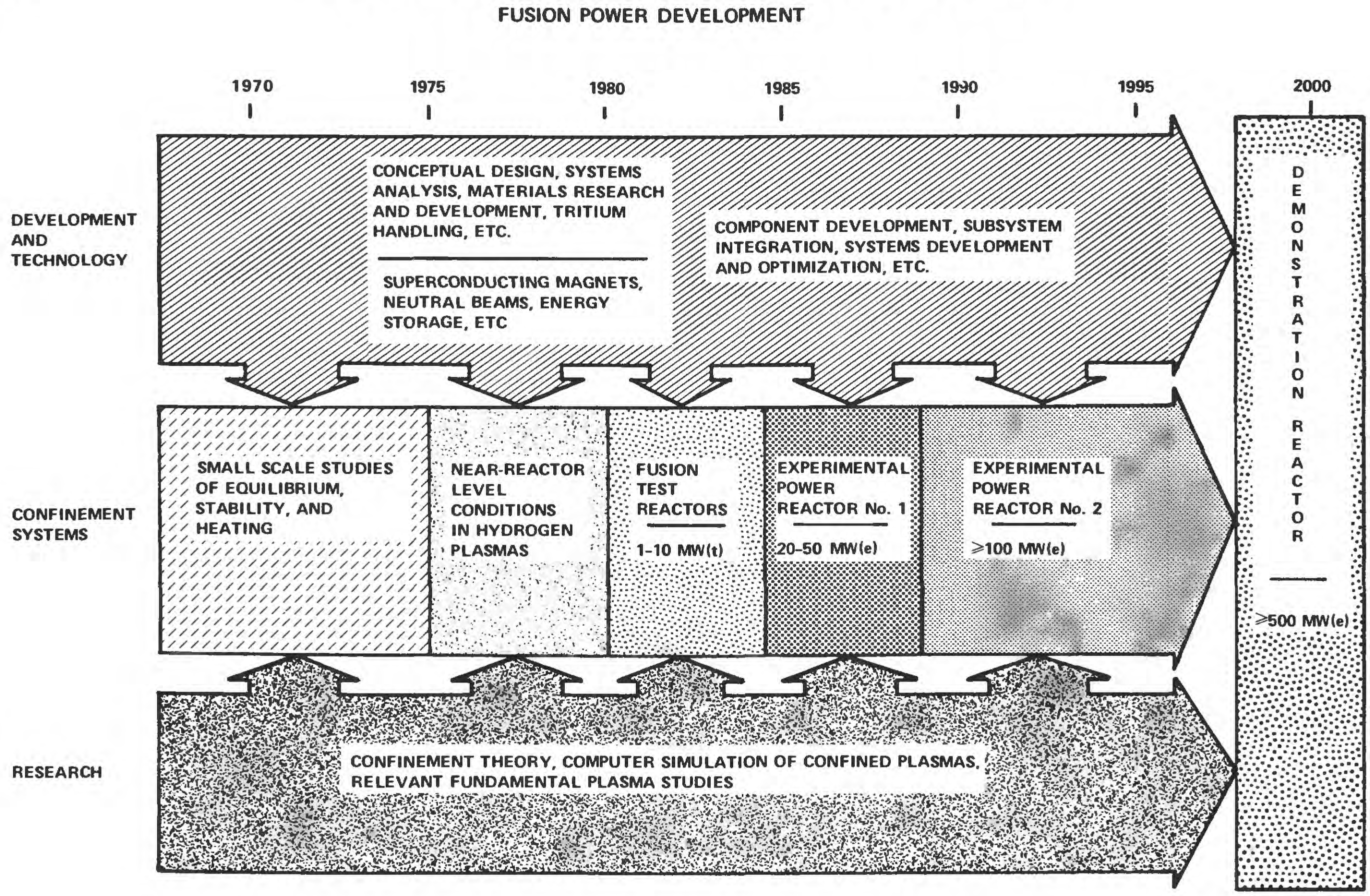


FIGURE 14.—Fusion power development plan.

example, nuclear fission, space exploration, and so forth). The point in time at which implementation begins is chosen by the following arguments.

Commercial fusion power reactors will be built after utilities and vendors are satisfied that fusion power is an energy source competitive with alternative technologies. Purchasing decisions will depend on the total cost of fusion power as compared with that of competing technologies. Disadvantageous characteristics of all energy sources are assumed to be included in costs. This accounting procedure is not uniformly practiced today but certainly will be before the end of the century.

If the DEMO is operating in 1998, then it is expected that the first order for a commercial reactor will be placed several years later, say in the year 2000. Subsequent orders would be placed in a fashion typical of most new technologies. Assuming that the time from order to operation is seven years, achievable for nuclear plants today, then the operation of the first commercial reactor would not take place until the year 2007. We will take this point in time as the implementation date of commercial fusion power with the implementation rate following the order rate but lagging by seven years. Consequently, we assume for the sake of this assessment that lithium will not be required for fusion power reactors in commercial quantities until the year 2007.

Note that fusion electric power does not take over the market completely. This occurs because there usually will be cases where unique circumstances make an alternative more attractive (economically, environmentally, socially). The saturation level here is taken to be about 80 percent of new orders, but there is no quantitative basis for this choice. The effect, however, is not too important.

This reactor type we will consider is the tokamak as this concept seems the most promising at this time. Since the breeding characteristics of fusion reactors are relatively design independent, this choice will not bias the analysis. Two types of blankets will be considered which represent the extreme of the lithium demand range. Table 9 presents the inventory and annual replacement lithium requirement for both concepts. The first type is the liquid lithium blanket which performs the simultaneous functions of tritium breeding and reactor cooling. This blanket type has a large lithium inventory but has such a small fractional burnup rate of lithium-6 that periodic refueling is normally not required. The second blanket type is the gas cooled solid lithium breeder

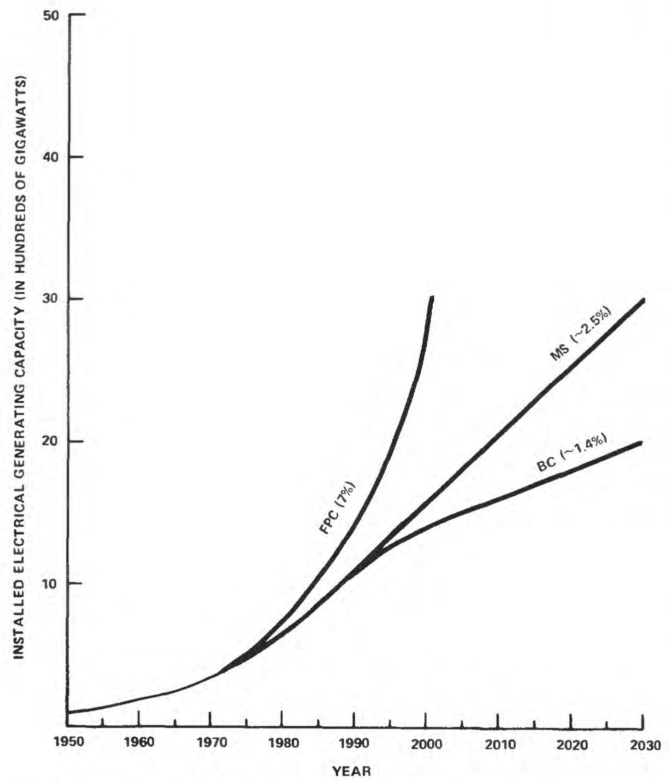


FIGURE 15.—Installed electrical generating capacity as a function of time for Project Independence Base Case and Major Shift to Electricity scenarios with the FPC 7 percent growth rate for comparison. BC, Base Case, MS, Massive Shift, and FPC, Federal Power Commission.

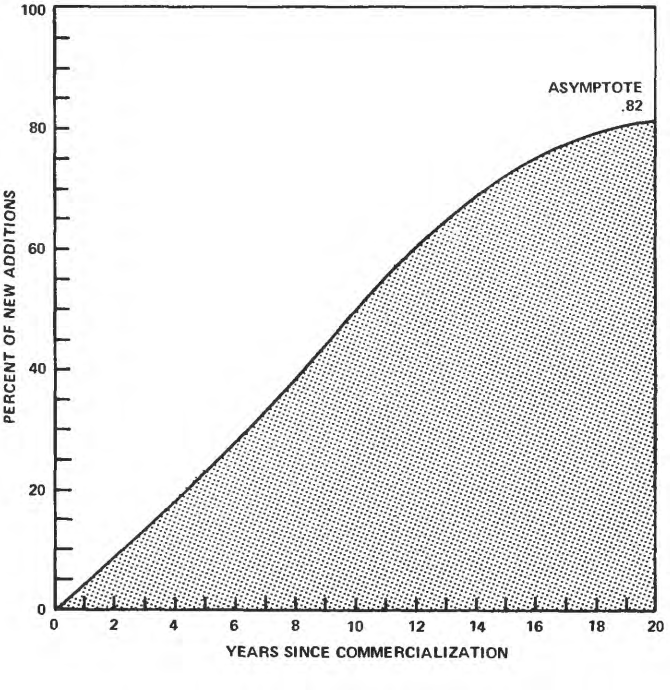


FIGURE 16.—Projected penetration of fusion into electrical generating market.

TABLE 9.—*Blanket lithium requirements*

	Liquid[1] breeder/coolant (MT/MWe)[3]	Solid[2] breeder (MT/MWe)	
	Natural	High tails (2.5 percent)	Low tails (0.3 percent)
Inventory	1.15	.0553	.03918
Annual replacement*	0	.00338	.00239

*At a thermal conversion efficiency of 40 percent and a plant factor of 80 percent.

[1] UWMAK-I University of Wisconsin Blanket.

[2] UWMAK-I Brookhaven National Laboratory Blanket.

[3] MT, Megatonnes.
MWe, Megawatts electric power.

which is enriched 90 percent in the isotope lithium-6. Very small lithium inventories are required but there is need for a neutron multiplier such as beryllium to achieve a tritium breeding ratio of greater than unity. Furthermore, the fractional burnup rate of lithium-6 is relatively high and frequent refueling is required (perhaps as often as two years).

A notable feature of the gas cooled solid breeder concept is that the lithium material "tails" resulting from the enrichment process (depleted in lithium-6) become available for non-nuclear applications. Consequently, the lithium demands computed for this particular blanket concept are not absolute in the sense that all the lithium is removed from the marketplace.

The natural lithium demand in the *i*th year for fusion power reactors, being commercially implemented in the year 2007, is defined to obey the following expression:

$$D_i = XI_i + Y(A_{i-1} + I_i/2),$$

X ≡ Natural lithium inventory demand in Kg/MW(e) of installed fusion reactor capacity,
I_i ≡ Incremental fusion reactor capacity in MW(e) installed in the *i*th year,
Y ≡ Natural lithium required to replace burn-up in Kg/MW(e) of installed fusion reactor capacity with an 80 percent duty factor and a conversion efficiency of 40 percent,
A_{i-1} ≡ Cumulative installed fusion reactor capacity in MW(e) at the end of the $(i-1)$th year.

The accumulated natural lithium demand at the end of the year j simply is

$$D = \sum_{i=1}^{j} D_i = D_1 + D_2 + \ldots + D_{j-1} + D_j.$$

For the case of the solid breeder enriched in the isotope lithium-6, the natural lithium demand as a function of enrichment is calculated from the following expression

$$X \text{ (or } Y) = Z \left[\frac{(a-b)}{(.0742-b)}\right],$$

where

X or Y ≡ Natural lithium feed per MW(e) of installed fusion reactor capacity,

Z ≡ Enriched lithium feed per MW(e) of installed fusion reactor capacity,

a ≡ The percentage of the Li-6 in the fusion reactor fuel,

b ≡ The percentage of the Li-6 in the lithium enrichment plant tails,

.0742 ≡ The Li-6 fraction of natural lithium.

The natural lithium demand associated with the solid breeder concept will be calculated for two tails fractions. The first case is 2.5 percent lithium-6 remaining in the tails which possibly could represent the most economical process. The second tails fraction is selected to be 0.3 percent which presently is characteristic of the U-235 fraction remaining in depleted uranium. One may wish to have such low tails fraction if lithium were indeed to become a very dear commodity after the turn of the century. In this case, one would attempt to extract as much lithium-6 as possible out of the natural lithium.

RESULTS

Tables 10 and 11 present the annual and cumulative natural lithium demand posed by a growing fusion reactor energy economy for both the Massive Shift and the Base Case. Table 10 suggests what might be required of the lithium industry while table 11 presents the potential impact on the resource base itself. It is clear that the choice of the basic breeder concept strongly affects both the annual and the cumulative demand and is more

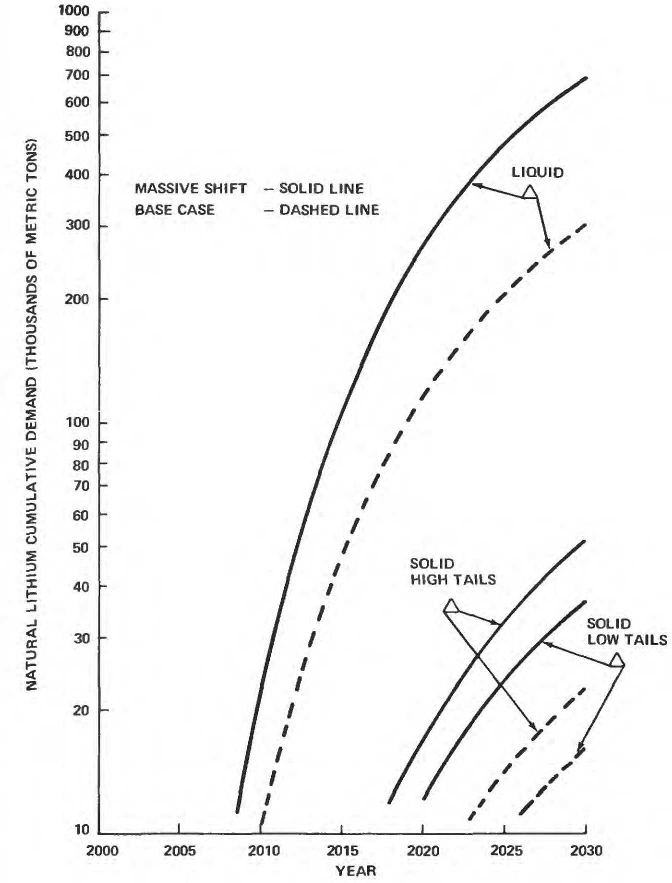


FIGURE 17.—Cumulative lithium demand curve for different reactors.

Table 10.—*Annual natural lithium demand*

	Massive Shift					Base Case				
Year	Electric capacity (GWe)	Fusion capacity (GWe)	Liquid breeder/ coolant (MT)	Solid breeder, high tails (MT)	Solid breeder, low tails (MT)	Electric capacity (GWe)	Fusion capacity (GWe)	Liquid breeder/ coolant (MT)	Solid breeder, low tails (MT)	Solid breeder, high tails (MT)
2000	1600	DEMO	~0	~0	~0	1400	DEMO	~0	~0	~0
2005	1825	DEMO	~0	~0	~0	1500	DEMO	~0	~0	~0
2010	2070	19.8	8,700	470	335	1600	8.6	4,140	220	160
2015	2280	92.6	24,800	1,470	1,040	1700	41.8	10,120	615	435
2020	2525	239.6	38,900	2,620	1,860	1800	101.8	15,870	1,085	765
2025	2770	425.8	42,800	3,440	2,430	1900	180.4	20,490	1,565	1,110
2030	3000	614.4	43,400	5,000	2,900	2010	270.6	20,750	1,880	1,330

TABLE 11.—*Cumulative natural lithium demand*

	Massive Shift					Base Case				
Year	Electric capacity (GWe)	Fusion capacity (GWe)	Liquid breeder/ coolant (MT)	Solid breeder, high tails (MT)	Solid breeder, low tails (MT)	Electric capacity (GWe)	Fusion capacity (GWe)	Liquid breeder/ coolant (MT)	Solid breeder, low tails (MT)	Solid breeder, high tails (MT)
2000	1600	DEMO	~0	~0	~0	1400	DEMO	~0	~0	~0
2005	1825	DEMO	~0	~0	~0	1500	DEMO	~0	~0	~0
2010	2070	19.8	22,780	1,200	850	1600	8.6	9,890	520	365
2015	2280	92.6	106,500	6,080	4,300	1700	41.8	48,070	2,745	1,945
2020	2525	239.6	275,600	16,940	11,990	1800	101.8	117,070	7,245	5,130
2025	2770	425.8	489,700	32,830	23,250	1900	180.4	207,480	13,950	9,880
2030	3000	614.4	706,600	52,050	36,860	2010	270.6	311,210	22,750	16,110

than a factor of 10 larger for the liquid lithium breeder/coolant concept (fig. 17).

For the liquid breeder/coolant concept, the cumulative inventory lithium requirement reaches 7×10^8 kg by the year 2030 in the Massive Shift case. This quantity corresponds to currently reported estimates of between 5×10^8 and 10^9 kg of economically recoverable domestic reserves. For the more conservative Base Case, the demand could exceed the reported reserves by the year 2040, even before the first plant, operating in 2007, was retired. In both cases, the potential cumulative natural lithium requirement for a fusion reactor economy is compared against what presently is regarded as the economically recoverable reserves. Experience shows that as one is willing to spend more for feedstock, more feedstock becomes available. Consequently, the demand posed by liquid lithium coolant/blanket concepts may only serve to increase the lithium supply at a higher, but yet to be quantified, cost.

The solid breeder concepts for both the high and low tails cases are far less demanding on the lithium supply. Furthermore, there does not seem to be a significant advantage to operate at the very low tails fraction of 0.3 percent. This result is placed in even greater perspective by the fact that most of the lithium is returned to the marketplace after the lithium-6 has been removed. For example, with a tails fraction of 2.5 percent Li-6, 94.38 percent of the calculated lithium demand is returned to the marketplace. This compares with only a modest decrease to 92.06 percent if the tails fraction was reduced by a factor more than eight to 0.3 percent. It is evident that only if lithium separative work were to be very cheap or if lithium were to be very expensive would there be an incentive to maintaining a low tails fraction.

CONCLUSIONS

Fusion power reactors may place a significant demand on what presently is thought to be the economically recoverable reserves of lithium if lithium is used for reactor cooling in addition to tritium breeding. The enriched solid breeder concept is far less demanding on the domestic lithium resource since much less feed is required and most of the feed is returned to the marketplace after the Li-6 isotope is removed. However, the solid breeder concept has a neutron deficit which must be made up by using neutron multipliers such as beryllium. Other multipliers exist but all, including beryllium, have potential technological or resource limitations. It is premature to select either the breeder/coolant or solid breeder concept as the most likely candidate for fusion reactors. Furthermore, there may exist attractive alternatives which lie within the lithium demand extremes represented by those two concepts.

The lithium supply should be more than adequate to meet the long term needs of fusion power. Even if the cost of lithium rises to many times its present level, utilization of lower grades of lithium bearing materials, including seawater, appears economic. A paper to be presented later in this symposium will indicate that the cost of lithium extracted from the oceans is only three to four times the present market price. This mild rise in cost is well within allowable limits for fusion power reactors.

Since the question of fuel resources is so fundamental to all energy supply options, we will continue to study the implications of blanket choices on lithium demand. However, with respect to fusion, it is premature to embark on programs to increase the supply or to stockpile material. Fusion power reactors are too far in the future to warrant the expenditure of present funds for these purposes given the current domestic lithium resource estimates.

Our real needs at this time lie in two areas. First, is an assessment of the total domestic and world supply of lithium as a function of both its cost and availability. Second, and perhaps more important, is a coordinated study of the different potential demands for lithium and how they will be met.

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U.S. LITHIUM SUPPLY AND DEMAND AND THE PROBLEMS INVOLVED IN COMPILING STATISTICS

By Hiram B. Wood, U.S. Bureau of Mines, Washington, DC

ABSTRACT

The United States has the reserves and the capability to more than satisfy all current domestic demands for lithium products. For the 1970–75 period, U.S. exports of lithium averaged about 21 percent of U.S. production. The U.S. is the largest exporter of lithium chemicals, exceeding Russia for the past 3 years. Currently, only three U.S. companies are producers of primary lithium products. The total 1974 U.S. published annual production capacity was about 4,500 metric tonnes (5,000 tons) of contained lithium. For the 1970–74 period, U.S. production ranged from 65–70 percent of world estimated production. Predicting the future demand for lithium products requires predicting the future growth of the many industries that use lithium products. For the 1970–74 period, the industry grew at the rate of 6 percent per year. Because of the current worldwide industrial slump, the 1975 growth was much lower, and a conservative growth rate of 5 percent annually is predicted through 1980. But a breakthrough, such as in nuclear fusion or lithium batteries, could by 1980 double the 1975 demand. The compilation of dependable statistics has been hampered by the lack of standard terminology, by difficulties with surveys, and by some reluctance on the part of private companies to reveal their production.

The United States and the world in general have the lithium reserves and the capabilities to supply demands at the current growth rate at least through this century. The 1975 world production and/or demand was about 6,300 tonnes (6,900 tons) of contained lithium. During the 1970–74 period, the United States exported about 20 percent of its production, and U.S. exports equaled about 14 percent of world production. For the same period, the U.S. accounted for 65 to 70 percent of world production.

Throughout the world, in the 1972–74 period, demand for lithium carbonate by the aluminum and ceramic industries increased notably. Demand for lithium hydroxide also continued strong. Demand decreased during the last quarter of 1975 making 1975 production about the same as 1974. Details on world trade of lithium compounds are available from trade tables published by the major industrial countries. Most of these countries, including West Germany, Italy, and France, import both raw mineral concentrate and lithium compounds and then export a variety of lithium chemicals and lithium metal. Only the United States and Russia are known to produce lithium mineral concentrate and to support significant quantities of lithium compounds and lithium metal.

Until 1965, the largest producer and exporter of mineral concentrate, mostly petalite, was Rhodesia. At that time the United Nations applied trade restrictions to that country, and since then export figures for Rhodesia have been obscured. On the Bureau of Mines world production tables, it was assumed that Rhodesia had continued to mine at the same rate of about 860 metric tonnes (950 tons) of contained lithium in mineral concentrates as in 1965. Based on verbal information, however, their production decreased greatly in 1974 and 1975.

There are only three U.S. producers of lithium, and two of these have been responsible for 98 percent of domestic output; consequently, the U.S. Bureau of Mines cannot publish domestic production figures received from these companies. However, the Bureau can use production capacity data which have been published either in company reports or in trade magazines, and it can publish U.S. Census Bureau export and import figures. From these data, we have prepared table 12.

All figures in table 12 are shown as tons of contained lithium. Three classes of marketable material are presented. As previously explained, lithium mineral production figures for the United States, which were reported to the U.S. Bureau of Mines as spodumene flotation concentrate containing 5 to 6.8 percent lithium oxide, are not shown. They have been small and erratic. Imports, which are mostly lepidolite, have been small.

The production of lithium compounds and metal represent published figures. These figures of estimated production capacity, consumption, and exports were compiled from different sources. The United States production estimates published by Lithium Corporation of America (LCA) and by the Canadian Department of Energy indicate an 8 percent annual growth rate. The estimate by Roskill Information Service for only a 3-year period indicates only a 4 percent growth rate. These estimates appear to be realistic, considering U.S. industry demands and exports, but the production tonnage estimates for 1972 through 1974 are notably different. From these figures, it is apparent that the United States production for 1974 and 1975 was between 4,200 and 4,600 tonnes (4,600 and 5,100 tons) of lithium.

The sale by the U.S. General Services Administration (GSA) of lithium hydroxide monohydrate from excess stocks is listed to show how much of this material has been made available to industry. These were published sales with the material going to the highest bidder whether a U.S. or a foreign country. All of this lithium hydroxide monohydrate came from USAEC (now U.S. Energy Research and Development Administration,

TABLE 12.—*U.S. salient lithium statistics*
[Lithium content in short tons (tonnes in parentheses)]

	1970	1971	1972	1973	1974	[e]1975
Lithium mineral concentrate:						
Shipments:						
Chemical and ceramic grade	W	W	W	W	W	W
Exports	------	------	------	66 (60)	81 (73)	38 (34)
Imports[1]	63 (57)	128 (116)	36 (33)	170 (154)	88 (80)	NA
Lithium compounds and metal marketed:						
Production est. Lithcoa[2]	2,444 (2,217)	2,820 (2,558)	3,008 (2,729)	3,290 (2,985)	NA	NA
Production est. Canadian[3]	3,200 (2,903)	3,200 (2,903)	3,600 (3,266)	4,280 (3,883)	[e]4,700 (4,264)	5,170 (4,690)
Production est. Roskill[3]	NA	NA	5,120 (4,645)	5,450 (4,944)	5,820 (5,280)	NA
Exports of metal and compounds[3]	747 (678)	516 (468)	503 (456)	805 (730)	894 (811)	[e]850 (771)
Lithium hydroxide ($LiOH \cdot H_2O$):						
Exports[1]	113 (103)	39 (35)	91 (83)	86 (78)	99 (90)	NA
General Services Admin.						
Excess sales	None	None	None	157 (142)	433 (393)	61 (55)
Price per pound	------	------	------	$0.65	$0.87	$0.95
Inventory, Dec. 31	1,071 (972)	1,071 (972)	1,071 (972)	914 (829)	482 (437)	420 (381)
Yearend prices:						
Spodumene mineral concentrate, per ton	NA	NA	$80	$88	$107	$130
Lithium carbonate, per pound	$0.52	$0.54	$0.55	$0.58	$0.78	$0.80
Lithium metal, per pound	$8.17	$8.17	$8.43	$8.53	$9.38	$11.30

[e] Estimate; W, withheld; NA, not applicable.

[1] U.S. Census Bureau and Roskill Information Service.

[2] Source: Roskill Information Service, p. 30

[3] Source: Roskill Information Service. Production by Canadian Department of Energy and Resources, p. 30, 1974–75 projections by USBM; Exports of Metal and Compounds, p. 9: Production estimate by Roskill, p. 32.

ERDA) stockpiles and was devoid of the isotope, lithium-6. A recent published report stated that ERDA has in stock about 36 million kg (80 million pounds) of lithium hydroxide monohydrate.

For those who are not familiar with the prices of the major lithium products, table 12 lists the approximate yearend price for spodumene mineral concentrate, lithium carbonate, and lithium metal from the Chemical Marketing Reporter. The price of lithium mineral concentrate increased more than 60 percent in the past 4 years, and lithium carbonate increased more than 45 percent.

The estimated world capacity, by country, and total estimated world production from 1970 through 1975 are shown on table 13. The tonnage estimates compiled by the U.S. Bureau of Mines may disagree notably from the world consumption estimates by Luckenback and from the production estimates by the Canadian Department of Energy and Mines as shown on the bottom two lines. The totals do not include GSA stockpile sales, but they do include tonnages of similar lithium hydroxide monohydrate, also devoid of isotope lithium-6, which were exported from the USSR. The U.S. Bureau of Mines world production figures indicate, for the 1970–74 period, a 6 percent annual growth. The estimated world production capacity figures for the same period indicate a 9.4 percent annual growth, and Luckenbach's figures for the same period indicate a 10.5 percent annual growth.

Table 13 shows that the United States, Russia, Rhodesia, Brazil, and South Africa have been and still are the major mineral producing countries. Although there does not appear to be much difference between the estimated production and the estimated production capacity, the important implication shown is that, if necessary, world production can in 1 or 2 years be increased 25 to 30 percent. Beyond that, new mines would have to be opened and new beneficiation and chemical plants built. The most significant production increases can most readily come from the United States, Canada, Rhodesia, Russia, Southern Africa, and Brazil. In time and with proper demand, new production may be realized in Chile and Zaire. The Zairetain mining company recently announced plans to build a $4 million spodumene concentrator at Manono.

Table 14 is included to show world trade for lithium. The exports from the United States, Russia, West Germany, and some other countries were derived from published trade statistics and show shipments mostly to western European countries and to Japan. This table shows West Germany as both a major importer and exporter, but they are not a primary ore producer. Trade data on the United Kingdom and Canada should be included in this table, but 1974 trade books from these countries had not arrived. This table does not show all world trade shipments, but it is probably 85 to 90 percent complete.

In general, current market conditions and future predictions are favorable.

Although the 1970–74 growth rate averaged 6 percent per year, it dropped to about 2 percent in 1975, and unless industry rebounds notably in 1976, the growth this year will not be much better. However, any good growth in any one of the major consuming indus-

TABLE 13.—*Estimated maximum world production capacity of lithium contained in mineral concentrate or brine solutions*
[Short tons (tonnes in parentheses)]

	1970	1971	1972	1973	1974	*e*1975
United States	3,600	4,000	4,500	5,000	5,200	5,500
	(3,266)	(3,629)	(4,082)	(4,536)	(4,717)	(4,990)
Argentina	5	5	5	10	10	10
	(4.5)	(4.5)	(4.5)	(9)	(9)	(9)
Australia	20	40	40	40	30	30
	(18)	(36)	(36)	(36)	(27)	(27)
Brazil	60	120	150	150	150	150
	(54)	(109)	(136)	(136)	(136)	(136)
Canada	40	40	40	90	90	100
	(36)	(36)	(36)	(82)	(82)	(91)
Mozambique	10	10	20	20	20	10
	(9)	(9)	(18)	(18)	(18)	(9)
Portugal	10	20	25	40	40	10
	(9)	(18)	(23)	(36)	(36)	(9)
South Rhodesia	950	950	950	950	950	950
	(862)	(862)	(862)	(862)	(862)	(862)
South Africa, Republic of, and Southwest Africa	100	250	250	250	300	300
	(91)	(227)	(227)	(227)	(272)	(272)
U.S.S.R.	700	1,500	1,500	1,800	1,800	2,000
	(635)	(1,361)	(1,361)	(1,633)	(1,633)	(1,814)
Total world capacity	5,495	5,935	7,480	8,350	8,590	9,060
	(4,985)	(5,384)	(6,786)	(7,575)	(7,793)	(8,219)
Total world production[1]	5,100	5,300	5,900	6,500	6,800	6,900
	(4,627)	(4,808)	(5,352)	(5,897)	(6,169)	(6,260)
Total world consumption W. F. Luckenbach[2]	3,055	2,886	3,478	4,653	5,020	NA
	(2,771)	(2,618)	(3,155)	(4,221)	(4,554)	
World lithium production[3]	5,060	5,290	5,842	6,532	NA	NA
	(4,590)	(4,799)	(5,300)	(5,926)		

*e*Estimated; NA, not applicable.

[1] U.S. Bureau of Mines.

[2] Source: Mining Journal, Mining Annual Review (1975, p. 112).

[3] Canadian Department of Energy Mines and Resources.

TABLE 14.—*World trade*
[Imports of lithium compounds and lithium metal as short tons of contained lithium (tonnes in parentheses)]

Importing countries[1]	Exporting countries									
	U.S.A.		U.S.S.R		West Germany		Other countries		Total	
	1973	1974	1973	1974	1973	1974	1973	1974	1973	1974
Belgium and Luxemborg	2		13		33	56	12	----	60	56
	(1.8)		(11.8)		(30)	(51)	(10.8)		(54)	(51)
France	75	77	59	36	91	70	----	29	225	212
	(68)	(69)	(54)	(33)	(83)	(64)		(26)	(204)	(192)
Italy	11	3	----	----	68	55	47	19	126	77
	(10)	(2.7)			(62)	(50)	(43)	(17)	(114)	(70)
Japan	301	375	305	302	----	----	----	7	606	684
	(273)	(340)	(277)	(274)				(6.4)	(550)	(621)
Netherlands	3	11	----	4	24	26	----	1	27	42
	(2.7)	(10)		(3.6)	(22)	(24)		(0.9)	(24)	(38)
West Germany	322	327	264	104	----	----	72	41	658	472
	(292)	(297)	(239)	(94)			(65)	(37)	(597)	(428)
Other countries[3]	111	115	NA	NA	119	78	NA	NA	230	193
	(101)	(104)			(108)	(71)			(209)	(175)
Total	825	908	641	446	335	285	131	97	1,932	1,736
	(748)	(824)	(582)	(405)	(304)	(259)	(119)	(88)	(1,753)	(1,575)
			*e*750	*e*550						
			(680)	(499)						

*e*estimated; NA, not applicable.

[1] Data from trade tables of respective importing countries, exclusive of United Kingdom.

[2] Data from West German export tables.

[3] U.S. exports of lithium hydroxide to other countries were estimated, based on partial data.

tries will certainly reflect a proportional increase in lithium demand. When one tries to predict the future demand for lithium and its seemingly unlimited number of compounds, one also has to predict the future growth for such industries as the aluminum, ceramic, glass, rubber, refrigeration, nonferrous alloys, industrial machinery, and organic chemicals, and also the unpredictable potential demand for automobile batteries, for nuclear fusion reactors, and the switching to absorption refrigeration to avoid use of fluorocarbons. A 5 percent per annum growth over the next 5 years is a conservative but practical estimate. Increased use of lithium carbonate by aluminum companies who currently do not use lithium carbonate to improve the thermal stability and electrical conductivity of their potlines will account for most of this growth. Undoubtedly, this is why Foote Mineral Company is building a new carbonate plant at Kings Mountain and why LCA, in their 1974 annual report, discussed plans to increase their output 50 percent. Without a scientific breakthrough, the conservative 5 percent annual growth would easily require by 1980 at least an additional 1,180 tonnes (1,300 tons) of lithium or 6.35 million kg (14 million pounds) of lithium carbonate. A higher growth rate for the European nations and Japan is anticipated because more severe energy shortages could force them to use more lithium carbonate in their aluminum smelting potlines.

In view of the present embryo state of the lithium industry, I think a U.S. demand of about 5,700 tonnes (6,300 tons) and a world demand of 9,070 tonnes (10,000 tons) of lithium by 1980 is reasonable. However, a breakthrough in any of the potential fields just mentioned could triple the growth rate to 15 percent annually. If the growth should increase 15 percent annually by 1980, U.S. and world production would have to double to 9,100 and 12,700 tonnes (10,000 and 14,000 tons) annually.

A warning on overenthusiasm in predicting future growth should be given because even if there is a breakthrough in 1976 or 1977, the consuming industry could not tool up and make the changes necessary to demand this much more lithium by 1980.

Terminology is one of the worst problems involved in compiling U.S. and world lithium statistics because production may be reported as lithium ore, lithium mineral concentrate, or lithium compounds. Often the lithium or lithium oxide content of the ore or concentrate is not given. If the kind of lithium mineral concentrate, such as spodumene, petalite, lepidolite, or amblygonite is listed, a fair estimate of the lithium content may be made. But in the international trade books, which list foreign shipments, lithium assays are seldom recorded. For years, the U.S. Bureau of Mines, in the producers canvass survey, has asked for shipments of lithium minerals, but seldom did the producers list the lithium oxide assays. In 1975, a new survey form was designed to be more specific. Also, in the U.S. Census tabulations, only the lithium hydroxide monohydrate is listed separately. All of the other lithium compounds are grouped under a blanket category which may include lithium amide, borate, bromide, chloride, carbonate, fluoride, and so forth. Also, the producing companies, in their annual reports or in trade magazines, report capacity and sometimes U.S. production as lithium carbonate equivalent. Usually, the lithium carbonate equivalent includes only the lithium compounds, some 30 or more that are produced commercially, and lithium metal. These estimates may or may not include the lithium mineral concentrate produced. Only the lithium companies can standardize their terminology and permit their output figures to be published; however, with only two significant, competitive companies in the industry, there are understandable reasons for their reluctance.

THE LITHIUM INDUSTRY

By Gerald J. Orazem,
Lithium Corporation of America, Gastonia, NC

ABSTRACT

The image of the lithium industry in the past has been clouded by lack of information available to the industrial world. The industry consists of several ore producers and marketers, but only three major basic producers of lithium chemicals; Lithium Corporation of America, Foote Mineral Company, and the USSR. The USSR exports to the Free World, but their supply is unpredictable in any one year. Their exports consist mostly of chemicals depleted in the lithium-6 isotope, a byproduct of their atomic energy program. Foote Mineral extracts lithium from brines at Silver Peak, Nev., and Lithium Corp. from spodumene concentrates in North Carolina. A minor producer is Kerr-McGee Chemical Company at Trona, Calif. Besides the basic producers, there are several converters, the most important of which are Metallgesellschaft in West Germany and Honjo Chemical in Japan. The major lithium chemicals are carbonate for use in ceramics and the aluminum industry, hydroxide in the grease industry, bromide and chloride in air conditioning, hypochlorite in sanitation, metal in pharmaceuticals, and butyllithium in synthetic rubber.

The Free World demand for lithium chemicals, based on carbonate equivalents, was about 21 million kg in 1974 and 17 million kg in 1975. The United States capacity for lithium chemicals was 20 million kg in 1975.

The largest potential in the next 5 years for lithium demand is the aluminum industry. The lithium battery is not expected to have a major impact on the lithium industry until the early 1980's.

LITHIUM RESOURCES—PROSPECTS FOR THE FUTURE

By Ihor A. Kunasz, Foote Mineral Company, Exton, PA

ABSTRACT

The future of the lithium industry will be controlled by the demands for lithium ores, chemicals, and metal. The ability of the lithium industry to meet any large future commitment must be appraised not only in terms of reserves, which are based on economic and legal extractability at the present time, but also in terms of identified resources, which represent sources economically and legally extractable at some time in the future. The point in time at which they will become reserves will be determined by the rate of lithium demand.

Consequently, all important identified resources must be considered if an accurate representation of the potential of the lithium industry is to be made. These resources are:

Tin-Spodumene Belt, North Carolina, U.S.A.
Clayton Valley, Nevada, U.S.A.
Bikita Tinfields, Rhodesia
Preissac-Lacorne District, Quebec, Canada
Bernic Lake District, Manitoba, Canada
Great Salt Lake, Utah, U.S.A.
Salar de Atacama, Chile
Manono-Kitotolo District, Zaire

These represent producing districts, districts with past or planned production, and districts with large identified resources. An evaluation of these deposits and the probability of discovery of additional resources in existing districts suggest that lithium resources will support the needs of the lithium industry for several decades.

INTRODUCTION

In reviewing the recent activity in the field of lithium, it appears that a great deal of attention has been devoted to it. In addition to last year's edition of Industrial Minerals and Rocks, lithium has been reviewed by Norton in U.S. Geologic Survey Professional Paper 820 in 1973, by Industrial Minerals of London in 1974, by Roskill Information Services of London in 1975, as well as by members of the newly created Lithium Exploration Group of the U.S. Geologic Survey. To these one must add the regular annual reviews prepared by the U.S. Bureau of Mines, the Engineering and Mining Journal, Mining Engineering, and Mining Journal. This surge in interest can be attributed to the anticipated potential of lithium in battery and possibly in thermonuclear power development. The continued interest in this fascinating element was amply demonstrated by the impressive attendance at this symposium.

RESERVES AND RESOURCES

The contents of the publications reveal two opposing viewpoints. Some maintain that resources are sufficiently large to satisfy future demands. Others suggest a serious forthcoming shortage by the end of the decade because of the large quantities of lithium predicted for battery and thermonuclear power development.

This disparity of opinion is not unusual or surprising. It is the result of a grave concern over the dependence of our economy on the imports of a significant number of strategic mineral commodities. This has led to a reevaluation of our mineral industry on the basis of a new reserve concept (McKelvey, 1973). This concept has been used by the U.S. Geological Survey in the recent evaluation of the lithium industry (Vine, 1975). In addition to a reserve evaluation, attempts to "estimate" probable lithium yields to be expected from the industry by the year 2000 have also been made. The "estimates" constitute the basis for a shortage prediction by some people.

While recognizing the validity of the reserve concept as it is proposed and applied to the evaluation of the lithium industry at the present time, one must nevertheless exercise great caution in using reserves (and even more, probable yields) to predict the ability of the lithium industry to fulfill future commitments, such as the battery or thermonuclear power. Such commitments are based on tenuous data. A contradiction seems apparent. Since reserves are defined on the basis of present steady state technological and economic conditions, they can only validly predict a steady state future. Demands resulting from battery and thermonuclear power development will create unsteady state conditions which may alter existing technological and economic conditions. For this reason, the future of the lithium industry cannot be precisely, nor validly, predicted on the basis of today's reserves.

This point can be illustrated by lithium's past history (fig. 18). Following World War II, the lithium industry experienced a period of slow growth consistent with commercial demand. In the few years which preceded the Atomic Energy Commission (AEC) program, the industry did not have the capacity necessary to meet the AEC requirements. And yet, within the amazingly short period of 24 months, Foote Mineral Company, Lithium Corporationn of America, and American Potash and Chemicals Corp. were able to meet this excessive demand. Clearly, had the lithium industry been evaluated on the basis of reserves and of "probable yields," the results could not have justified the initiation of an AEC program. In fact, economic parameters had changed drastically, and resources became reserves practically overnight.

While the industry was able to fulfill its commitment by increasing its capacity, the latter caused its downfall as well. From 1955 to 1960, commercial demand for

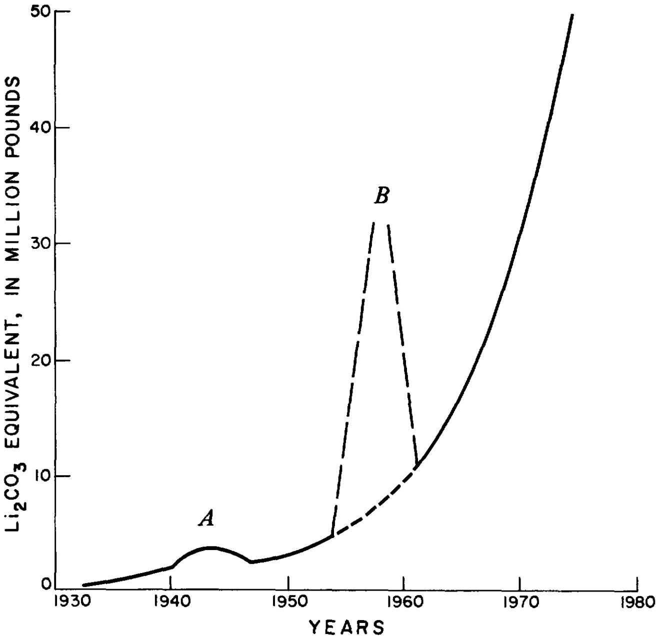

FIGURE 18.—History of lithium production in the United States. *A*, Use (during World War II) of large quantities of lithium hydride to inflate rescue apparatus, and in the development of multipurpose lithium greases. *B*, Lithium purchase program of the U.S. Atomic Energy Commission.

lithium had only doubled, while the industry was faced with a 500 percent overcapacity. Plants operated at about 20 percent of their installed capacity, and the lithium industry experienced a period of economic depression.

In order to determine the ability of the lithium industry to meet future requirements, a comprehensive study of the lithium industry must be made. It is proposed that a valid evaluation can only be made on the basis of identified resources and not on the basis of reserves.

IDENTIFIED RESOURCES

An evaluation of identified resources reveals that in addition to existing producing districts, there are several areas around the world which must be included in a proper evaluation of the lithium industry. These areas contain identified resources (conditional resources) which could justify chemical processing centers in the future. The following paragraphs review existing and potential districts in the United States, Canada, Africa and South America.

TIN-SPODUMENE BELT, NORTH CAROLINA, U.S.A.

As stated by Kunasz (1975), the tin-spodumene belt of North Carolina constitutes the largest developed reserve of spodumene in the world. Following a short period of mining activity during World War II, Foote Mineral Company began the mining of spodumene in 1951. In the 1960's, Lithium Corporation of America opened up its own mine some 5 miles northwest of its Bessemer City, North Carolina plant. Although Foote Mineral Company also produces significant quantities of lithium carbonate from its Silver Peak brine operation in Clayton Valley, Nev., the tin-spodumene district constitutes the most important source of lithium in the world today.

In 1959, when Foote Mineral Company completed its drilling program over the main portion of its ore body, a total resource of about 36,000,000 tons of pegmatite was reported (Kesler, 1960). In the following 16 years, several million tons of ore have been mined out.

The pegmatite belt is known to extend through the remaining portion of the Foote property—its resource potential essentially unknown. As a result of a recent modest drilling program, a resource of 38,000,000 tons has been identified over approximately one-half of the Foote property. Resources on the remaining half of the property are still unknown but will be identified in the next few years. Drilling increased the pegmatite resources by a full 20 percent, not only replacing the mined out ore, but adding several million tons of a new resource.

Lithium Corporation of America has more than doubled its reserves from 13.6 million tons grading 1.4 percent Li_2O to 30.5 million tons grading 1.5 percent Li_2O. A preliminary mining plan indicates that 27.5 million tons are recoverable by open pit mining methods. The outlined pegmatite remains open downdip (Evans, 1976).

Under an extensive exploration program which would take place under conditions of increased lithium demand, the probability of discovery of considerable additional reserves and resources is considered high.

CLAYTON VALLEY, NEVADA, U.S.A.

A benchmark in the history of lithium has been the discovery of this element in the brine of Clayton Valley, Nev. The uniqueness of this brine deposit lies in the fact that lithium is a primary, and not a co- or by-product.

The resources of Clayton Valley have been a subject of controversy and need to be clarified. As pointed out by Norton (1973), the large resources previously reported also included lithium contained in Tertiary and Quaternary lacustrine sediments present in the valley. In the last edition of AIME's Industrial Minerals and Rocks, an updated resource figure was reported (Kunasz, 1975). The new figure of 775,000 tons as Li includes only that amount calculated to be contained in the brine body. In addition, a yield of 44,500 tons of Li as recoverable product was estimated under present economic and technological conditions. This is only a small fraction of the resource present in Clayton Valley. Favorable technological and economic conditions will increase the yield since weaker and deeper hypothetical brine resources are not being exploited or included in published data.

The yield estimate for Clayton Valley has been recently misinterpreted by Vine (1975) in a paper entitled "Are Lithium Resources Adequate for Energy Self-Sufficiency?" Using the published yield of 44,500 tons Li and assuming a 50 percent recovery factor, Vine calculated and reported lithium resources at 90,000 tons, instead of the 775,000 tons reported by Kunasz (1975). In a similar evaluation of the tin-spodumene belt, a probable yield of 680,000 tons as Li is reported. In this case, however, even hypothetical resources have been included in the estimation of the yield. Clearly, the yield from a hypothetical source can only be zero. An artificial set of numbers has thus been generated and used to predict the potential of the lithium industry. The validity of such an evaluation is questionable and, more importantly perhaps, is misleading.

GREAT SALT LAKE, UTAH, U.S.A.

The Great Salt Lake constitutes a considerable resource of lithium. The importance and the reality of this source was well demonstrated when the Gulf Resources Corp. announced production plans. However, since the production of lithium is tied to the production of other salts such as potassium sulfate, sodium sulfate, magnesium chloride, contractual difficulties resulted in a postponement of the project.

Total resources in the Great Salt Lake have been reestimated at 526,000 tons as Li (Whelan, 1976). The quantity of lithium which can be extracted from this body of brine is restricted by the production levels of primary salts and by the efficiency of the extractive technology. An agreement with the State requires Gulf Resources Corp. to return all waste salt streams back to the lake. This eliminates waste disposal problems and results in a more subdued alteration of the brine salinity of the lake.

CANADA

In Canada, there are two significant sources of lithium raw materials. One is located in the Preissac-Lacorne area of Quebec and the other in the Bernic Lake area of Manitoba.

In the Preissac-Lacorne region, several pegmatites occur in an area approximately 8,000 feet long and 2,000 feet wide. The identified resources have been calculated at 15,000,000 tons, carrying 1.2 percent Li_2O (Mulligan, 1965). In 1955, the Quebec Lithium Division of the Sullivan Mining Group estimated their resources to last 45 years at current production rates. The property is developed with an underground mine, a mill, and a chemical plant. Its operational capacity is 1,000 tons of ore per day with a rated capacity of 2,000 tons per day. Although inactive at the present time, the company did operate for a number of years when it supplied the Lithium Corporation of America's North Carolina chemical plant. Following completion of the AEC contract, Quebec Lithium operated at reduced levels until 1965. The overcapacity in the lithium industry created by the 5 year noncommercial demand by the AEC, forced the closure of the operation.

In Manitoba, Tanco began the exploitation of a complex zoned pegmatite which probably constitutes the world's richest tantalum and cesium mine. The pegmatite contains an uncommonly rich spodumene zone which averages almost 3 percent Li_2O. A previously unknown spodumene zone has been intercepted beneath the main spodumene ore body by exploratory drilling (Pearse, 1973). The resources of this new body are unknown. Resources for the main spodumene ore body are reported at 5,000,000 tons.

In 1972, Tanco undertook a pilot plant study to evaluate the possibility of spodumene production. No significant commercial production has yet been achieved, as this company has been plagued by a number of financial problems. In 1974, Kawecki-Berylco Industries bought a 24.9 percent interest. In addition to their cesium and rubidium interest, Kawecki-Berylco plans the production of about 10,000,000 lb of lithium carbonate and about 15,000 tons of spodumene concentrates per year (Pearse, 1973). Production is scheduled to begin in 1977.

BIKITA TINFIELDS, RHODESIA

The Bikita ore body became important in the 1950's as a result of the AEC program. In order to partially satisfy the needs of the program, American Potash and Chemicals processed Bikita lepidolite in Texas.

Although United Nations sanctions have been imposed on Rhodesian trade, eliminating an important source of petalite for the U.S. ceramic industry, Rhodesian ores are still mined and sold.

Resources have been reported at about 6,000,000 tons (Symons, 1961) with an average composite grade of 2.9 percent Li_2O. The pegmatites contain petalite, spodumene, lepidolite, and eucryptite. This appears to be a deposit similar to Bernic Lake in Manitoba. A chemical processing plant is, therefore. not inconceivable.

ZAIRE

The pegmatites of Manono and Kitotolo were discovered in 1910. Exploitation for cassiterite and tantalite began in 1929 when the Belgian company, Geomines, undertook the project.

A report by Barzin, Managing Director of Geomines, states that the pegmatites are both 5.5 km long and average 400 metres wide (Barzin, 1952). The pegmatite sills have been proven to a depth of 125 metres by drilling. A calculation using these dimensions shows that resources are enormous. Barzin reports, however, that up to 50 metres are kaolinized and altered. On the other hand, exploratory drilling ended in pegmatite, indicating the presence of additional resources. Over the years, low cost mining of cassiterite and tantalite has been achieved from the upper decomposed layer. The pegmatites of Manono and Kitotolo probably represent the largest spodumene resource in the world. However, they have never constituted reserves because of their remote location in south-central Africa. The tin and columbium production is exported via the Angolan port of Lobito, located some 2,000 km away. Nevertheless, this deposit must be included in an appraisal of the future of lithium. In fact, the government of Zaire must think so, because plans for the production of lithium carbonate have been officially announced. The document states that Zaire will become the third producer of lithium carbonate in the world. Zairetain (50 percent government controlled) is planning a production of 10,000,000 lb of lithium carbonate per year beginning in 1980.

SALAR DE ATACAMA, CHILE

The latest development in the field of lithium has been the announcement by the Chilean government of the discovery of a large brine field containing unusually high lithium values. The statement indicated concentrations of 2,000 ppm Li and resources on the order of 1,200,000 tons of lithium, presumably as Li.

In January 1975, Foote Mineral Company entered into a contract with the Chilean government and has since undertaken a program of geological, hydrological, and chemical research in order to assess the feasibility of producing lithium chemicals from the brines of the Salar. The Chilean government is also interested in recovering potash in order to develop its fertilizer industry.

The geology of the Salar de Atacama and of the surrounding areas has been described in several publications (Dingman, 1967; Chong, 1971; Moraga and others, 1974; Stoertz and Ericksen, 1974). The Salar has been interpreted as a graben (Frutos, 1972), bounded on the east by the Andean Cordillera and on the western side by the Cordillera de la Sal, a structural block which consists of evaporites including halite.

The Salar lies at an elevation of 7,500 feet. The southern portion consists of a halite nucleus which occupies an area of 1,400 km^2. The surface of the nucleus is very rugged, and the halite occurs as razor-sharp jagged ridges. The area is extremely arid. Several streams drain into the Salar. The largest of these is the Rio San Pedro which enters the basin from the north. Although the resources reported by the government have not yet been verified, the work Foote has done to date supports their earlier claim.

CONCLUSIONS

The deposits which have been described do not constitute hypothetical resources of lithium. These are all reserves or conditional resources.

Today, lithium chemicals are produced in North Carolina (Kings Mountain and Bessemer City); in Virginia (Sunbright); Silver Peak, Nevada; Exton, Pennsylvania; New Johsonville, Tennessee; and Searles Lake, California. Under favorable economic conditions, one may expect production from Quebec and from new centers such as Manitoba, Utah, Rhodesia, Chile, and Zaire.

An evaluation of the resources held in all these deposits yields a total of 4,100,000 tons as Li. If we assume as little as 15 percent recovery from these resources, there is 617,000 tons of Li available (table 15).

If only existing and actually announced capacity is considered, an annual production rate of 90,000,000 lb lithium carbonate may be reached by 1980. This represents 9,000 tons as Li. If we assume a consumption of 200 kg of Li per one thousand MW(e) (Mills, 1975), a 500,000 MW(e) capacity would require 100 tons of metal. This corresponds to the total 1970 U.S. electric power consumption. In addition, approximately 100,000 tons of metal will be needed in the reactor blanket. The projected industrial capacity could supply this quantity in 11 years. Obviously, the lithium industry will not devote 100 percent of its capacity for this exclusive use. However, since such a thermonuclear power capacity is predicted for the year 2020, the industry would have ample time to expand if and when this use appeared likely. The projected capacity suggests that commercial as well as thermonuclear power and battery requirement can be met by the lithium industry.

As a final comment, one must again ask the question of the fate of the lithium industry after the peak de-

TABLE 15.—*Major identified resources of the world*

	Short tons Li	Production	Reference
Tin-spodumene Belt, North Carolina, U.S.A	473,000	Active	Kunasz (1975); Evans (1976).
Clayton Valley, Nevada, U.S.A	775,000	do	Kunasz (1975).
Great Salt Lake, Utah, U.S.A	526,000	Planned	Whelan (1976).
Preissac-Lacorne, Quebec Canada	84,000	Temporarily inactive.	Pearse (1973).
Bernic Lake, Manitoba, Canada	69,000	Announced	Pearse (1973).
Bikita, Rhodesia	81,000	Active	Symons (1961).
Atacama, Chile	1,200,000+	Possible	
Manono, Zaire	1,000,000+	Announced	
Total	4,208,000+		

mand for batteries and thermonuclear power has been met. A hasty increase in capacity installed to meet a projected demand based on tenuous data may have harmful consequences. Existing data suggests that resources are sufficiently large to satisfy projected higher lithium demands in the future. The existing and announced capacity of the industry are likely to satisfy the demands for a considerable number of years.

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LITHIUM ORES

By R. Keith Evans, Gulf Resources & Chemical Corporation,
Houston, TX

ABSTRACT

Chemical differences and commercial advantages of the principal lithium ore minerals—spodumene, petalite, lepidolite, eucryptite, and amblygonite—are described. Ores and concentrates of these minerals are used directly in specialty glasses, glass ceramics, porcelain enamels, fritted glasses, raw glazes, ceramics (whitewares), and refractories. These lithium minerals can also be used in the production of lithium chemicals and lithium metal. The quality requirements for these uses are not as stringent as they are for "direct usage" ores.

An estimate of the demand for "direct usage" lithium ores under conditions of normal trading suggests a probable demand between 3.2 and 4.5 million kg (7–10 million pounds) of lithium carbonate equivalent. The inherent uncertainties in making this estimate are discussed. Potential consumption of "direct usage" lithium ores would constitute a significant percentage of the total Free World lithium production if such ores were more readily available.

LITHIUM MINERALS

Although lithium occurs in a variety of minerals, those of principal economic interest are spodumene, petalite, lepidolite and, to a much lesser extent, amblygonite and eucryptite. In the future, lithium-containing clays could assume some economic significance, but neither clays nor lithium-containing brines fall within the scope of this short paper.

In terms of volume usage, spodumene is much the most important mineral; it constitutes the feed to the western world's current and proposed major lithium chemical plants. In addition, it meets a high percentage of the current demand for "direct use" ore, or concentrate for the manufacture of glasses and similar products. The current bulk of sales for this purpose is as low-iron (about 0.1 percent Fe_2O_3) concentrates grading between 6 and 7 percent Li_2O; historically significant tonnages of a quartz-spodumene intergrowth similar in chemical composition to petalite and grading about 4.5 percent Li_2O have been sold, both for direct usage and chemical manufacture.

Prior to the imposition of the United Nations sanctions against Rhodesia, petalite grading approximately 4.3 percent Li_2O and 0.03 percent Fe_2O_3 was the principal lithium mineral used in the glass and related industries. New deposits have been brought into production, stimulated by the virtual absence of Rhodesian ore, but these have either been smaller and of poorer quality than the source they have sought to replace or have lacked the consistency of the grade of Rhodesian material.

In most applications petalite and spodumene of comparable iron content can be substituted for one another. The silica/alumina ratios are different, but in the case of glass manufacture, for example, these can be balanced by the volume of other additives. This interchangeability, however, is only true in cases of total melting; petalite behaves in a more refractory manner than spodumene with no volume change accompanying its conversion from an alpha to beta phase and is the preferred lithium mineral in strictly ceramic applications. The more refractory nature of petalite makes it a marginally less attractive feed for chemical production. Following phase conversion, petalite retains a strong resistance to the fine grinding which is a normal prerequisite for efficient acid attack, whereas the phase change in spodumene coincides with decrepitation.

In the bulk of nonchemical uses the choice between the use of spodumene and petalite is dictated by the price of each per lithia unit and by the relative concentrations of deleterious constituents. The latter vary with end use, but the key ones are iron, soda, and potash.

Lepidolite differs from the two other major minerals in that it contains significant percentages (2–4 percent) of both fluorine and rubidia. The added fluxing powers of these make the ore an attractive one for certain glass and porcelain enamel compositions. Until recently lepidolite was the preferred source of lithia for a high percentage of the world's monochromatic television tube glass.

Although known high grade sources are rare, adequate flotation capacity exists to produce upgraded acceptable concentrates (3.8–4.3 percent Li_2O) to meet a declining demand due to the increased concerns regarding fluorine emissions. Lepidolite was the ore feed for large scale lithium hydroxide production in the United States in the 1950's.

Bikita, Rhodesia, is the only known source of economic tonnages of eucryptite where it is a co-product from the mineral assemblage there. The mineral in its alpha form has no current unique commercial application. Amblygonite rarely occurs in large tonnages but because of its high lithia content (8 percent Li_2O) is generally saleable for use, particularly, in certain porcelain enamel formulations. Amblygonite is the feed for small scale chemical production in Brazil.

DIRECT USAGE ORES

Apart from the production of lithium chemicals and metal, the principal current uses of lithium ores are in glasses, glass ceramics, porcelain enamels, fritted glazes, raw glazes, ceramics (whitewares), and refractories.

Glasses are formed when mixtures of inorganic substances are melted and subsequently cooled in a manner which usually prevents crystallization. The main ingredient is normally silica sand but, to reduce the melting temperature to an economically acceptable level, an alkali flux is added. This flux is normally in the form of soda ash; lime is added as a stabilizer. These soda-lime-silica glasses constitute the bulk of the world's glass output.

Small amounts of alumina, magnesia, boric oxide, and other chemicals are added to impart specific properties in response to market demands. Each glass is a compromise with soda being the principal source of alkali because of its cost, inspite of the fact that its use introduces many undesirable qualities.

Although lithium results in the lowest increase in undesirable qualities, the difference in price and the tolerance of these in normal applications generally restricts its use to specialized glasses.

Specific advantages of lithia additions include the following: viscosity reductions; reduced melting temperatures; the reduction in the thermal expansion of the glass; increased density resulting in good electrical properties and high chemical durability; increased surface hardness; and other improvements which cannot be commented upon with brevity.

The use of lithia in container glasses is limited and generally restricted to those few low-tonnage types that require a high thermal shock resistance. Glass lenses subject to rapid temperature fluctuations, such as many sealed beam headlight glasses and borosilicate opal glasses, contain lithia.

High-barium monochromatic television tube production results in a major demand for lithium ores, principally as a melting aid. Similarly in much foam glass production, lithium is utilized as a replacement for other potentially polluting additives. There is increasing usage of lithium in the glass fiber industry. Lithium is added to the glass batch for the production of large telescopic mirrors to help the glass withstand a prolonged annealing process. It is also added to a wide variety of other low tonnage glasses, where one or more of the unique properties of lithium are necessary.

Glass ceramics are nonporous crystalline materials derived from noncrystalline glass containing nucleating agents. When reheated under very careful control, the nuclei act as centers of crystal growth. Many formulations have been devised, but the most commercially important are those for end products requiring a high thermal shock resistance. These are produced in Europe, the United States, and Japan and the resulting demand for lithium is substantial. Originally the demand was almost exclusively for high quality ores. The shortage of good grade ores coupled with increasing quality demands, especially in respect to low potash and soda contents, has resulted in a partial replacement of ore by lithium chemicals, particularly lithium carbonate.

Vitreous or porcelain enamels are essentially fritted glasses that are fused to metals for decoration and corrosion resistance. Properties attributable to the use of lithia in glasses apply equally to enamels; lithia is a common constituent in a wide range of formulae.

A high percentage of domestic United States' lithium demand for these applications is as lithium carbonate. This is because the large volume formulae are low in alumina, and the addition of lithia as ore minerals results in a significant and intolerable alumina addition. Elsewhere, low-alumina enamels are less common; providing the ore is of acceptable purity, the choice of the lithia source is based on the relative costs of ore and carbonate.

Glazes in general vary in type from "raw" to fully fritted, with composition differences from enamels which generally allow longer firing times. With increasing pressure against the use of lead oxides in glazes, there is a continuing increase in lithium usage because of its low fusion point and low viscosity, to provide brilliance, luster, and smoothness. In terms of tonnage, lithium ore usage is greatest in glazes on low expansion ceramic bodies.

The benefits of adding lithia to ceramic (whiteware) bodies to allow rapid firing have been well publicized. Apart from some low volume specialized ceramics, usage is small, except in Japan where large tonnages of petalite are used in inexpensive ovenware.

There appears to be a great potential for lithium ore usage in the ceramics industry for domestic and industrial use. In the domestic field, technical problems exist in producing glazes with coefficients of thermal expansion to match the very low thermal expansion ceramic bodies possible with the use of petalite.

Finally, a moderate amount of lithium ore is used in some refractories and kiln furniture.

ORES AS CHEMICAL PLANT FEED

All of the principal lithium minerals are, or have been, used as feedstock for lithium chemical production in the United States (spodumene, petalite, and lepidolite), Canada (spodumene), Brazil (amblygonite), England (petalite and eucryptite), West Germany (petalite and spodumene principally), Italy (spodumene and spodumene-quartz intergrowth), and Japan (petalite).

The remaining operations in other countries are small, while others have been abandoned completely as uneconomic. The closures, in part reflect the cyclical nature of the industry in its earlier years, but also demonstrate the generally inherent uncompetitiveness of lithium chemical plants located away from their ore sources.

Even the theoretical maxima of lithia contents in the common minerals are low. Pure spodumene grades a theoretical 8 percent Li_2O; 7 percent material is producible if one is prepared to sacrifice recovery, but optimisation of recovery and grade generally results in the production of chemical feed concentrates grading between 5 percent and 6.5 percent Li_2O. Petalite and lepidolite normally grade between 3.5 percent and 4.5 percent Li_2O, and this cannot be improved upon.

Quality requirements for chemical feed are not as stringent as for direct usage ores. Iron content is not a major concern, but other elements such as soluble alumina, phosphates, fluorine, and particularly magnesium result in complicated processing requirements and higher costs.

DEMAND

Approximate lithium ore requirements for lithium chemical production can be translated back from published chemical production statistics by making reasonable assumptions regarding recoveries in milling and processing.

Direct usage ore demand is more difficult to estimate because nearly 90 percent of the Free World's supply originated from a source that is no longer open to the major consuming nations.

There are uncertainties concerning the decline in ore demand in certain key consumption areas such as (1) monochromatic television tubes and enamels, (2) the problem of more stringent specifications for certain high technology products resulting in an increasing demand for lithia as a chemical rather than an ore, (3) problems concerning fluorine emissions resulting from lepidolite usage, and (4) others which may be offset by increased ceramic demand. Finally there is the question of the relative prices per lithia unit of ores and lithium chemicals.

My personal opinion is that in normal trading conditions current lithium ore demand for uses other than chemical production would amount to between 8,000 and 12,000 tonnes/year for lepidolite (on a 4 percent Li_2O basis) and between 40,000 and 50,000 tonnes/year for petalite or spodumene if reduced to a common 4 percent Li_2O basis. These are approximately equivalent to lithium carbonate demands of between 3.2 and 4.5 million kg (7.0–10.0 million pounds) a year and, thus, represent a significant percentage of total current lithium demand.

LITHIUM PRODUCTION FROM SEARLES VALLEY

By Larry E. Rykken,
Kerr-McGee Chemical Corporation, Trona, CA

ABSTRACT

Lithium occurs in Searles Lake brine, which is processed primarily for other minerals. A portion of this lithium is recovered as a crude concentrate in a two-stage foam-flotation process. This concentrate (dilithium sodium phosphate) is then converted to a relatively pure lithium carbonate by digestion using sulfuric acid and conversion using sodium carbonate.

INTRODUCTION

Lithium in the form of lithium carbonate is produced as a byproduct of the Trona, Calif., Plant main-plant-cycle process. In this process, a dry-lake brine, pumped from permeable salt beds, is essentially evaporated to dryness in triple-effect evaporator units. Potash (KC1), borax ($Na_2B_4O_7 \cdot 10H_20$), salt cake (Na_2SO_4), and soda ash (Na_2CO_3) are recovered by a series of fractional crystallizations in a cyclic process. Lithium in the form of dilithium sodium phosphate (Li_2NaPO_4) is separated from a process stream by foam flotation. This separation is part of the refinement process for the production of salt cake and soda ash in the soda products section of the main plant cycle. The lithium values in the dilithium sodium phosphate are then converted to a refined lithium carbonate (Li_2CO_3) product, while the phosphate values are converted to a 78-percent-crude orthophosphoric acid (H_3PO_4). Annual production is approximately 153,000 kg as lithium (900 tons/year of lithium carbonate), which represents recovery of approximately one-third of the lithium contained in the brine fed to the main plant cycle.

DEVELOPMENT

The first attempts to remove part of the lithium-bearing slimes from the soda-products liquors were prompted by the problems they presented in processing (foaming of liquors, poor filtration, product contamination) rather than by their potential sales value. The recovery of lithium concentrates (licons in plant terminology) was started in 1936 by processing the foam from a process vessel on a campaign basis. Liquor was drained from the tank, water added, and the slurry circulated several hours through a line in which steam was injected to remove entrained air. The wet licons were removed on a Sweetland filter press, washed with water, partially air-dried, scraped from the press leaves, and hauled to drying plates, where the material was sun-dried for a week or two and them sacked for shipment.

Only minor improvements in this process occurred until May 1942, when the Federal War Production Board issued an urgent request to triple the lithium tonnage. An intensified research and development program was inaugurated, which resulted in the design and construction of a commercial-scale flotation plant in 1943. The original plant has undergone considerable revision since then, although the air-flotation principle has been retained.

The dried licons were sold until late 1951 when the lithium carbonate plant in Trona began operation. This plant was plagued by heavy tarlike gums, which formed when the licons were digested with sulfuric acid. This problem resulted in the addition, in 1954, of a Herreshoff furnace for burning off the organic material from the licons. The last major addition was a second-stage flotation unit in 1956; only minor refinements to the process have been made since then.

FLOTATION-PROCESS DESCRIPTION

The Searles Lake brine contains from 0.007 percent to 0.008 percent lithium (~0.015 percent Li_2O). Most of the lithium-bearing salt is precipitated in the main-plant-cycle evaporators and accompanies the burkeites through the classification and dewatering steps. The burkeites are double salts of sodium sulfate and sodium carbonate, which constitute the feed to the soda products section. After further processing a burkeite filter cake is dissolved in water, leaving the relatively insoluble lithium-bearing solids in suspension. The exact molecular structure of the lithium salts is in question, but the constituents closely conform to the formula Li_2NaPO_4 or dilithium sodium phosphate. It is relatively insoluble in neutral or basic water solutions, but very soluble in even slightly acidic solutions.

The lithium-plant flotation process uses soap as a flotation agent. The soaps are derived from coconut-oil fatty acids, which are added to the alkaline liquors at the main-plant-cycle evaporators. The fatty acids serve an additional function as foam-control agents in the evaporators. The sodium soaps of the fatty acids are believed to coat the near-colloid licon particles, making them relatively insoluble. Residence time is minimized between the solution of the lithium-containing burkeite and the flotation because the amount of dissolved lithium increases with time. The best recovery is obtained from a near-saturated solution of burkeite at a temperature just above the crystallization temperature of glauber salt (~80°F). Water addition at the burkeite dissolver is controlled by the density of the liquor leaving the dissolver. The dissolver liquor is cooled by passing it through two induced-draft spray-cooling towers.

Flotation is carried out in two stages, with air added at both feed-pump suctions. The air is compressed by a pressure-controlled surge chamber at the discharge of each feed pump. Release of pressure in the flotation units results in the formation of a multitude of tiny air bubbles, which collect the soap-coated licon particles and float them to the surface.

The first-stage flotation takes place in four 10,000-gallon (37,850-l)-capacity tanks. The tanks contain an inner cone-bottomed tank. The liquor is released tangentially along the bottom of the outer tank, rises through the annular space surrounding the inner tank, and then sinks downward in the inner tank. The lithium froth overflows the lip of the outer tank into a foam trough, and the liquor is discharged from the bottom of the inner cone-bottomed tank. Liquor levels are automatically controlled and maintained within 2–3 inches (5–7.6 cm) of the top.

The second stage consists of an industrial pneumatic foam separator. The aerated feed liquor (discharge from first stage) is released inside a hooded skirt in the center of the unit: it spreads to the outer wall, then down and under the wall and up through risers to discharge into a circular launder. Lithium froth forms on the surface and is removed by a sweep. Additional foam is obtained from a sweep on the surface of one of the soda-products process tanks, which is kept at a constant liquor level.

The foam is collected in tanks where it is agitated and heated to break down the foam. The lithium salt is filtered from the foam-storage tanks in a batch process using two Sweetland filter presses. The cake is washed, dried with an air-stream mixture, and removed into hoppers. Conveyor belts carry it to the licons roaster, where the organics are removed by roasting and bleaching with sodium nitrate in a six-hearth, gas-fired Herreshoff furnace.

LITHIUM-CARBONATE PROCESS

In early 1945, work was started on the production of a comparatively pure salt of lithium in place of the crude lithium concentrates. Several possibilities were investigated, but a process for the production of lithium carbonate was finally decided upon. The availability of sodium carbonate as an in-house product for the conversion and the marketability of the carbonate form of lithium were factors in this decision. Actual production did not begin until 1951.

In the lithium-carbonate process, the licons are first digested with concentrated (93 percent) sulfuric acid. The digestion reaction may be represented as:

$$2\,Li_2NaPO_4 + 3H_2SO_4 \rightarrow 2\,Li_2\,SO_4 + Na_2SO_4 + 2H_3PO_4.$$

This reaction is accomplished in a 6,000-gallon (22,710-l) tank equipped with a top-entering agitator and a double-walled inner tank or pachuca. The double-walled pachuca serves as the heat-exchange surface for both heating during the digestion of licons and cooling the batch preparatory to the separation of the precipitated solids. The lithium and sodium sulfates (called mixed sulfates) are centrifuged from the digester tank, washed, and dissolved in water. The filtrate is a 45–50 percent orthophosphoric acid solution, which is evaporated down to a 78 percent phosphoric acid solution. The evaporation reduces the lithium in solution from about 3 percent as Li_2O to less than 1 percent, thus increasing recovery. After evaporation, the solids (Li_2SO_4 and Na_2SO_4) are settled out and recycled as a sludge back to the digester.

The dissolved, mixed-sulfate solids are introduced into a saturated solution of sodium carbonate at a temperature of 200°F. The lithium carbonate has a solubility of about 0.6 percent as Li_2O versus about 4 percent for the lithium sulfate. The lithium carbonate precipitates out according to the reaction

$$Li_2SO_4(l) + Na_2CO_3(l) \rightarrow Li_2CO_3\downarrow + Na_2SO_4(l).$$

The lithium-carbonate solids are centrifuged out, washed, dried in a steam-heated rotary-drum air dryer, and packaged in 50-pound (22.7-kg) sacks and 325-pound (147-kg) fiber drums for shipment. Lithium recovery is increased by treating the end liquor (lithium carbonate centrifugal filtrate) using dilute phosphoric acid and evaporating to near $-Na_2SO_4$ saturation. The phosphate ions cause precipitation of Li_3PO_4 as a result of the decreased solubility of Li_3PO_4 (<.15 percent Li_2O versus 0.6 percent Li_2O for Li_2CO_3). The reaction is

$$3\,Li_2CO_3(l) + 2\,H_3PO_4(l) \rightarrow 2\,Li_3PO_4\downarrow + 3\,CO_2\uparrow + 3\,H_2O.$$

The Li_3PO_4 solids are settled out and recycled to the digester. Lithium is also recovered from spillages by pumping sump liquors back to the end-liquor evaporator.

"Theoretical" lithium losses are reduced to those dissolved in concentrated phosphoric acid and treated end liquor. Theoretical recovery is 92–94 percent, whereas actual recovery has averaged about 88 percent.

THE LITHIUM-RESOURCE ENIGMA

By James D. Vine,
U.S. Geological Survey, Denver, CO

ABSTRACT

The identified lithium resources of the United States that may be recoverable by the year 2000 will probably yield less than one million tonnes. About a third of this will be used in conventional ways, leaving about two-thirds for new energy-related uses, including use in batteries for electric vehicles. Exhaustion of our recoverable lithium resources for these uses would limit the development of thermonuclear power in the early decades of the next century. Depletion of a commodity essential to future energy independence can best be prevented by identifying new resources of lithium. A program of exploration for new deposits well in advance of the demand would help to assure a stable price and a steady growth and would be of benefit to the American public as well as the lithium industry. The best chance of finding new deposits of lithium is in association with nonmarine salt bodies. Undiscovered resources may exist in other geologic environments that have not as yet been evaluated. A modest U.S. Geological Survey effort to search for such deposits shows promise.

THE NEED FOR RESOURCE DATA

Previous estimates of the availability of lithium tend to be misleading to those who plan to use this rare metal in alternative energy applications. Reasons for an overly optimistic outlook are twofold: (1) Geologic estimates of resources (for example, Norton, 1973) summarize data on amounts of lithium in the ground without regard to recoverability and (2) all recently published estimates are biased by an unrealistic preliminary forecast of lithium available from one large brine field in Nevada. Although brine fields account for a large part of the lithium resource base, they will represent a much smaller fraction of the identified lithium recoverable by the year 2000. That is because, in practice, a large part of the resource base is inaccessible as a result of technical or other problems. Many of these other problems, including economic, political, and environmental restrictions, can be as difficult to overcome as any technical problem.

An accurate forecast of the amount of lithium available to the market place rather than a measure of the lithium contained in various inaccessible parts of the earth is desirable, in order to plan for the effective development of lithium batteries for automobiles and for storage of off-peak power for utility nets. Furthermore, if the scarcity of the Li_6 isotope, which is required in the production of tritium, is a limiting factor in the development of controlled thermonuclear power, as suggested by Hubbert (1969, p. 230–233), consideration should be given to stockpiling this isotope prior to using the rest of the lithium for batteries and other conventional uses.

Any mineral industry, such as the lithium industry, is concerned with the quantity of ore that can be profitably extracted from the ground.[1] This is the category of resources that we call reserves, and it may represent only a small fraction of the total resource base. Most companies will attempt to block out an ore reserve adequate to supply 5–10 years of mill product, or whatever is required to amortize the capital investment in mining and milling facilities. Under the pressure of competition they may tie up additional mineral leases, but most companies cannot afford the investment required to hold leases that they do not anticipate using for a few years.

Even if available to the government, the proprietary data on company-held reserves would not be adequate for long-range government planning. Thus, from the broader perspective of the long-term economic health of the nation, various agencies of government may need data on the total resources of a commodity, including company-held reserves, identified but subeconomic resources, and the undiscovered resources that may be predictable on the basis of geologic probability. Reasonably accurate forecasts are required for many different uses—from the ranking of national priorities to military and diplomatic strategy.

REVISED LITHIUM RESOURCES

A classification of lithium resources that includes an estimate for three main categories of resources, revised to include information up to February 1976, is shown in table 16. The categories include (1) identified reserves, which are economic at today's prices and technology; (2) identified low-grade resources, which are not economic at today's prices and technology but may become economic at a higher price or improved technology, and (3) hypothetical and speculative resources, which will have to be discovered and developed in order to bring the cumulative yield by the year 2000 up to 1 million metric tonnes. All classes show both the "in place" resources, which refers to the amount of lithium that is in the ground, and the probable yield, which refers to the

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[1] The latest definitions for various categories of reserves and resources can be found in U.S. Geological Survey Bulletin 1450–A.

TABLE 16.—*Classification of U.S. lithium resources in millions of tonnes of contained lithium*

Sources	In place	Estimated percent recoverable by 2000[1]	Probable yield
Reserves (economic)			
Kings Mtn., N.C.[2]	0.510	35	0.185
Clayton Valley, Nev[3]	.080	50	.040
Searles Lake, Calif[4]	.009	50	.005
Total	0.599		0.230
Low-grade resources (subeconomic)			
Kings Mtn., N.C.[2]	0.840	25	0.200
Clayton Valley, Nev[3]	.625	10	.060
Searles Lake, Calif[4]	.027	10	.003
Imperial Valley, Calif[5]	1.000	1	.010
Oilfield brines[6]	1.000	1	0.10
½ Great Salt Lake, Utah[7]	.263	5	.010
Borate mine waste[8]	.060	7	.004
Black Hills, S.D.[4]	.010	30	.003
Total	3.825		0.300
Hypothetical and speculative resources[9]			
Clays	0.800	25	0.200
Brines	1.000	20	.200
Pegmatites	.350	20	.070
Total	2.150		0.470

[1] various sources, including hearsay.

[2] "In place" reserves estimated for two known ore bodies (Keith Evans and Ihor Kunasz, oral commun., Jan. 1976). Total resources for the district from Norton (1973, p. 372).

[3] Calculated from the estimate of recoverable reserves and total resources listed by Kunasz (1975, p. 796).

[4] Calculated from Norton (1973, p. 372).

[5] Extrapolated from two analyses and the geometry of the brine field suggested by White (1968, p. 312–313).

[6] Based on analytical data of Collins (1974, p. 16–20). No data on brine volume.

[7] Estimate by J. D. Whelan (oral commun., Jan. 1976) incorporating recent downward revision of the volume of brine in the lake by Carol A. Peterson.

[8] Calculated from data presented by Robert B. Kistler (oral commun., Jan. 1976).

[9] This amount, in addition to reserves and low-grade resources, must be discovered and developed to produce a cumulative yield of 1 million tonnes in the years 1976 through 2000.

amount of lithium one might expect to be recovered and made available to the market place. While the in-place resources are a measured volume of rock times the grade of ore, the accuracy of which may be good (±10 percent) or poor (±100 percent), the factor of recoverability is not a measurable quantity. Recoverability involves unpredictable economic and technical factors that can be determined only in practice. Although the accuracy of the resulting data may be questioned, the totals probably represent a reasonable value. For example, a marked price increase relative to other products and services could increase the total yield by a factor of 10 or 20 percent, to more than a million tonnes of lithium, but additional restrictions on the use of land for mining could reduce the total by an equal or greater amount. Although the existence of hypothetical and speculative resources can be predicted on the basis of geologic probability, the quantities listed here are uncertain and will be a function of the imagination applied by geologists and the incentives available for exploration. It seems reasonable to forecast that the United States will produce somewhere between 750,000 and one million tonnes of lithium by the year 2000, but such production will require an economic climate that provides incentive for considerable exploration and development of lithium in previously unknown deposits.

COMPARISON OF RESOURCES AND REQUIREMENTS

In the years 1971 through 1974, conventional uses for lithium grew at an average rate of 8.8 percent, according to proprietary data. If this figure is projected into the future, conventional uses may consume about 3×10^8 kg of lithium by the year 2000. Requirements for new energy-related uses for lithium, including batteries for electric automobiles, batteries for the off-peak storage of power for utility nets, absorption-type refrigeration and air-conditioning units, and controlled thermonuclear power plants, are much more difficult to predict. Requirements for these uses depend on the success of current technologic research and its acceptance by the American public. Estimates of these requirements, as detailed in a previous report (Vine, 1975b) are from 3 to 15×10^8 kg for battery applications alone. Thermonuclear power plants are not expected to require much lithium before the year 2000 but may need as much as 5×10^8 kg by the year 2020.

Thus, about one-third of our presently identified recoverable resources will be consumed by conventional uses by the year 2000. The remaining two-thirds could easily be spent in battery applications before the year 2000, leaving nothing for thermonuclear power, unless we start now to search for and develop new deposits. Failure to identify new resources of lithium may be regarded as irresponsible by those of the next generation.

UNDISCOVERED RESOURCES

An appraisal of lithium resources would be incomplete without discussion of undiscovered resources, which include extensions of identified resources in known districts plus identification of new districts previously unknown. Whereas the rate of discovery of new oilfields can be extrapolated from the past history of exploration and discovery for petroleum, no such record of exploration exists for the lithium industry. Moreover, the number of known districts is too small to constitute a statistical basis for projection. Even prospecting guides to aid in the exploration for lithium are minimal. Small lithium-bearing zoned pegmatites, such as those in the Black Hills of South Dakota, are generally characterized by large crystals, as much as 1–2 metres in length; their size makes them easy to recognize and unlikely to be overlooked when exposed at the surface, but their irregular distribution makes prediction of covered pegmatites nearly impossible. Unzoned pegmatites, such as those in the Kings Mountain tin-spodumene belt of North Carolina, are large features that may extend for many kilometres; hence they are unlikely to be overlooked, except in areas of deep weathering or jungle cover. Thus, the chances of discovering a major new pegmatite district within the conterminous United States seem rather poor. The chances of discovering a new brine field, on the other hand, are relatively good, because relatively little effort has been devoted to searching for brines. Furthermore, lithium-rich rocks or minerals may be associated with nonmarine salt bodies, volcanic rocks, and vein deposits, none of which have received more than casual attention with respect to lithium (Vine, 1975a).

Whereas, by definition, reserves are identifiable, measured amounts of a commodity, the concept of resources is abstract in that the values can change with changes in economics, technology, and geologic understanding. For example, the possibility of discovering previously unrecognized lithium resources is very good because previous exploration was minimal and limited to a few geologic environments. Hence, a program of exploration for lithium in previously untested geologic environments could greatly improve the outlook for lithium resources.

If the future growth of the lithium industry is dependent on presently identified resources, a considerable price increase in lithium can be predicted, which will bring today's subeconomic resources into the category of economic reserves. However, any marked price increase would seriously limit the economically feasible uses of lithium, especially in direct consumer products such as electric automobiles. On the other hand, an exploration program that appraises previously untested geologic environments may result in a more optimistic forecast of resources because of the probability of discovering new deposits. Thus, a program to search for such deposits could make the difference between reasonably priced electric automobiles and some other form of personal transportation that might be too expensive for the average consumer.

Although private industry is capable of conducting a program of exploration for lithium, little incentive to do so exists at the present time, because industry has sufficient reserves for the short term and no assurance that major investments in exploration would ever be returned. Meanwhile, large amounts of money are being spent to develop new energy-related uses for lithium, partly based on the assumption that lithium will be available at a reasonable price when the manufacturers are ready to start up production lines. However, if new resources are not identified and developed well in advance of this need, any sudden increase in demand will be met by a spectacular rise in price which will justify having to mine and mill lower grade lithium ore. A crisis in demand does not permit the time required to develop new resources. Moreover, a spectacular price rise would be self-defeating because less desirable but less expensive substitutes could be found to replace lithium in batteries.

A stable price for lithium would be beneficial to both the industry and the American public. The best way to assure both a stable price and a steady growth in the demand for lithium would be to conduct a program for the exploration of new deposits well in advance of the actual increase in demand. A modest program along this line has already been initiated by the U.S. Geological Survey and has begun to produce encouraging results. Those of us involved in this program solicit both the confidence and encouragement of the lithium-producing industry as well as the support of the scientists and engineers from national and private laboratories who are concerned with the development of new energy-related uses for lithium.

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LITHIUM RESOURCE ESTIMATES—WHAT DO THEY MEAN?

By JAMES J. NORTON,
U.S. GEOLOGICAL SURVEY, DENVER, CO

ABSTRACT

Lithium resources have been poorly known, mainly because there has been little need for information. The supply of lithium in known deposits, minable under prevailing conditions, has been far more than adequate to meet demand. Potential resources are very much larger.

Most of the major mines are in deposits that had been discovered long before they were developed or were found more or less by chance. Systematic exploration for new deposits, especially new kinds of deposits, has been meager, and thus experience with exploration techniques is slight.

Anticipated large demand, now centering on lithium for storage batteries, greatly changes the outlook but can probably be met, though to justify the costs of exploration and development requires assurance that the demand will in fact materialize.

Mutual understanding among those who will participate in enlarging the supply of lithium and those who develop new uses is a necessity. Confidence arising from large resource estimates can be seriously misplaced; the resources must first be developed and made ready for market.

The most reliable category of resources consists of the lithium proved to be recoverable under current conditions from known deposits. Almost equally important in an expanding market is lithium in known deposits that is almost but not quite minable now. The large expected demand, however, can be met only if new deposits are found, as they probably can be.

BACKGROUND

The decision to publish the articles in this volume was triggered by misunderstandings of lithium resource estimates, by shortcomings in published statements, by a tendency to misuse the estimates because of inadequate comprehension of what underlies them, and by need for better communication among those who plan future uses of lithium, those who do the geologic work, and those who mine or will mine lithium.

An article of mine (Norton, 1973) is at the center of some of the problems. Many of the users of that article are not mining engineers or geologists. They have tended to quote the resource estimates without studying the text of the article to understand the data on which the estimates are based.

But I too have been at fault, in that article and in personal communications, by accepting premature company announcements of lithium reserve estimates for Clayton Valley, Nev., which later proved to be too large and which seriously distorted the total estimated reserves for the United States. One awkward aspect of compiling mineral resource estimates is that companies ordinarily do not reveal the data on which their calculations are based, and the shortcomings in their announcements may not be visible even to themselves.

In a generally overlooked paragraph (Norton, 1973, p. 375), I protested against a tendency to call my lithium resource estimates conservative in disregard of the fact that they have been the largest that available data would allow, but added that any truly large new demand would cause a search for new deposits and probably still larger estimates of resources. The conclusion of the paragraph emphasized the necessity of finding deposits and determining their lithium content before any large use actually begins.

Such uses now appear to be forthcoming. Hindsight shows that my 1973 article was defective in not being written so as to be more useful to persons not connected with mining or geology. A particular shortcoming was the absence of discussion of the outlook for lithium mining under various sets of possible circumstances.

Lithium almost certainly can become in ample supply to meet even the largest needs now foreseen for the remainder of this century, but the end of the century is not far away. The problem of how to bring demand and supply together at acceptable costs must be understood by all persons involved or likely to become involved with lithium.

MINERAL RESOURCE CLASSIFICATION AND NOMENCLATURE

The word "reserves" is widely misinterpreted as including all material expected ever to come to market. Idiosyncratic usage of the term is not unusual among mining engineers and geologists, and the published record contains definitions that are incompatible with one another.

More rigorously defined, "reserves" include only material that can be profitably mined, or at least is expected to be profitable, under present economic and technologic conditions, and for which considerable information has been obtained. The drilling, geologic investigation, chemical analyses, and other work necessary to outline reserves are ordinarily time consuming and costly: Reserves may be said to be "bought" rather than "found," though at some single point in the process there is, of course, a discovery and at the same time or a later time there is a decision that profitable mining is possible.

"Resources" is the term used to include all material, discovered and undiscovered, profitable and now unprofitable, which seems likely to become a source of a mineral commodity.

The nature of the various categories of mineral resources has been greatly clarified by what has come to be known as the McKelvey diagram, a simplified version of which is shown as figure 18A. This is the basis for the current U.S. Department of Interior nomenclature and classification of mineral resources, most recently described in comprehensive form by the U.S. Geological Survey (1975). Among the many other publications discussing the diagram are McKelvey (1972), Brobst and Pratt (1973), and Schanz (1975).

Resources may, as a first step, be divided into four categories: (1) those classified as reserves because they have already been discovered and can now be worked at a profit, (2) those yet to be found that would also be profitable, (3) discovered material of too low quality to be used, and (4) material that is both undiscovered and unprofitable.

Reserves is the most important category for the next few years. The undiscovered but profitable category generally takes second rank, especially when the time span is some decades. Yet under special circumstances the known low-quality deposits can take over the second or even the first position, as during times of great increase in demand or price, or after a major technological change, or when conventional sources are cut off by war or embargoes. The necessity for speed in mining may then be too great to allow time to explore. An example for lithium was the intensive mining in the 1950's of deposits in granitic pegmatites that previously had been only moderately attractive. The possibility of finding nonpegmatitic deposits was already suspected, but there was no time to look for them. If demand again increases greatly and if exploration of brines, clays, and so on is insufficiently intense or is unsuccessful, pegmatitic deposits will again assume their earlier importance, despite their probably higher costs of mining.

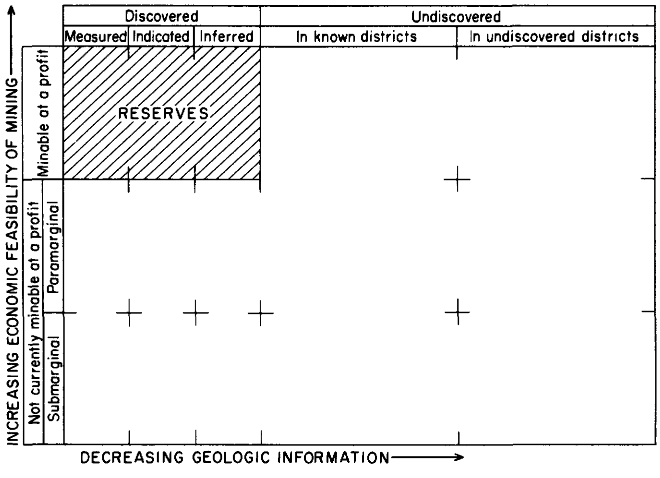

FIGURE 18A.—Classification of mineral resources. Modified from McKelvey (1972, fig. 3).

Industry's interest is generally in or near the category represented by the rectangle labeled reserves on figure 18A. Most industry reserve estimates are for single mines or small groups of mines, chiefly for the purpose of acquiring the information needed to plan operations and to keep financial arrangements on a firm footing. Government has broader and longer term responsibilities, and thus tends to be concerned in considerable degree with other segments represented by the diagram.

Reserves are customarily divided into smaller categories on the basis of how much is known about the position, size, shape, grade (ordinarily expressed as the percentage of a metal in the deposit), amenability to processing, and other factors necessary to appraise a deposit.

In figure 18A, reserves are divided into classes called measured, indicated, and inferred, following the practice of the U.S. Department of Interior. The mining industry prefers the terms "proved," "probable," and "possible" ore (Banfield and Havard, 1975). Measured and proved are generally agreed to have nearly the same meaning. They refer to ore that is so well known as to be ready for development and extraction. Neither the words "probable" and "indicated" nor "possible" and "inferred" seem to be equivalent, but the issue does not need to be discussed here.

A formerly unprofitable deposit is promoted to the reserve category usually because of higher prices, technological advances leading to lower costs, or an increase in demand permitting larger scale and hence more efficient operation. A deposit can also cease to be profitable and lose its standing as a reserve, as by a decrease in price caused by lowered demand.

Many other circumstances can cause a body of ore to move into or out of the reserve category or even to be a reserve for one company and not another. Construction of public highways or railroads can make mining more feasible. A deposit can become of value through an opportunity for cheap transport of the product in ships; loss of such an opportunity can return the deposit to worthlessness. After the gold mine closing order of World War II, many operators of small gold mines were unable to keep their facilities in working order and never reopened the mines; their unmined ore ceased to be reserves. Other governmental actions, such as starting or ending a price support program, can move deposits from one category to another. The opening of better mines can cause other mines to become unprofitable, as has happened twice with lithium: (1) in the

1950's, when greatly increased demand led to the opening of large mechanized mines and ultimately to the closing of the old small handsorting mines and (2) when the Clayton Valley, Nev., brine operation caused the Quebec Lithium mine, near Barraute, Quebec, to be no longer competitive. Some mineral deposits may be profitably worked by a company that already has a large plant nearby but not by a company that must build new facilities. Other possibilities can be conceived by anyone who gives a little thought to the subject.

What constitutes a profit introduces questions. A mining company expects a rate of return commensurate with its risks. Certainly the prospective return must be greater than the yield of high-grade bonds to be attractive. Yet once a mine has been developed and a plant built, mining will continue as long as cash income exceeds cash outgo, even if part or all of the capital cost must be written off.

Individuals making reserve calculations may have different motives that can lead to different results from essentially the same data. Congressman Harold Runnels (U.S. Congress, 1975, p. 28) has expressed this neatly by saying that a person borrowing money to develop a newly discovered oilfield will want the largest possible reserve estimate, but when evaluating the same oilfield for an estate he would want the smallest possible estimate. Mining company reserve calculations made during the planning process that precedes the large financial outlays necessary to start mining have a tendency to be low: Caution can do no harm to the company except to lead to missed opportunities, but recklessness can do the company very serious financial damage.

If the reserve concept is so complex and the calculations are hard to evaluate, it is not suprising that those who estimate undiscovered resources open themselves to disputes. The test of the precision of a calculation is the reproducibility of results obtained by different persons using different methods. Oil is currently the most instructive example, partly because the urgency of its problems has given it wide attention but mainly because an enormous quantity of information is available. The disparities in the estimates of undiscovered oil in the United States seem extraordinary to many persons, but actually the spread is equivalent merely to several decades of U.S. consumption at its current rate. Though this spread is important in planning the future of U.S. energy usage, its size is insignificant compared to what would result from similar examination of most other mineral commodities.

A mineral commodity for which reserves are much larger than required by the market presents great uncertainties. Lithium is a good example. Most of the major known lithium deposits were easily found in surface exposures, and the others were found virtually by chance. Their lithium content is far greater than has ever been needed to meet the demands for lithium. The circumstances create little reason to search for more deposits, thus offering slight experience or information to use as a guide in estimating the magnitude of undiscovered resources. My recent estimates of undiscovered resources (Norton, 1973, table 73, p. 372) were little more than informed guesses, as the text of the report makes clear, but they have been widely credited with more accuracy than they possess.

Resource estimates for coproducts and byproducts have problems which are neglected in figure 18A and which rarely, if ever, are examined in the literature, though the mining industry is well acquainted with them. The lithium produced as one of the minor products, along with several major products, from brine at Searles Lake, Calif., is a useful example. A change in the processing plant to add to the overall efficiency of the operation could have the side effect of making the lithium unrecoverable. The reserve (if it ever should have been called a reserve, for the lithium content is only about 70 ppm) then no longer exists. Other lithium brines have marketable components that must be produced to make mining economically viable. A lithium company can thus be put into another business in which it has little expertise and little influence, hence complicating the appraisal of its outlook for lithium production.

In short, resources of various categories can change through time for a great variety of reasons. Estimates of their magnitude range from careful, elaborate, and expensive measurements to mere guesses. These estimates are furnished by persons who cover the whole spectrum from those of indisputable expertise and objectivity to those of questionable reliability. Persons who provide estimates should explain how their results were obtained so that others can make independent interpretations. With lithium the chief shortcoming in existing resource estimates is lack of information caused by the little past need for exploration.

METHODS OF EXPRESSING RESOURCE ESTIMATES

Metal mining companies ordinarily state reserves in terms of the tonnage of ore and its grade. Grade is generally expressed as the percentage of a metal in the ore. Not all of the metal is recovered during mining and processing, but few companies issue estimates of the recoverability. In making broad appraisals of metals reserves, the lack of such estimates is rarely important because recoverability of metals tends to be near enough to 100 percent so as not to introduce errors that are much if any greater than the errors made in the normal reserve estimating process. Some mines actually recover more than 100 percent of the measured reserves, for unanticipated ore may be found during mining or low-grade ore not originally calculated in the reserves may, inadvertently or by necessity, be extracted.

The practices in stating reserves of deposits of industrial minerals and rocks (commonly called nonmetals) are too varied to be discussed briefly. The products may be rocks, minerals, chemical compounds, elements, or manufactured materials. A deposit's grade (in the sense applied to this word in the metals industry) may be no more important than many of its other properties.

Recoverability is critical in the oil industry's examination of its resources, for only about a third of the oil in the ground can be obtained profitably. The oil industry emphasizes what it calls "proved reserves," which includes only the amount that is reasonably certain to be recovered under existing conditions. Of course the oil terminology also provides for estimates of the total in the ground and for methods of expressing other estimates serving various purposes.

For lithium the practice has been to state tonnage and grade, but recoverability is also very important. Of all the lithium ever extracted from pegmatites, probably at least one-third and possibly nearly half has been lost during mining and the elaborate processing needed to make the many kinds of lithium products on the market. In the brine at Silver Peak, Nev., the most recent estimate by Kunasz (this report) indicates a known content of 775,000 tons of lithium but a recoverable amount of only 44,500 tons. Applying the word "reserves" to the 775,000 tons, as has been done by Kunasz (1975, p. 796), is akin to the practice of the metal mining industry; applying it to the 44,500 tons follows the methods of the oil industry. This difference illustrates a vital problem in expressing lithium reserve estimates.

RELATION OF RESERVES TO PRODUCTION

Often since the beginning of this century, it has been noticed that the reserves of many mineral commodities were adequate to last only a few decades. With the passage of time, reserves in most of the mineral industry stayed ahead of production by about the same amount. Some have attributed this experience to transitory good luck by prospectors, to the incompetence of geologists, and to machinations of mining companies. The principal reason is none of these. It is merely that the size of reserves depends largely on the magnitude of production, which in turn reflects demand. In the phraseology of mathematics, reserves are a function of production. They are also a function of the geologic availability of deposits, accessibility, political environment, and many other influences.

A hypothetical example will clarify this point. Suppose all the world's copper deposits were identical in every way that affects how the copper is mined, processed, and sold. Suppose also that the deposits contain enough copper to last thousands of years, and that price, rate of consumption, and other economic factors will remain unchanged. The effect of these assumptions is to reduce all the variables to a constant except reserves and production.

Now suppose the lifetime of every deposit, at the most efficient rate of mining, is 100 years. Each year some deposits will be abandoned as mined out, and an equal number of deposits will begin to be mined. The reserves in operating mines will at all times amount to 50 years of supply, despite the existence of very large resources.

No authority would disagree that the recoverable reserve of lithium in the United States is at least 350,000 tons. At the 1975 production rate of probably between 4,600 and 5,100 tons (estimated from Wood, this report), this reserve would last about 70 years. Such a large reserve-production ratio is unusual, and seems in conflict with the belief that reserves tend to be kept at the minimum necessary level. Actually reserves are so large relative to demand not because there has been any need for large reserves but merely because some lithium deposits are of such great size that dividing a small number (production) into a big one (reserves) yields a large result. As a consequence, reserves are not only adequate to meet the assured market but also provide leeway to prepare to meet larger, less certain needs.

Other articles in this volume suggest that annual demand for lithium will greatly increase by the end of this century. If demand thereafter is expected to continue at a high level, then reserves must be correspondingly increased to maintain an adequate backlog for subsequent years.

HOW RAPIDLY CAN PRODUCTION OF LITHIUM BE INCREASED?

An astonishing assumption underlying many discussions of future uses of lithium and whether supply will meet demand is that if resource estimates are large enough, there need be no worry about supply.

Actually, the chief concern should be whether lithium can be brought to market in suitable amounts when needed. Theoretically one should also be concerned about whether the inadequately explored or undiscovered resources exist and can eventually be converted to reserves, but on this score I remain an optimist.

A way of visualizing the circumstances is to look at the McKelvey diagram (fig. 18A) as if it were three dimensional and the third dimension is time. In this third dimension, the reserve box would be continuously depleted by mining and continuously replenished by discovery of additional deposits and by raising low-grade material to a profitable level. How fast this can be done is a critical and difficult question, especially with a commodity for which there has been very little exploration.

Figure 18B presents the problem in a different light. Wood (this report) suggests a 5-percent growth rate in U.S. production for the next 5 years. If this growth rate were to continue, the production in the year 2000 would be about 15,000 tons of lithium. At the other extreme, Chilenskas and others (this report) suggest a consumption for storage batteries alone in the year 2000 at somewhere between 90,000 and 170,000 tons. The maximum likely figure for U.S. annual demand at the end of the century seems to be about 180,000 tons.

The disparity between 15,000 and 180,000 tons raises obvious enough uncertainty to those who must find deposits, drill them out, develop mines, and build plants. A further problem lies in the rate of change in demand. Curve 1 of figure 18B shows the most probable form of increasing annual consumption if lithium batteries do come into common use—a modest expansion in the next few years and a great upswing at the end of the century. A curve of this shape cannot, of course, continue upward forever. It must eventually turn downward because of a shortage of lithium, because of something else affecting lithium usage, or through other ancillary circumstances. Curve 2 represents merely a straight-line increase. Curve 3 has the shape to be expected if lithium resources minable at acceptable costs turn out to be hard to find or if the demand for lithium has a dimishing rate of increase at the end of the century.

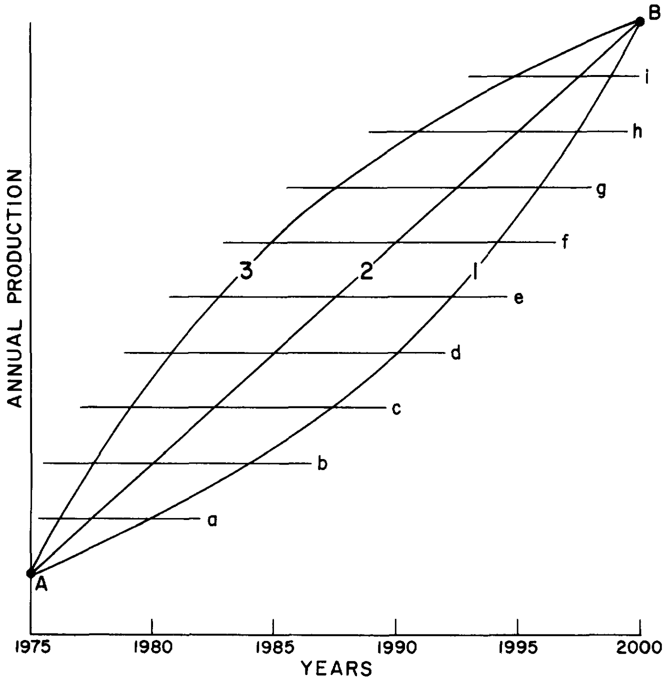

FIGURE 18B.—Schematic graph of how an increase in lithium production may proceed in the years 1975 to 2000. Lines 1, 2, and 3 are possible generalized curves showing annual production (the actual curve will, of course, be far more irregular). Point A is 1975 production, which in the United States was probably somewhat less than 5,000 tons of contained lithium. Point B is U.S. demand in the year 2000, which may be as small as 15,000 tons or as great as 180,000 tons. Lines a through i signify production levels at which new mines and plants must start operation.

Along any curve representing increasing production, there are points at which new mines and plants must start operating. These are represented schematically by the horizontal lines labeled a through i. The lines indicate considerable uncertainty about when new mines will be needed. This uncertainty is important for anything that requires as long a lead time as a mine, especially a mine in a new kind of deposit requiring experimentation with processing methods. Mining companies in lithium and the other so-called rare elements have heard about many anticipated large new uses that did not materialize, and they have learned the importance of caution and skepticism.

The outlook beyond the end of the century can also be influential, though its importance may be little more than theoretical now. Nevertheless it can affect the rate at which capital costs must be amortized and the prudence necessary in developing new mines.

The history of other mineral products that have gone through large increases in demand can give hints about how large an increase is practicable in lithium.

Let us assume that the production capacity desired for the United States by the year 2000 is 150,000 tons of lithium. Starting from a current capacity of not much more than 5,000 tons (Wood, this report), an approximately 30-fold expansion in 25 years would be needed.

Increases of this amount are rare in segments of the mineral industry controlled mainly by private markets. For oil, which has an outstanding reputation as a growth industry, U.S. output increased 58-fold in the 75 years from 1896 through 1970, which was the peak year. The increase from 1921 through 1970 was merely 7.5 times. Copper increased only eight-fold from 1896 through 1970, also the peak year for it.

To find increases that were proportionately much greater and took place over a shorter time, it is best to search among commodities which had small production until recently and for which there was assistance from the Federal Government. Uranium is the greatest success story. U.S. uranium production increased from virtually nothing in the late 1940's to a high peak in 1960. Meanwhile world production, in the non-Communist group of nations, increased 22-fold.

Niobium (columbium) is especially pertinent because in 1950 its situation was similar to that of lithium today. The main difference between the two is that notice of an increase in niobium demand, chiefly for use in jet engines, came very suddenly. The geologic literature available in 1950 indicated, as with lithium now, that major deposits of niobium probably could be found, and notes in trade journals implied that some were ready for development. A U.S. Government purchase program began that exceeded the wildest expectations, and after its end in 1959 world production increased even more rapidly. Niobium output of the world, outside the Communist segment, was about 14,565 tons in 1975 (U.S. Bureau Mines, 1976, p. 45), in contrast to about 500 tons in 1950 (when production data were, for several reasons, imprecise). The increase was about 30-fold.

With such experiences in the background, and if one can assume the availability of adequate lithium resources, there seems little reason for pessimism about increasing lithium production enough to meet the maximum demands anticipated for the end of the century. In lithium, unlike niobium in 1950, the United States is already the world's largest producer and has the world's largest reserves as well as favorable geologic environments for the discovery of more deposits. For the expansion to be orderly and not too costly, new deposits must be found and the demand must be assured long enough in advance for the construction of producing facilities.

PROBLEMS IN RECENT ESTIMATES OF LITHIUM RESOURCES

Several articles in this volume treat various aspects of existing information about lithium resources. The principal assessments of resources are in the articles by Vine and by Kunasz. Their tables of resource estimates may, to the casual reader, seem greatly different, but actually the main difference is in their approach to the available data. Vine emphasizes the very proper view that the critical figures are for lithium that almost certainly can be mined by the end of the century, for this is the only lithium that users can be sure to obtain. Kunasz takes the equally proper view that in an expanding market the known resources that are less adequately known or are of lower quality will take on increasing importance. Both of them would undoubtedly agree that search for new deposits is necessary if U.S. demand is indeed going to increase greatly by the year 2000. If a proper reserve base should amount to at least a 30-year supply, and if the annual production at the end of the century is to be 180,000 tons of lithium, reserves at that time should be about 5,400,000 tons, which is larger than either of their estimates of known resources and far larger than any estimate of reserves.

My own recently published appraisal of resources (Norton, 1973, p. 372–375) is not fundamentally incompatible with those of Vine and Kunasz. The most obvious difference is that I estimated or (in more correct words) made guesses of undiscovered world resources; Kunasz makes no such guesses and Vine does so only for the United States, arriving at a total (if his Kings Mountain, N.C., low-grade resources are included) similar to mine but via a different route. Both Vine and Kunasz use Great Salt Lake brines, which I chose to disregard. Vine also uses oil field brines, for which I had virtually no information. Kunasz promotes the Zaire and Chilean deposits to identified resources, chiefly on the basis of recent information.

A source of some contention has been the estimates for Clayton Valley, Nev. The original claim was 2.5 to 5 million tons of lithium "reserves" (obviously meaning "resources"). My examination of the published data (Norton, 1973, p. 374) led to assigning 500,000 tons to reserves and relegating the rest to more dubious categories of resources. Kunasz (this report), using newer information, now estimates the identified resources at 775,000 tons of lithium, of which only 44,500 tons is currently recoverable. He adds that the total resources in the valley, apparently in clay as well as brine, are undoubtedly very much larger, though when and how these resources can be mined seems questionable. Vine (1975 and this report) stresses the 44,500-ton figure, because one can rely on obtaining this amount. Yet to say that no more than this quantity of lithium will ultimately be extracted from Clayton Valley may be too conservative, though some such event as the development of better deposits elsewhere, making Clayton Valley not competitive, could prevent enlargement of its supply of recoverable lithium for a long time.

OUTLOOK FOR INCREASING LITHIUM RESERVES

Questions about the future success of lithium exploration are difficult to answer, and the answers are impossible to quantify. The small amount of exploration and geologic study has yielded a correspondingly small amount of information about where and how to search for new deposits.

The traditional source of lithium has been pegmatite. Most lithium pegmatite has about 0.7 percent lithium, apparently for geologic reasons summarized recently (Norton, 1973, p. 368–369). The main economic difference between a good and a not-so-good lithium pegmatite is size: A large one can be mined more cheaply than smaller ones. Another difference is accessibility. The Zaire deposits may be the best in the world except for their remote location and the political environment.

Pegmatites are the source of several unusual mineral products and for this reason they have been prospected carefully in much of the world. Not many large lithium pegmatites exposed at the surface seem likely to have remained undiscovered. The stage of exploration probably is near maturity. Nevertheless, the great disparity between the amount of known lithium pegmatite in

North America and in the rest of the world suggests some hope for the potential of other continents.

Exploration is decidedly immature for lithium pegmatites concealed beneath the surface and for small but possibly useful pegmatites. Kesler in this report makes suggestions about how to find additional large deposits in the Kings Mountain region, North Carolina.

Several clay deposits are known to contain about 0.2 percent lithium, but none have been mined for lithium. For these deposits, little laboratory work on extraction processes has been attempted, the geology is poorly known, and all the discoveries were little more than accidental. A grade of 0.2 percent by weight seems very low, but opportunities for low cost mining and processing may offset this defect. Furthermore, weight percent is somewhat misleading with elements of low atomic weight: for example, spodumene ($LiAlSi_2O_6$), the principal lithium mineral of pegmatites, contains 10 percent lithium in terms of atoms but only 3.7 percent by weight.

The likelihood of finding lithium-rich brines was suspected long before the more or less fortuitous discovery of the Clayton Valley deposit, which is now probably the second most productive deposit in the world. The deposit in the Salar de Atacama, Chile, reputedly also found by chance, appears to be richer than Clayton Valley and probably also large. Whether even better deposits are awaiting discovery is unknown and will be beyond even guessing until the geology and geochemistry of lithium brines have been investigated much more thoroughly.

In short, exploration for lithium brines and clays is at a very immature stage.

No other kinds of lithium deposits are known, but they may exist. The source of the lithium in lithium-rich pegmatites is uncertain (Norton, 1973, p. 368–369). The lithium may have been obtained by partial melting of lithium-bearing metamorphic rocks. If so, some of the lithium pegmatite regions of the world may also contain nonpegmatitic deposits. Because nearly all lithium pegmatite localities were first prospected for tin, the association between tin and lithium may be worth examining. Many publications indicate that rocks allied with the Cornwall, England, tin deposits have lithian mica, and one wonders if they have other lithium minerals.

Ocean water has often been cited as a potential source of lithium. Its content of only about 0.2 ppm lithium multiplied by the large tonnage of ocean water is impressive, but actually does nothing but reaffirm the eye-catching effect of such arithmetic. With so many better possible sources of lithium to test, one cannot regard ocean water seriously except perhaps for byproduct lithium. In processing ocean water, other commodities would probably be more remunerative, and the lithium output would depend on their market. This is not to say that the work of Steinberg and Vi-Duong Dang (this report) is not a useful contribution to the chemical engineering of extracting lithium from seawater. The subject has been so much discussed that its technology must be examined.

HOW TO ADAPT RESOURCE NOMENCLATURE TO LITHIUM

Three aspects of lithium resources have caused most of the misunderstandings and disputes: (1) the difference between the lithium contained in the deposits and the amount recoverable, (2) the existence of deposits that are not now minable at a profit but are equal in quality to deposits mined in the past and in some instances have actually been mined, and (3) the potential for finding new deposits.

Uncertainty about undiscovered deposits can be alleviated only by geologic work of many kinds coupled with exploration to teach us where, how, and at what rate new resources can be found. If uses in the next 25 years are to become as large as now anticipated, a sizable body of geologic data must be acquired soon.

The problems with recoverability and with marginal deposits can be clarified by dividing the resource estimates into the smallest feasible categories. Resources in operating mines, closed mines, and undeveloped but known deposits should be separated from one another. Resources in different kinds of deposits should also be segregated, because future technological advances may have different effects on the various categories. Separation of deposits by size, grade, mineralogy, and other traits would also be worthwhile. As Singer (1975) shows, "disaggregated" information of this kind will facilitate the process of predicting the supply outlook for the various possible combinations of future economic and technologic circumstances.

Reserves should include only lithium that is currently recoverable, and should exclude lithium now lost in mining and milling. In other words, reserve estimates should encompass only material reasonably certain to enter market channels. The unrecoverable lithium is not a reserve in this sense, but because the recoverability may increase or the lithium in mine dumps and mill tailings may someday become obtainable, it is of potential value. Companies may be reluctant to reveal recoverability, but probably in most instances they can hide the data they prefer not to release. Certainly frank statements of recoverable reserves would eliminate a major source of confusion that may endanger the future of the lithium business.

The importance of marginal resources is illustrated by the Quebec Lithium Corp. deposit at Barraute, Quebec, which could quickly assume its former status as one of the world's best and most productive deposits. The decision to stop operation because of inability to compete with Clayton Valley brine made it no longer a reserve but merely a paramarginal resource. However accurate this term may be, it implies that the deposit's standing is lower than it really is. Other pegmatite deposits have a similar problem. They have often been called reserves, and some of them are in fact either reserves or so near to being reserves that misunderstanding is created by treating them slightingly.

Lithium seems unready for a well-organized, systematic, and exact procedure for stating resources, but a step in that direction would be well taken. One can more easily be optimistic that knowledge of the lithium potential of the United States can and probably will be greatly increased in the next decade.

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OCCURRENCE, DEVELOPMENT, AND LONG-RANGE OUTLOOK OF LITHIUM-PEGMATITE ORE IN THE CAROLINAS

By THOMAS L. KESLER (retired), HENDERSONVILLE, NC

ABSTRACT

Unzoned lithium pegmatites occur in a narrow area 50 km long in the Carolina Piedmont. The pegmatites are composed of approximately 20 percent spodumene that contains about 7.5 percent Li_2O. The ore bodies are as much as 90 m thick and 1,000 m long. Tens of millions of tonnes of ore are minable by open pit. Development began gradually in the 1930's, and two large mines are now in operation. The area containing the pegmatites occurs mostly within and parallel to the strike of metamorphosed shallow-water sediments of the Kings Mountain belt and bounds the east side of the Permian(?) to Mississippian(?) Cherryville Quartz Monzonite of the Inner Piedmont. Pegmatites elsewhere in and around the monzonite do not contain lithium minerals. The quartz monzonite provided the main components of the lithium pegmatites, but the lithium was probably derived from contiguous evaporites in the metasedimentary rocks. Deep pegmatites of long-range interest for underground mining are probably west of those now known, because the metasedimentary rocks dip westerly and should dip less steeply at depth.

GEOLOGIC SETTING

The western world's largest reserves of lithium are in the pegmatites of an area of metamorphic rocks in the Carolinas. Geologic maps of much of the area (Sterrett, unpublished map, 1912; Keith and Sterrett, 1931; Kesler, 1942, 1944, 1955; Griffitts, 1958; Espenshade and Potter, 1960) have been used in the preparation of figure 19, which shows features related to this discussion.

Most of the area is in the western part of the Kings Mountain belt of the Piedmont. The country rocks are mostly metasedimentary and of lower metamorphic rank than those to the east and west. They include quartzite, conglomerate, fine-grained schist with traces of pyroclastic texture, chloritoid schist, biotite schist and gneiss, thin-layered amphibolite, crystalline limestone, and phyllitic metashale that is interbedded with the other types of rocks.

The more quartzose of these rocks underlie a series of ridges, of which Kings Mountain is the most prominent (figs. 19 and 20). The less quartzose rocks, which strati-

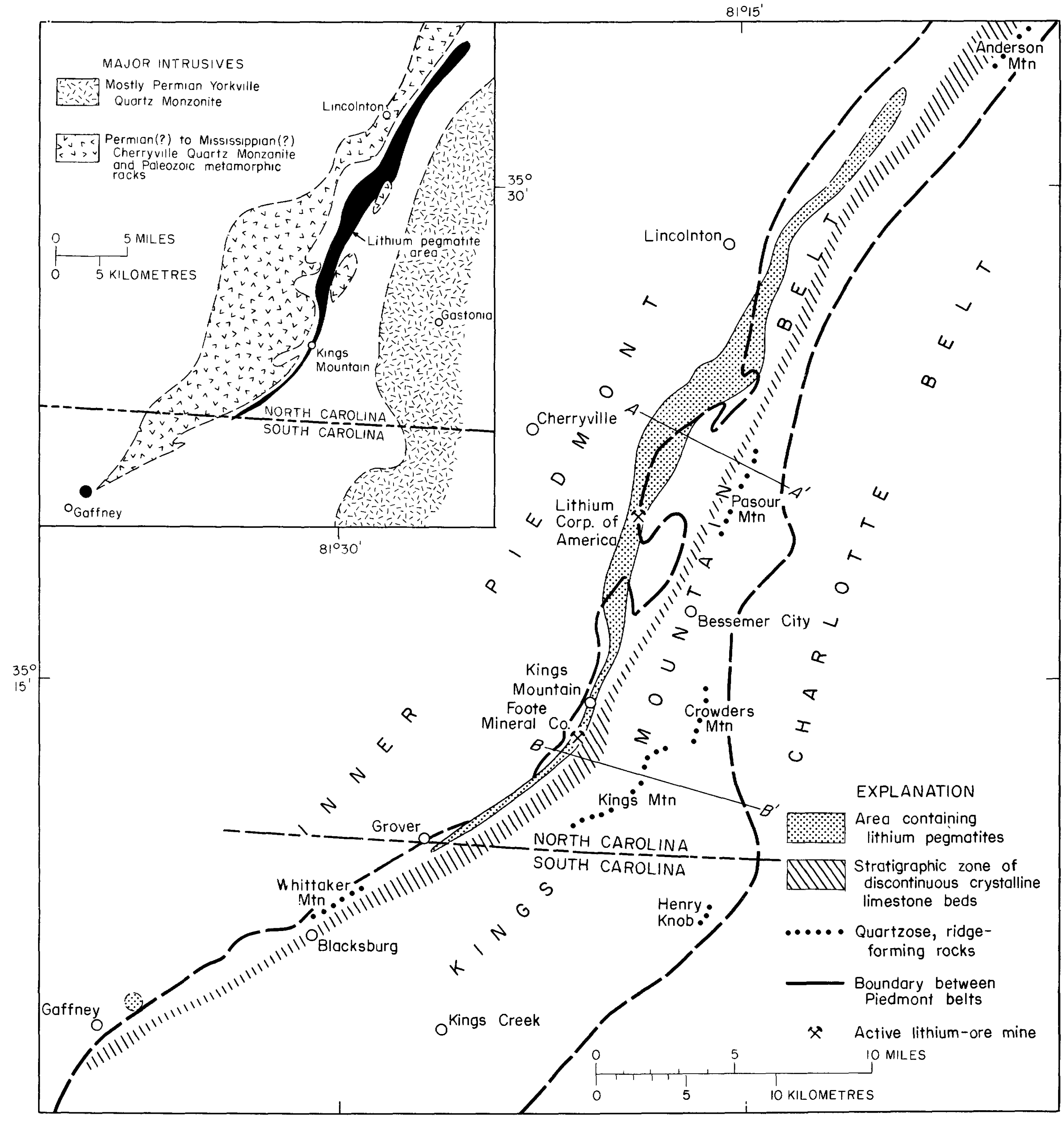

FIGURE 19.—Areal features of the Carolina lithium region.

graphically overlie the quartzose rocks, crop out west of the ridges with uniform westerly dip except at Gaffney, where the beds are overturned. These west-dipping rocks identify the western limb of an arch originally more than 15 km wide, and vertical isoclinal folds mapped in the ridges by Espenshade and Potter (1960) identify the strongly compressed core of the structure.

In the northern part of the belt (section *A–A'*) the eastern limb of the arch is missing, having been displaced by a major intrusive of the adjoining Charlotte belt. This is the biotitic and porphyritic Yorkville Quartz Monzonite of Permian age (Overstreet and Bell, 1965).

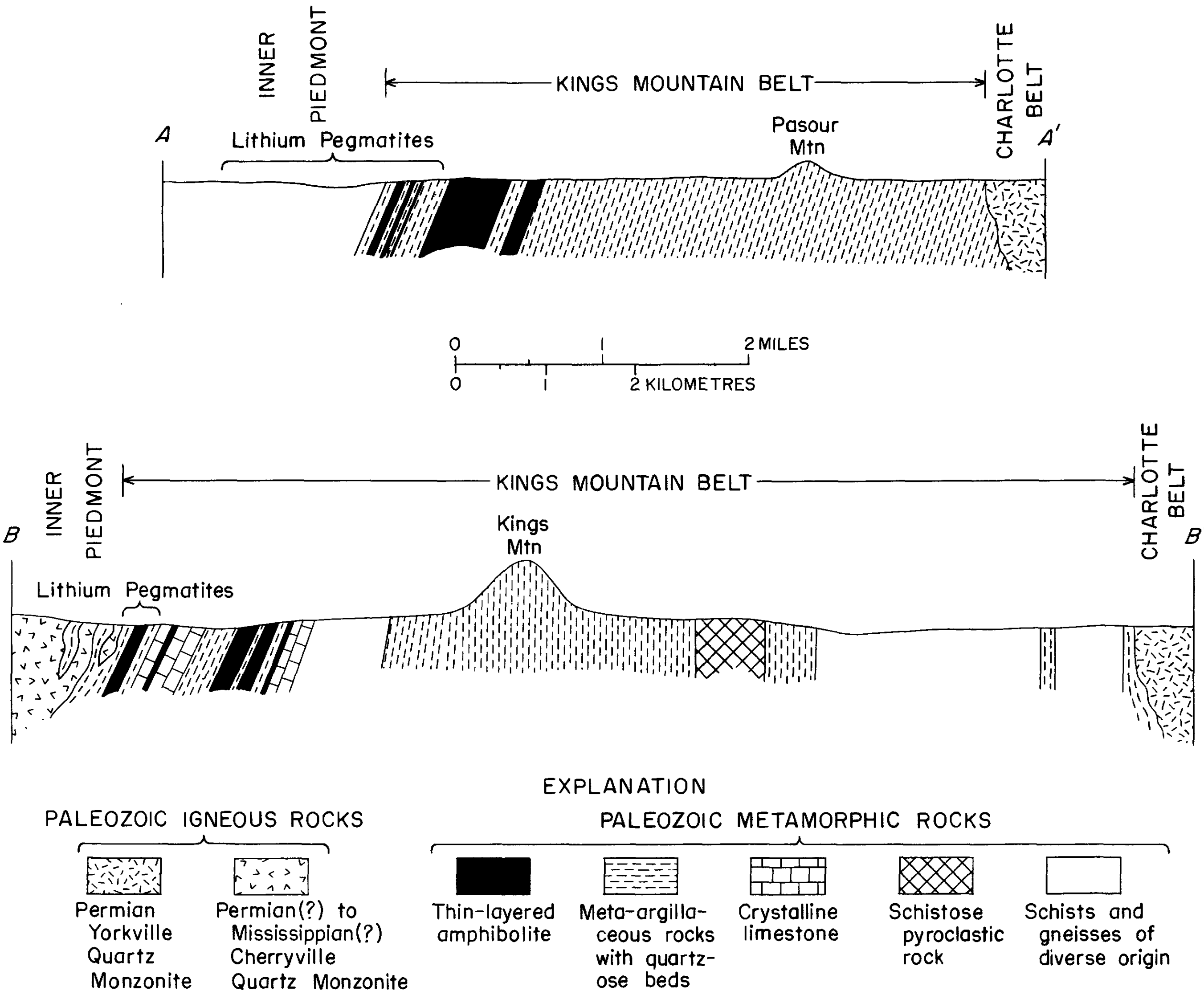

FIGURE 20.—Cross sections showing geologic relations of the pegmatites. Location of sections shown in figure 19.

The forceful intrusion of the Yorkville left discordant contacts and contact-metamorphic effects (Espenshade and Potter, 1960; Overstreet and Bell, 1965), but this intrusive shows no relation to the lithium pegmatites.

Along the western boundary of the Kings Mountain belt there is a transition involving four features: (1) a gradual decrease in dip from that shown in figure 20; (2) an increase in metamorphic rank; (3) a change from the northeast structural grain of the Kings Mountain belt to a complex of diversely oriented, broad, open folds characteristic of the Inner Piedmont; and (4) a profusion of large and small bodies of a muscovite-biotite quartz monzonite of the Cherryville, many of which occur as concordant sheets. Limited data on the Cherryville yield radiometric ages ranging from 375 to 260 million years, a spread regarded by Overstreet and Bell (1965) as inconclusive. Whether this results from inadequate sampling or from a long and relatively passive intrusive history is unknown. However, the Cherryville differs from the Yorkville in that it does not truncate major country-rock structures.

The Cherryville contains nonlithium pegmatite, and similar pegmatite also occurs in the surrounding country rock; however, it is only along the east side of the intrusive that the outermost of the pegmatites are lithium bearing. Of particular significance (Kesler, 1961) is a compound pegmatite 30 m wide within amphibolite and 60 m from the quartz monzonite to the west and lithium pegmatite to the east. In composition, this body grades eastward across its strike from simple quartz-monzonite pegmatite to spodumene-bearing pegmatite. The Cherryville, therefore, shows a genetic relation to the lithium pegmatites; this relationship is considered further in discussing future exploration.

THE PEGMATITES

The lithium pegmatites occur at close intervals in an area about 50 km long and less than 3 km in maximum width (fig. 19). Sporadic spodumene crystals also occur in pegmatite near Gaffney, 19 km farther south. The bodies are as much as 90 m thick and almost 1,000 m long. To date drilling has reached a maximum depth more than 200 m below outcrop without encountering any change in the geologic characteristics of pegmatites or wall rocks.

In general, pegmatite was intruded parallel to the foliation of mica schist. Thin-layered amphibolite, where not interlayered with schist, was ruptured irregularly with respect to dip, but parallel to strike. Thin pegmatites were intruded into joints with diverse trends in massive hornblende gneiss.

Five minerals make up about 99 percent of the lithium pegmatites. As previously reported (Kesler, 1961), long-term control on the milling of crude ore showed an original content of 20 percent spodumene, 32 percent quartz, 27 percent albite, 14 percent microcline, 6 percent muscovite, and 1 percent trace minerals including cassiterite in which there has been recurrent mining interest since the 1880's. Only near the collapsed shaft of the old Ross tin mine near Gaffney have pegmatite cores been recovered in which spodumene is very scarce. Elsewhere it is common and averages about 7.5 percent Li_2O (theoretical maximum 8.03). Thus, crude ore with 20 percent spodumene should grade about 1.5 percent Li_2O, or 7,000 parts per million Li. The pegmatites, with rare and small-scale exceptions, are not zoned, and the grade of crude ore is fairly uniform as shown in published assay sections (Kesler, 1961). This feature has also stimulated the recovery of feldspar and mica byproducts, which are liberated in grinding the ore.

Late features include contact-alteration selvages between pegmatite and amphibolite, rarely as much as 0.5 m thick, consisting of rare-alkali biotite, holmquistite, calcite, and apatite. Near some of the large pegmatites, dynamically brecciated amphibolite containing fractured black tourmaline has been altered to coarse chlorite rock containing much pyrrhotite and a little holmquistite and chalcopyrite. Extreme weathering of such breccia leaves only a conspicuous float of fragmental black tourmaline. A few nearly vertical, northwest-trending faults of very small displacement cut some of the pegmatites. The walls are separated by a few centimetres to nearly a metre of amphibolite breccia and gouge, partly altered to a biotitic rock that resembles minette.

DEVELOPMENT

In 1938, our government's concern with supplies of strategic minerals caused a renewed interest in the cassiterite content of the pegmatites. The U.S. Geological Survey assigned me and other personnel to an investigation that included two seasons of detailed mapping, and the results (Kesler, 1942) indicated a large potential for developing minable reserves of lithium ore.

Others had foreseen this possibility. Limited prospecting was started in the mid-thirties by the Tennessee Mineral Products Company, by Phillip Hoyt, and by L. M. Williams, who was still active when our survey began.

On leases of Williams, the Solvay Process Company operated a mine and flotation plant in the early forties and did considerable diamond drilling. This effort ended in 1945, and uncertain market conditions following World War II prevented further work until 1951, when Foote Mineral Company reactivated the mine and mill and did more extensive drilling. An account of all exploration on this property through 1959 has been published (Kesler, 1961). Shortly after Foote started its operation, the Lithium Corporation of America began construction of a chemical plant at Bessemer City and did some preliminary mining at two localities 8 km south of Lincolnton. Their present mine is near Tryon School, 6.5 km northwest of their plant, where much exploratory drilling has also been done.

The large open-pit mines of Foote and Lithium Corporation are expanding, and during their early years purchases of lithium by the Atomic Energy Commission caused a flurry of prospecting in the Carolina area as well as in Canada, its nearest potential competitor. In fact, until early in 1956, published articles had listed 286 lithium interests in 16 areas in 3 Canadian provinces plus the Great Slave Lake region. The Canadian activity had a strong influence on developments in Carolina and finally matured into temporary competition. The domestic industry should not forget.

MINING

The mines in the Carolinas must penetrate the zone of weathering before encountering the fresh ore that gives best recoveries in milling. The base of the zone of weathering is irregular, mostly from 10 to 20 m below the surface in pegmatite, but generally deeper in the country rocks. Little of the pegmatite in the zone of weathering is decomposed, but substances deposited from ground water stain the cleavage surfaces of the minerals. Flotation reagents therefore cannot reach clean surfaces, and only part of the stains are acid soluble at practicable concentration. Separation by heavy media requires crushing that preferentially shatters the spodumene, which has better cleavage than the other minerals. Power requirements for abrasive scrubbing of total crude ore to remove the stains would become increasingly uneconomic because of rising fuel costs, and this disadvantage would also apply to any effort to bypass the concentration of spodumene by roasting the crude ore for treatment. Whatever may be the solution to this problem, it must be found to eliminate a continual drain on ore reserves.

LONG-RANGE OUTLOOK

It is generally agreed (Kesler, 1961; Norton, 1973) that reserves of minable lithium ore in the Carolina area amount to tens of millions of tonnes. The rate at which they will be consumed is unknown, but their location gives them a competitive advantage over other pegmatite ores. The advantage will continue until mounting costs of open-pit stripping and initial stages of underground mining bring competition from foreign sources.

As reserves in the Carolina area are depleted and costs increase, the lithium industry will then enter a second stage in which the domestic market may be divided between domestic and foreign suppliers. A third stage will eventually be reached in which foreign sources will also experience rising costs, bringing the location of ore reserves back into major importance. At that time the domestic industry, if it prepares well in advance, can be in position to recapture lost segments of the world lithium market.

The preparation will require exploration beyond anything yet attempted, based on the certainty that all ore of sufficient bulk for open-pit mining will have been discovered and that new targets will be much deeper. Where and how these efforts should be directed requires consideration of the origin of the Carolina lithium pegmatites.

Scarcely half of the Cherryville Quartz Monzonite as illustrated in figure 19 actually consists of monzonite. The remainder consists of Inner Piedmont metamorphic rocks with widely divergent structural trends, a feature also characteristic of Inner Piedmont rocks marginal to the Cherryville. The quartz monzonite is accepted as the source of all pegmatites in and around its area of outcrop, but only those containing lithium occur in an area having a preferred and essentially straight trend. That trend is along the west side of the Kings Mountain belt and parallel to its structural grain as reflected by the zone of limestone shown in figure 19. Thus, the distribution of the lithium, considered apart from the nature of its host, seems to be more closely related to the Kings Mountain belt than to the Inner Piedmont.

In an effort to account for high concentrations of pegmatitic lithium without an obvious source, Norton (1973) has suggested that deep melting, or anatexis, of lithium-rich metasedimentary rocks could form the pegmatite magma. This concept, though not entirely compatible with known conditions in the Carolina area, provides a new approach.

The low metamorphic rank and well-preserved sedimentary structures of the rocks at Kings Mountain preclude their having reached conditions usually specified for anatexis, but their lithology suggests an original shallow-water environment that could have included evaporites. All of the rocks are thin bedded, and the bedding planes are sharp and continuous along the trend of the belt without appreciable distortion. The limestone is lenticular and was originally silty; the quartzite is relatively pure and reflects good sorting; the conglomerate is mostly fine textured, but contains pebbles as much as 7.5 cm in diameter; and the meta-argillaceous rocks are nonuniform in composition, particularly their micas. These features show that the original sediments at Kings Mountain were deposited under conditions of variable currents, in water too shallow for massive, poorly sorted deposits to be formed. They were apparently deposited in a basin bordering an area that would later become the Charlotte belt (fig. 19) on whose margin Espenshade and Potter (1960) have found evidence of volcanism, and therefore a possible source of thermal waters.

The final stage in the filling of such a basin could have included the formation of evaporite deposits whose position would have been in the present downdip section beneath the eastern edge of the Inner Piedmont. During the slow invasion of the Cherryville Quartz Monzonite, volatiles expelled into the rocks of the Kings Mountain belt would have served as collectors of loosely bonded elements, including lithium if present; such volatiles are essential parts of pegmatite magma.

This hypothetical framework implies that rocks of the Kings Mountain belt should persist in depth as the wallrocks of the lithium pegmatites. Their normal dip is westward beneath the rocks of the Inner Piedmont (section *A–A'*) and adjacent to the Cherryville Quartz Monzonite. In the entire extent of the Cherryville and the metamorphic rocks (fig. 19), the many bodies of the monzonite are so uniformly concordant with the Inner Piedmont metamorphic rocks that abrupt departure from this habit is unlikely. The eastern limit of the Cherryville Quartz Monzonite and its bordering fringe of lithium pegmatites can therefore be expected to shift westward at depth, and deeper pegmatites of interest for future exploration should lie west of the axis of present outcrops.

Outside of this area, the apparently barren gap between Grover and Gaffney could reflect an original divide between evaporate deposits, but the presence of spodumene near Gaffney requires reconsideration of that area. Closer study is also needed beyond the presently known limit of the pegmatites to the northeast, where conditions are not clear (Broadhurst, 1956) but where the continuity of typical metasedimentary rocks in the Kings Mountain belt may indicate continuity of lithium source beds.

There is no known physical reason why underground mining of the strategically located Carolina ore bodies cannot reach depths many times the present maximum; it is also an economic probability for the future, not only because mineral values rise as raw materials are depleted, but also because essentially the entire mineral content of this ore has large-scale industrial use.

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A COMPARISON OF THREE MAJOR LITHIUM PEGMATITES: VARUTRÄSK, BIKITA, AND BERNIC LAKE

By E. Wm. Heinrich
University of Michigan, Ann Arbor, MI

ABSTRACT

A reassessment of the mineralogical and geological characteristics of three major lithium pegmatites, Varuträsk, Sweden; Bernic Lake, Manitoba; and Bikita, Rhodesia, shows that Bernic Lake and Bikita are mineralogically and structurally very similar. Both also contain significant reserves of lithium, especially in very low iron secondary spodumene which is especially suitable for utilization as glass-ceramic raw material.

INTRODUCTION

Three of the world's most highly localized major Li-Rb concentrations are the structurally and mineralogically complex pegmatites of Varuträsk, Sweden; Bikita, Rhodesia; and Bernic Lake, Manitoba, Canada. This paper compares these deposits and assesses their past importance and future potential as Li-Rb sources.

The writer has examined all three: Varuträsk first some 25 years ago; Bikita, in 1966 and 1967; and Bernic Lake several times beginning in 1972.

PEGMATITIC LITHIUM MINERALOGY

There are some 26 different "independent" lithium minerals, of which nine silicates and eight phosphates occur in granitic pegmatites. Five other lithium minerals occur almost exclusively in highly alkalic subsilicic pegmatites (nepheline-syenitic) and related deposits.

Of the many subordinate elements that characterize granitoid pegmatites, lithium is undoubtedly one of the most versatile and, indeed, is so in several ways. It not only forms its own pegmatitic species but can also appear vicariously in other minerals, including such diverse groups as pyroxenes, amphiboles, micas, and tourmalines. Its granitic pegmatitic minerals are equally varied: the pyroxene, spodumene; the amphibole, holmquistite; the micas, lepidolite, zinnwaldite; and the zeolite, bikitaite. Both a variety of silicates and of phosphates (for example, amblygonite, triphylite) are represented. In alkalic granitic pegmatites lithium may even appear as the fluoride, cryolithionite.

In granitic pegmatites lithium minerals appear in all three structural types of pegmatites: unzoned, zoned, and structurally complex. In addition, holmquistite occurs as an exogenic wallrock constituent (Heinrich, 1965). In zoned pegmatites, spodumene and amblygonite-montebrasite are not uncommonly multigenerational, with differences among generations in form, crystal size, and composition (Heinrich, 1953). Lepidolites of complex pegmatites are normally multigenerational with conspicuous variations among generations in color, grain size and form, and, of course, in composition (Heinrich and Levinson, 1955; Heinrich, 1967).

The lithium minerals range, paragenetically, from such earliest species as phenocrysts of iron-rich spodumene, through the intermediate magmatic stages (spodumene, petalite, amblygonite, triphylite), through the post magmatic replacement period (lepidolites), into intermediate to low-temperature hydrothermal alteration stages (eucryptite, bikitaite, cookeite, and secondary phosphates).

PARAGENETIC TYPES OF SPODUMENE

Recent studies (Heinrich, 1975; 1976) have identified three distinct paragenetic types of spodumene in pegmatites:

1. Phenocrystic spodumene in essentially unzoned pegmatites of the "King's Mountain type." These laths, usually less than a foot long, commonly are greenish and contain essential Fe^{3+} in substitution for Al^{3+}, usually in the range of $Fe_2O_3=0.6-0.9$ percent.
2. Zonal spodumene, commonly as large laths that occur in intermediate zones and cores of well-zoned pegmatites. This spodumene is low in iron ($Fe_2O_3=0.01-0.03$ percent). It may contain significant manganese (×.0−0.× percent), and whereas most is white, some is pink or lilac (kunzite).
3. Secondary spodumene. Produced by the isochemical decomposition of petalite:

   $$\text{petalite} \rightarrow \text{spodumene} + \text{quartz}$$
   $$LiAlSi_4O_{10} \rightarrow LiAlSi_2O_6 + 2SiO_2$$

   This spodumene is relatively fine grained; commonly the aggregate retains the crystal form and basal cleavage of the parent petalite. It is white and has very low iron ($Fe_2O_3=0.007-0.03$ percent), because of the low-iron content of the parent petalite.

The substitution of even small amounts of Fe^{3+} for Al^{3+} in spodumene markedly increases its thermal stability field (Appleman and Stewart, 1968). Iron spodumene was synthesized in air at 1,100°C and is stable up to at least 800°C at 2Kb H_2O pressure compared to ~565°C at 2Kb for essentially iron-free spodumene. Geothermometric data obtained by Sheshulin (1963) from fluid-inclusion studies, indicate that early (his Generation I) spodumenes crystallized between 600° and 640°C, whereas younger (his Generation II) spodumenes crystallized at 330°–390°C. Thus phenocrystic spodumene, which is iron rich as compared to paragenetically younger intermediate zone and core spodumene, represents a higher temperature spodumene.

After secondary spodumene has been formed from petalite, it may be recrystallized and texturally rearranged, becoming coarser, unoriented, and very difficult to distinguish from primary white inner zone spodumene. Some such spodumene occurs at Bernic Lake where Černý and Ferguson (1972) distinguish three types of spodumene: Type A, tabular aggregates of fibrous spodumene intergrown with quartz, clearly pseudomorphous after petalite which constitute 90 percent of all spodumene in the pegmatite. Type B, laths up to 1.5 m long, in the intermediate core-margin zone, not associated with petalite, and identified as primary zonal spodumene. Type C, fibrous to columnar spodumene in quartz, but not tabular (may be secondary).

VARUTRASK, SWEDEN

The Varuträsk pegmatite, described in 37 articles by Percy Quensel and his students (see Quensel, 1952, 1956) is "C"-shaped in plan with the "C" open to the north, the western, thinner limb which trends northwestward dips inward to the northeast at a low angle, whereas the eastern thicker limb which trends northeastward dips 30° NW. Thus the pegmatite is synclinal with the trough plunging to the north at a shallow angle.

The internal structural units are as follows:

1. Border zone, 1–3 cm, fine-grained, quartz and muscovite.
2. Wall zone, up to 5 m, coarse-grained, quartz, muscovite, schorl, and locally beryl.
3. Outer intermediate zone, microcline-perthite, quartz, muscovite.
4. Inner intermediate zone, microcline-perthite, quartz, muscovite, amblygonite, spodumene-quartz pseudomorphous after petalite, petalite remnants. Units 3 and 4 together are 40–75 m thick.
5. Pollucite masses (Quensel's "Caesium replacement unit"), as much as 5 m across, which in the eastern limb are marginal to the core.
6. Core, quartz, 12 m across.
7. Lepidolite replacement unit. This is centrally located in the western limb and replaces mainly rock of the inner intermediate zone. In the eastern limb it also replaces parts of this zone but in addition transgresses into the outer intermediate zone and the wall zone.
8. Cleavelandite replacement bodies, irregularly developed in all older units.

BERNIC LAKE, MANITOBA

The geology of the Tanco pegmatite at Bernic Lake, Manitoba, has recently been described in detail in a series of papers by Cerný and Ferguson (1972). The east-west-striking pegmatite is an almost horizontal sheet that crops out only in the bed of Bernic Lake from whence it dips at a low angle to the north and plunges slightly both toward the east and west. As in most flat-lying pegmatites, the zonal configuration is markedly asymmetric with outer zones 1, 2, 4, and 5 (see below) forming a series of shells that enclose the lensoid to tabular inner units 3, 6, 7, 8, and 9 (see below). Of these inner tabular units the albitic fine- to medium-grained assemblages are concentrated in the lower interior, whereas lithium- and silica-rich assemblages with giant-crystal dimensions predominate in the upper interior.

The sequence of units in probable order of formation is (Crouse and Černý, 1972):

1. Border zone, albite, quartz, locally tourmaline.
2. Wall zone, albite, quartz, microcline-perthite, locally tourmaline.
3. Sheet and lenses of aplitic ("sugary") albitite.
4. Lower intermediate zone, microcline-perthite, albite, quartz, spodumene + quartz, (replacement of petalite), locally amblygonite.
5. Upper intermediate zone, spodumene (laths), spodumene + quartz (replacement of petalite), quartz, locally amblygonite and petalite.
6. Central intermediate zone, microcline-perthite, albite, quartz, locally beryl and wodginite.
7. Core units, lenses and sheets of quartz in several different positions.
8. Lens-shaped bodies of pollucite in zone 5 and between zone 6 and hanging-wall zones 1 and 2.
9. Sheets and pods of lithian muscovite rock in zone 6.

BIKITA, RHODESIA

The Bikita pegmatite is an irregular sheet that strikes north-northeast and dips 14–45° eastward.[1] It ranges in thickness from 95 to 210 ft and has been explored over a strike length of 5,100 ft. Again the internal zonal structure is strongly asymmetric, and there are major changes in the sequences of units along the strike. Our first knowledge of the internal structure stemmed from Symons (1961) and Cooper (1964) who both unfortunately use a variety of nonequivalent terms (mineralogical, structural, textural, and grade) to designate the units. Studies by Gallagher (1962) and by the writer in 1966 and 1967 (Heinrich, unpublished company report, 1966) have supplied additional information on the units. Table 17 is an attempt to decipher and interpret the interrelationships.

COMPARISON

The three pegmatites are compared in table 18. The reassessment of the nature of the finer grained units in the Bikita pegmatite demonstrates that Bikita and Bernic Lake are structurally very similar, both having aplitic albitites (some wavy banded) and lepidolite replacement units. The latter is centrally located in both but is much more strongly developed, both in size and grade, at Bikita than at Bernic Lake. At Bikita the lithium mica is chiefly lepidolite, whereas at Bernic Lake it is predominantly lithian muscovite. As at Bernic Lake, the aplitic albitites at Bikita are concentrated in the lower part of the pegmatite.

One of the main differences between Bikita and Bernic Lake is in the extent to which the petalite has been transformed to spodumene + quartz. At Bikita about 50 percent of the petalite has been converted; at Bernic Lake probably about 90 percent of the petalite has been transformed.

RESERVES

VARUTRÄSK

There has been no mining at Varuträsk since early 1950, but in late 1960 "some stockpiles of lithium minerals" still were available (Erland Grip, written commun., 1967). Doubtless these are small, and the total amount of lithium in all reserves at Varuträsk (petalite, spodumene, lepidolite, amblygonite) is small, possibly no more than about 100 tons of ore.

BERNIC LAKE

Lithium reserves for the Bernic Lake pegmatite were calculated by Howe and Roundtree (1967) who estimated lepidolite reserves at 107,700 tons containing an average of 2.24 percent Li_2O and spodumene reserves at 4,727,263 tons containing an average of 2.01 percent Li_2O, excluding ore that must be left in a pillar unless the overlying lake is drained. These data indicate a total of 45,000 tons of lithium (Norton, 1973). Since then drilling has considerably extended the dimensions of the spodumene ore body, and the total lithium reserves are at least 50 percent greater.

BIKITA

Symons (1961) calculated reserves of 6,700,000 tons of all lithium-mineral ores (petalite, spodumene, lepidolite, amblygonite, eucryptite) averaging 2.90 percent Li_2O or 90,000 tons of lithium (Norton, 1973). Calculations on measured reserves of all types of ores known at the end of 1965 available to the writer show that 76,000 tons of lithium were in these reserves. This total does not include the unmeasured resources of the northern extension and the two western "arms."

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[1] Actually the "main Bikita pegmatite" may be but one limb (the easternmost) of a much larger undulatory sheet. The eastern limb passes north of the Al Hayat sector into an anticlinal unit, and thus connects southwestward into a synclinal phase to the east of which lies a third main unit, an east-dipping synclinal limb (see Gallagher, 1962).

TABLE 17.—*Internal structure of the Bikita, Rhodesia, pegmatite from hanging wall downward to footwall*

Symon's (1961) and Cooper's (1964) designations			
Al Hayat Sector	Bikita Sector	Mineralogy	Interpretation (this paper)
Border zone	Border zone	f. gr. alb., qtz., musco	1) Hanging-wall border zone.
Wall zone—mica band	Wall zone—mica band	c. gr. musco., qtz	2) Hanging-wall wall zone.
Hanging-wall feldspar zone	Hanging-wall feldspar zone	micro.-perth., qtz., musco	3) Intermediate zone.
Intermediate zone: petalite-feldspar zone	Intermediate zone: petalite-feldspar zone	pet., micro.-perth., alb., musc., qtz	4) Intermediate zone.
Intermediate zone: spodumene zone	Intermediate zone: spodumene zone	spod.-qtz., in matrix alb., musco., qtz., eucryptite, bikitaite.	4a) The spodumene-quartz aggregates represent former petalite crystals.
Intermediate zone: feldspathic lepidolite zone		f. gr. lepid., alb., qtz	5) Aplitic lepiodolite albitite.
Intermediate zone: pollucite zone	Intermediate zone: pollucite zone	pollucite, lepid	6) Pollucite zone.
	Intermediate zone: feldspar-quartz	micro.-perth., qtz	7) Core-margin intermediate zone.
Intermediate zone: "all mix" zone	Intermediate zone: "all mix" zone	micro.-perth., qtz., pet., spod.-qtz., beryl + cleav., lepid.	8) Spodumene-quartz replace petalite. Clevelandite and lepidolite are secondary. Part of core-margin intermediate zone.
	Core zone: "High grade" ↓ lepidolite	lepid	9) Lepidolite replacement of a quartz core. Quartz increases downward.
	"Near solid" ↓ lepidolite	lepid., qtz	
	lepidolite-quartz shell	lepid., qtz., amblyg.	10) Remnants of quartz-amblygonite core.
	Lower intermediate zone "cobble zone."	lepit., alb., qtz	11a) Lepidolite "bands", lenses, veins in banded aplitic albitite.
	Lower intermediate zone feldspathic lepidolite.	lepid., alb., qtz	11b) Lepidolite disseminated in aplitic albite-quartz rock.
	Not recognized by Cooper	alb., qtz	11c) Aplitic albitite.
	Rhythmically banded beryl zone	lepid., alb., qtz., beryl, tant.	11d) Banded aplitic lepidolite albitite.
	Muscovite band	musco., qtz	12) Footwall wall zone.
Footwall feldspar zone	"Spotted dog" zone	alb. + blebs of musco.-qtz	13) Footwall border zone.

Abbreviations: alb. = albite; amblyg. = amblygonite; cleav. = cleavelanditic albite; lepid. = lepidolite; micro.-perth. = microcline-perthite; musco. = muscovite; pet. = petalite; qtz. = quartz; spod. = spodumene, tant. = tantalite; f. = fine; c. = coarse; gr. = grained; ↓ = sequence from center core outward.

TABLE 18.—*Comparison of Varuträsk, Bernic Lake, and Bikita pegmatites*

Characteristic	Varuträsk (1.7 b.y.)	Bernic Lake (2.6 b.y.)	Bikita (2.65 b.y.)
Shape and attitude	Flat-troughed sheet	Nearly horizontal sheet	Irregular to tabular gently dipping.
Size (strike and dip)	1,050 ft(+?)	4,000 by 1,500 (+)	5,100 (+)
Thickness	10–100 ft	60–280 ft	95–210 ft
Wall rock	Amphibolite	Amphibolite	Amphibolite.
Wallrock alteration	Albite, tourmaline	Biotite, holmquistite, tourmaline, apatite.	Biotite, tourmaline (?).
Internal structure	Relatively symmetric; lepidolite replacement.	Strongly asymmetric; aplitic albitites; lepidolite replacement.	Strongly asymmetric aplitic albitites; lepidolite replacement.
Major accessory elements	Li, Cs, Rb, B, P, F	Li, Cs, Rb, Ta, Ti, F	Li, Cs, Rb, Be, P.
Minor accessory elements	Nb, Ta, Ti, Sn, U, Mn Be, As, Sb.	Nb, Sn Mn, B, P, Mo, Bi	Nb, Ta, Ti, Sn B, Cu.
Lithium mineralogy	Petalite, spodumene, amblygonite, lepidolite, Li-muscovite, cookeite, triphylite -lithiophilite, ferri-sicklerite.	Petalite, spodumene, amblygonite, lepidolite, Li-muscovite, eucryptite, cookeite, triphyllite-lithiophilite, lithiophosphate.	Petalite, spodumene amblygonite, lepidolite, Li-muscovite, eucryptite, bikitaite.
Types of spodumene	Secondary (major); recrystallized secondary (minor).	Zonal (very minor); secondary (major) (minor).	Secondary; recrystallized secdondary (very minor).
Economic minerals	Petalite, spodumene-quartz, pollucite, lepidolite.	Spodumene-quartz, Ta minerals, pollucite.	Petalite, spodumene-quartz, lepidolite, amblygonite, eucryptite, pollucite, beryl, microcline, Ta minerals, cassiterite.

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NONPEGMATITE LITHIUM RESOURCE POTENTIAL

By JAMES D. VINE
U.S. GEOLOGICAL SURVEY, DENVER, CO

ABSTRACT

The lithium content of most sedimentary rocks ranges from about 0.0005 to 0.01 percent, but rocks deposited in basins that contain evaporite minerals may contain 0.01–0.1 percent lithium, and clay minerals related to hectorite containing 0.3–0.5 percent lithium have been reported from several localities in the western United States. Although marine evaporite sequences that include potassium salts may suggest conditions favorable for the entrapment of lithium-rich brines, nonmarine evaporite basins probably represent the most favorable trap for concentrated lithium brines. Areas known to contain such exotic salts as borates and nitrates in nonmarine basins of Tertiary age also contain anomalous concentrations of lithium in clastic rocks, volcanic ashes, clays, and magnesium-rich carbonate rocks.

Once dissolved, lithium tends to remain in solution in residual brines, even after evaporative concentration and precipitation of the salts of sodium, potassium, and magnesium. Brines associated with these evaporite minerals may contain as much as 1,000 times more lithium than seawater contains.

INTRODUCTION

The distribution of lithium is less well understood in sedimentary rocks than in igneous rocks where the concentration of lithium in the late stages of crystallization and in mineralizing fluids expelled from the magma chamber is fairly well documented (Heier and Billings, 1972). All the commercially important lithium minerals occur in pegmatites or greisen associated with igneous rocks. Recent studies (Horstman, 1957; Ronov and others, 1970; Tardy and others, 1972) suggest that most of the lithium content of sedimentary rocks is associated with the clay minerals. Because clays are so widely dispersed in sedimentary rocks and the manner of lithium fixation on clays is generally weak, lithium is only rarely concentrated in sedimentary rocks in amounts of more than a few tens of grams per tonne. The exceptions to this broad dispersal of lithium in sedimentary rocks are of special interest in the search for potential new sources of lithium.

NORMAL MARINE SEDIMENTS

Seawater has an average lithium content of slightly less than 0.2 mg/l (Goldberg, 1963), an amount that is equal to the influx from river waters in about 6.4×10^6 years (Wedepohl, 1968, p. 1010). Hence, the residence time for lithium in the sea is a relatively short interval of geologic time, equal to about one-tenth the interval of time since the end of the Cretaceous Period. Thus, an amount of lithium equal to the total quantity in the ocean must be removed every 6.4 m.y. Marine clays, which contain an average of about 60 g/t lithium, provide the reservoir for this excess lithium. However, this process of adsorption of lithium on clay particles is so uniform throughout the ocean that it is unlikely that any significant enrichment of lithium will occur in the sediments deposited in normal marine environments.

MARINE EVAPORITES

Local marine basins with restricted circulation may develop hypersaline environments, and in warm dry regions these waters will become concentrated enough to precipitate evaporite minerals, including gypsum ($CaSO_4 \cdot 2H_2O$), halite (NaCl), and various complex salts of potassium and magnesium. Such evaporite deposits have been estimated to compose no more than 1 percent of the total mass of sedimentary rocks (Wedepohl, 1969, p. 265), and most of these are of marine or marginal marine origin. However, lithium is so soluble it will not precipitate by evaporative concentration until after most of the sodium, potassium, and magnesium salts have been precipitated. Lithium precipitation is so rare a situation that natural lithium salts have never been observed.

In order for a restricted basin to accumulate a large quantity of salt, it must have a regular source of fresh seawater by transport across a shallow bar or by periodic flooding during storms. The heavier, more concentrated brines may be preserved by entrapment in the pore spaces of the already precipitated salts, but some brine may also be mixed and diluted with the fresh seawater. Some of the diluted brine will generally escape to the open sea by ebbtide or through gravity return across a permeable bar. Hence, in a basin of marine evaporites, if we sum the sodium and lithium in both the precipitated salts and the entrapped brine, the ratio Li:Na may be less than, but cannot exceed, the ratio (0.0001) for normal seawater.

With continued deposition and burial, the body of permeable salt and brine will recrystallize into a solid dry mass causing the brine that once filled the pores to be expelled into adjacent clastic rocks such as sandstone. Most of the lithium will be carried away from its original environment of deposition into these adjacent sediments.

Because only those salts deposited from the most concentrated marine brines contain potassium minerals, the occurrence of potassium may be an indication of the former existence of a lithium-rich brine. Lithium does not significantly substitute for sodium or potassium in the common salt minerals, but the salts deposited from the most concentrated brines may contain anomalous amounts of bromine. This relation provides a way to recognize areas favorable for potassium exploration, and it may help to guide the search for lithium brines or for neoformed lithium minerals that are a result of the interaction between a brine and the rock in which it was contained.

NONMARINE EVAPORITES

Nonmarine evaporites are the product of evaporative concentration of water in undrained basins within the continental landmass. Most rivers drain into the sea, but an undrained basin may occur where the crust of the earth is deformed so rapidly—or the rate of evaporation is so high—that the streams cannot maintain their course to the sea. Streams may also be blocked by volcanic activity, landslides, and glacial activity, but the larger basins such as Death Valley in California and the Dead Sea trough in Israel are the result of tectonic deformation of the earth's crust in an arid climate.

The Great Basin area in the southwestern United States (fig. 21) includes a relatively large area of undrained basins, both large and small. Some major rivers flow into this area and contribute to the load of dissolved mineral matter that is carried into a terminal lake or playa. The Owens River of California drains the eastern Sierra Nevada and terminates at Owens Lake, Calif. The Walker River also drains an area of eastern California and empties into Walker Lake, near Hawthorne, Nev. The Truckee River forms the outlet for Lake Tahoe in eastern California and flows into Pyramid Lake, northeast of Reno, Nev. The Bear River drains part of southeastern Idaho and southwestern Wyoming, and flows into the Great Salt Lake, near Ogden, Utah. The Sevier River, which drains central Utah, terminates at Sevier Playa, south of Delta, Utah. The Humboldt and Reese Rivers flow through a large part of central and northern Nevada and drain into Carson Sink, a large playa, near Fallon, Nev.

The structural framework responsible for these basins originated in mid-Tertiary time—some 20–25 m.y. ago—when faulting produced the system of basins and ranges extending from the front of the Wasatch Range, near Salt Lake City, Utah, across western Utah and Nevada to the eastern front of the Sierra Nevada, near Bishop, Calif. Since the initial breakup, some parts of this region have been integrated into the major drainage of the Colorado River. However, the present course of the Colorado River is geologically quite recent, and so some basins that contain upper Tertiary evaporites have only recently been exposed by erosion. One such body of salt is exposed along the Overton Arm of Lake Mead, Nev. Salt deposits of nonmarine origin differ somewhat from those of marine origin in not being laminated and in being very low in bromine. Moreover, the ratio Li:Na may be much greater in nonmarine evaporites than in marine evaporites.

Chemical differences between evaporite basins are pronounced. Great Salt Lake, Utah, and the Great Salt Lake Desert to the west are characterized by high concentrations of sodium chloride. Others, such as Railroad Valley, southwest of Ely, Nev., contain a large body of salt that includes a body of gaylussite ($Na_2Ca(CO_3)_2 \cdot 5H_2O$). Bristol Lake in California is characterized by an unusually high concentration of calcium chloride. Other basins in the Mojave Desert area in California are characterized by high concentrations of boron. Clayton Valley, southwest of Tonopah, Nev., is characterized by a high lithium-to-sodium ratio in a chloride brine. Attempts to explain these differences in terms of the chemistry of the immediate drainage basin are only partly satisfactory. This is because the history of the region is complicated. Many basins received overflow from other basins during previous wet climate periods, and some receive drainage by ground water flow from adjacent basins at the present time. Significant ground water flow has been suggested as the reason that some basins such as Clayton Valley have a wet surface while adjacent slightly higher basins have a hard dry surface.

The origin of most of the major constituents of nonmarine evaporites—including the sodium, calcium, magnesium, as well as the sulfate, chloride, and carbonate—can be explained either by weathering of rocks, including marine evaporites, within the drainage basin or by the airborne salt carried into the area by the prevailing westerly winds off the Pacific Ocean. How-

Figure 21.—Undrained basins in western United States.

ever, neither explanation seems to account for the unusually high ratio of lithium to chloride that distinguishes some of these brines, such as that of Great Salt Lake, from sea-water. Deep ground water circulation with subsurface heat and volcanic activity seems to be the best alternative explanation for the source of the lithium.

HYDROTHERMAL WATER

Although freshwaters generally contain only a few tens of micrograms per litre of lithium, many hot springs and geothermal waters contain 1–10 mg/l lithium, and a few contain more. The high ratio of lithium to sodium is so characteristic of geothermal waters that a ratio approaching 1:100 may be useful in recognizing a geothermal source, even where the water has been cooled and diluted by surface waters (Ellis, 1975, p. 516). The elevated temperature of geothermal water generally indicates deep circulation of ground water in the vicinity of a buried heat source, such as a magma chamber or volcano. Pore water in the rocks adjacent to such a heat source will tend to circulate as in a giant convection cell. Taylor (1974) has shown that the quantity of water pumped to the surface in this manner in mineralized districts such as Tonopah, Nev., is very large. Hot water is more effective than cold water in leaching lithium from rocks; hence, the amount of lithium carried to the surface in hot springs is probably very large. In Yellowstone National Park, and in similar geothermal areas, most of the lithium is lost to streams that carry it directly to the sea. However, the lithium mica lepidolite has been reported from a drill core in the Lower Geyser Basin in Yellowstone National Park (Bargar and others, 1973), and lithium-rich clays, from the Pliocene Teewinot Formation, have been reported south of the park near Jackson, Wyo. (J. D. Love, written commun., 1973).

Geothermal systems not only circulate lithium, but may in some areas represent the ore-forming fluid responsible for deposition of base and precious metals. A lithium asbestos, known as eckermannite, is associated with lead and other metallic ores at the Camp Albion district, Boulder County, Colo. (Wahlstrom, 1940). Another example is the Spor Mountain beryllium deposit, Juab County, Utah, where lithium occurs with beryllium, fluorite, manganese, and uranium. The possibility of finding commercially significant quantities of lithium minerals associated with hydrothermal mineral deposits should not be overlooked.

BURIAL METAMORPHISM

When sedimentary rocks are deeply buried, many changes take place that we associate with compaction, diagenesis, and burial metamorphism (Noble, 1963). Hydrous minerals that are stable during weathering at the surface of the earth are, when deeply buried, transformed to less hydrous or anhydrous species (Coombs and others, 1959; Jolly, 1974). Thus, at depth, hydrous clay minerals such as montmorillonite are transformed to anhydrous illite or mica, zeolites may be altered to feldspars, hydrous iron oxides related to limonite are transformed to hematite or may be reduced to pyrite, and gypsum is transformed to anhydrite. All these changes involve the loss of water, which can be quantitatively significant. Moreover, the lithium, which is lightly adsorbed by many of these hydrous minerals, may be released to solution. The water, released at depth, cannot readily escape to the surface but will be forced into fractures where it may be responsible for the deposition of various vein minerals, such as cookeite.

SUMMARY

Because pegmatites and brines have supplied sufficient lithium to date, there has been no pressing economic reason to look for new sources of lithium. The predicted future demand for lithium suggests that new sources of lithium will be needed. To find new resources, new prospecting techniques based on increased knowledge of the behavior of lithium in different geologic environments have to be developed. Hydrothermal sources of lithium may result in lithium deposits similar to the beryllium deposit at Spor Mountain, Utah. Concentrations of lithium in brines or sediments may also be associated with nonmarine evaporite deposits or with extremely concentrated marine evaporites. Cookeite deposits may be found in low-grade metamorphic terranes, and other lithium deposits associated with hydrothermal activity may also be found.

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LITHIUM CONTENTS OF THERMAL AND MINERAL WATERS

By DONALD E. WHITE, J. M. THOMPSON, and R. O. FOURNIER
U.S. GEOLOGICAL SURVEY, MENLO PARK, CA

Reported lithium contents of natural waters range from less than 0.01 ppm to more than 500 ppm (table 19). Although absolute contents are of major interest in commercial recovery, the ratios of Li to other major constituents are more significant in evaluating origin and diverse effects of evaporation, dilution, and water-rock interaction. The most useful single ratio is Li/Cl, which is emphasized in this text, but Li/Na has nearly equal usefulness.

Lithium/chlorine (by weight) is lowest in ocean water (0.00001, table 19) and becomes progressively higher in major North American rivers (0.00004) and in small streams and meteoric springs (variable and unreliable values because so dilute, but ranging from 0.001 to 0.1). For comparison, the ratios in major crustal types are granite, 0.15; basalt, 0.17; and shale, 0.38 (table 20).

Thermal and mineral waters of high salinity tend to have intermediate Li/Cl ratios, generally ranging from about 0.0001 to 0.001 (table 19). The median ratio for oil-field waters is probably near 0.0003, but a few ratios attain 0.001 and even higher; one notable example is brine from the Jurassic Smackover Formation of Texas and Arkansas, which averages 0.001. Individual analyses are greater than 0.002 and Li contents are as

TABLE 20.—*Lithium contents of average rocks, in ppm*
[Data from Krauskopf (1967)]

Rock type	Li	Na	Li/Na ratio	Cl	Li/Cl ratio
Crust	20	24,000	0.0008	130	0.15
Granite	30	28,000	.0011	200	.15
Basalt	10	19,000	.0005	60	.17
Shale	60	6,600	.009	160	.38

TABLE 19.—*Lithium contents of various waters, in ppm*

	Li	Na	Li/Na ratio	Cl	Li/Cl ratio	Source
Water						
Ocean	0.17	10,500	0.00002	19,000	0.00001	Krauskopf (1967).
North American rivers	.003	$\sim$9	.0003	8	.0004	Livingston (1963).
Meteoric warm springs, (median of 5, $\sim$50°)	.04	$\sim$30	.001	5	.008	Mariner and others (1975).
Salton Sea brine, Calif. ($\sim$350°C)	215	50,400	.043	155,000	.0014	White (1968).
Oilfield brines						
Jurassic Smackover Formation brines of Gulf Coast (average)	174	67,000	0.0026	172,000	0.0010	Collins (1974).
Alberta, Canada	81	42,000	.0019	113,000	.0007	White (1965).
Kern County, Calif	9.9	6,700	.0015	15,300	.0006	White (1965).
Evaporate brines						
Clayton Valley (connate?), Nev	380	66,200	0.0057	95,200	0.004	Kunasz (1970).
Searles (connate?), Calif	81	110,000	.0007	121,000	.0007	G. I. Smith (oral commun., 1975).
Permian Salado Formation (connate?), N. Mex	16	14,300	.0011	200,000	.00008	White and others (1963).
Permian Salado Formation (solution of salts), N. Mex	2.8	95,000	.00003	157,000	.00002	White and others (1963).
Pennsylvanian Paradox Member; Hermosa Formation (connate?), Utah	66	6,000	.011	241,000	.0003	White (1965).

much as 500 ppm (Collins, 1974). The interstitial waters of some evaporites, marine and nonmarine, are notably high in Li (table 19): 81 ppm in the upper salt brine of Searles Lake (Li/Cl ratio 0.007) and 300 ppm in the commercial Clayton Valley brines (Li/Cl ratio 0.004).

Nearly all saline waters of high temperature geothermal systems are much enriched in Li. The Salton Sea brine (350°C and 26 percent salinity) has 215 ppm of Li (Li/Cl ratio of 0.0014 and an estimated 1.0 million tonnes of Li in 5 km^3 of brine; White, 1968). Moderately saline geothermal waters exceeding 200°C and closely associated with young silicic volcanism range from about 1 to 50 ppm of Li and have the highest Li/Cl ratios of any major group of thermal and mineral waters, ranging from less than 0.001 to more than 0.02; the median ratio is about 0.004 (White and others, 1963). The relatively dilute thermal waters of Yellowstone National Park are especially notable, having an average Li content of about 3 ppm and an Li/Cl ratio of about 0.01. The calculated discharge of Li from Yellowstone Park is about 480 tonnes per year, or 48 million tonnes over the probable minimum activity of 100,000 years (table 21).

TABLE 21.—*Lithium contents of waters of Yellowstone National Park, Wyoming, in ppm*

[From Thompson and others (1975)]

Location	pH	Li	Na	Li/Na ratio	Cl	Li/Cl ratio	Temperature (°C[1])
Near-neutral chloride waters							
Upper Geyser Basin:							
Ear	9.2	5.2	335	0.016	417	0.012	95
Giantess	9.2	5.7	365	.016	439	.013	95
Punch Bowl	8.3	4.0	425	.009	295	.014	95
Sapphire	9.0	2.3	450	.005	308	.007	95
Interchange	8.6	3.2	300	.011	226	.014	74
Spring near Y–8	8.9	2.9	429	.007	293	.010	79
Myriad near C–1	9.9	4.0	310	.013	404	.010	94
Midway-Lower Basins:							
Rabbit Creek (Y–5)	8.4	3.3	375	.009	271	.012	95
Fountain P.P. near Clepsydra	9.4	2.8	380	.007	325	.009	92
Porcupine Hills near Y–13	9.2	4.6	341	.013	312	.015	93
Ojo Caliente (Y–3)	8.2	4.2	335	.013	331	.013	95
River Group	9.4	3.4	339	.010	323	.011	93
Fairy Meadows	8.7	3.4	390	.007	319	.011	87
Imperial Group	~9.1	2.4	290	.008	222	.011	93
Sentinel	~8.5	1.7	309	.006	300	.006	94
Sylvan	5.7	4.8	410	.012	531	.009	93
Norris:							
Cistern	7.1	4.3	316	.014	476	.009	93
Fenner drillhole	4.6	7.9	440	.018	720	.011	92
Porcelain Terrace, base	8.4	6.8	400	.017	713	.010	93
Pork Chop	8.0	6.3	470	.013	780	.008	91
Yellowstone Canyon (7 mile)	8.9	3.3	347	.010	376	.009	92
Vermillion Group	8.6	.35	430	.0008	244	.0014	67
Rainbow Group	8.4	.55	354	.0016	304	.0018	92
Heart Lake, Spike Group	9.5	6.7	400	.017	363	.018	93
Lewis Lake	8.0	.6	140	.004	79	.008	Hot
Shoshone Basin, Bronze Group	8.8	1.5	315	.005	167	.009	93
Lone Star (Y–6)	8.2	1.7	329	.005	417	.004	68
Travertine-depositing springs							
Hillside	8.6	0.84	151	0.006	73	0.012	83
Firehole Lake, Steady	8.4	.40	85	.005	44	.009	93
Terrace Springs	7.3	.75	305	.002	65	.012	59
Mammoth	7.3	1.6	130	.012	166	.010	73.5
Thermal, acid SO_4–Cl waters							
Norris Basin:							
Little Whirligig	3.2	4.6	345	0.013	582	0.008	93
Realgar[2]	3.2	3.6	334	.011	492	.007	88.5
Horseshoe[2]	2.5	2.8	235	.012	341	.008	86
Echinus[2]	3.2	.93	160	.006	103	.009	85
Emerald[2]	3.05	3.6	308	.012	460	.008	89
Unnamed	3.3	3.7	290	.013	468	.008	54
Green Dragon	~2.7	2.3	145	.016	216	.011	~93
Green Dragon	~2.7	4.0	273	.015	447	.009	92
Northwest of Fenner drill hole	acid	.70	63	.011	88	.008	63
Shoshone Basin	2.4	.16	60	.003	60	.003	93

TABLE 21.—*Lithium contents of waters of Yellowstone National Park, Wyoming, in ppm*—Continued

Location	pH	Li	Na	Li/Na ratio	Cl	Li/Cl ratio	Temperature (°C[1])
Thermal, acid SO_4 waters							
Summit Lake[2]	2.8	0.02	30	0.0007	5	0.004	94
Washburn	4.5	.02	14.8	.001	.1	.2(?)	~90
Hot Springs Basin	1.8	.01	11.0	.0009	.1	.1(?)	76
East of Sulphur Cauldron	2.0	.01	25.4	.0004	2.1	.005	88
Heart Lake[2]	2.8	<.01	2.2	<.005	3	<.003	87.5
Joseph Coats	1.8	.01	7.0	.001	.1	.1(?)	86
Dilute neutral waters							
Cold Streams							
Thumb Creek	7.5	0.04	27	0.0015	1.4	0.03	5
Little Thumb	7.4	.01	4.4	.002	1.3	.008	7
Elephant Back	7.3	.02	9.2	.002	.8	.03	Cold
Cold Springs:							
West of Black Sand	7.5	.02	6.7	.003	3.8	.005	14
Midway Picnic area	7.3	.12	32	.004	17	.007	21
Sylvan area	7.80	.02	3.0	.007	.2	.1(?)	5
Thermal meteoric waters:							
Fairy Meadows	not reported	.09	16.2	.006	1	.06	26
Southwest of Gibbon Hill	8.6	.12	63	.002	1.6	.08	68
North of Gibbon Falls	6.0	.1	24	.004	.8	.12	31
Specimen in Geyser Creek area	7.9	.05	65	.0008	5	.01	92
Hillside	7.4	.04	10.4	.0004	4.0	.01	32
North of Biscuit Basin	6.9	.01	10.0	.001	.8	.01	48

[1] Boiling at this elevation is 93°C. Springs above 93°C are superheated.
[2] Unpublished data of Thompson.

The most probable explanation for Li-enriched geothermal waters is selective leaching of part of the Li from rocks at temperatures above 200°C; 300° to 500°C may be especially favorable. The evidence for direct involvement of magmatic fluid high in Li and other constituents is a real but still controversial possibility.

Lithium is evidently removed from river and ocean waters and is fixed by low-temperature reactions in clay minerals. In simple evaporational processes, most brines require source waters that are higher in Li/Cl than is the brine. The Clayton Valley brine (table 19), which has an Li/Cl ratio of 0.004, probably requires a main supply from hot springs containing an Li/Cl ratio of 0.01 or higher and a localized evaporation basin with little inflow of other Cl. The upper Tertiary rhyolitic volcanism and hydrothermal ore deposits west of Clayton Valley may have been essential in supplying Li.

Diagenetic, metamorphic, and igneous-related water-rock interactions at moderate to high temperatures are probably essential in accounting for the relatively high Li contents of most thermal and mineral waters.

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LITHIUM RECOVERY FROM GEOTHERMAL FLUIDS[1]

By C. E. BERTHOLD, HAZEN RESEARCH, INC., GOLDEN, CO, and
D. H. BAKER, JR., U.S. BUREAU OF MINES, BOULDER CITY, NV

ABSTRACT

The lithium resource of the Imperial Valley, Salton Sea KGRA (Known Geothermal Resource Area), in southern California, appears to be of significant size, comparable to the Clayton Valley, Nevada, lithium reserve in quantity of contained lithium.

Lithium occurs, presumably as lithium chloride, in amounts of about 200 ppm (as Li) in the geothermal fluids obtained from depths of 5,000 feet or more (as typified by Sinclair No. 4 fluid).

Recovery of lithium from this resource can be achieved by chemical concentration (precipitation) techniques and ion-exchange methods, both liquid and solid, among others.

The paper will discuss in general terms the studies undertaken and preliminary results obtained in attempting to recover lithium from this resource.

INTRODUCTION

Geothermal fluids from various sources in the Western United States contain quantities of lithium ranging from the low parts per million level to concentrations of hundreds of parts per million (ppm). Some of these geothermal resources can be considered to be significant, if not major, resources or reserves of lithium.

In some studies on recovery of mineral values from geothermal fluids for the U.S. Bureau of Mines, a sampling survey was made of several hot springs and geothermal sites in the Western United States. Table 22 presents a summary of the lithium content found in some of these geothermal fluids and hot springs waters. As can be seen, the geothermal fluids of the Salton Sea Known Geothermal Resource Area (KGRA), Imperial County, Calif., contain significant concentrations of lithium. Lithium reserves within this KGRA site have been compared in quantity with those of the Clayton Valley, Nevada, area, that is, approximately 40,000 tonnes of contained lithium (Kunasz, 1975).

TABLE 22.—*Lithium contents of selected geothermal fluids and hot spring waters*[1]

Location	Lithium concentration (ppm Li)
Mesa L–6–1, Imperial County, Calif., pre-flash, 8,000-ft depth	55
Magmamax No. 1, Imperial County, Calif., pre-flash, 2,400-ft depth	143
Sinclair No. 4, Imperial County, Calif., post-flash, 5,400-ft depth	238
Coso Hot Spring, Inyo County, Calif., average of published analyses	Trace to 0.1
Darrough Hot Springs, Nye County, Nev. post-flash	.06
Golconda Hot Springs, Humboldt County, Nev.:	
No. 1	.45
No. 2	1.0
Beowawe Steam Well, Eureka County, Nev. post-flash	3.3

[1] From work performed by C. E. Berthold and others, June 1973 for the U.S. Bureau of Mines under contract No. SO 133084, Process Technology for recovering geothermal brine minerals.

The lithium content of the Salton Sea geothermal fluids appears to vary, both with respect to location within the reservoir and depth of the producing zone. As an example, Magmamax No. 1 well produces brine from the 2400-foot level and has a lithium content of about 150 ppm with a total salinity of approximately 180,000 ppm. Contrasted to this geothermal fluid are those of Sinclair No. 4 brine (well located one mile south of Magmamax No. 1) at 5400-foot depth, with over 200 ppm lithium and a total salinity of nearly 300,000 ppm. Figure 22 shows the locations of these geothermal wells in the Imperial Valley area.

Lithium occurs in the Salton Sea KGRA fluids, presumably as lithium chloride, since the predominant anion is chloride, with small amounts of bromide, fluoride, and sulfate also present. The major cations present in these geothermal fluids are sodium, calcium, potassium, and ammonia, with minor amounts of magnesium, rubidium, and cesium also present. Table 23 presents a partial analysis for Mesa, Sinclair, and Magmamax geothermal fluids, together with a comparison of lithium-sodium and lithium-calcium ratios for these geothermal fluids with other naturally occurring saline brines.

It appears that brine from Mesa L–6–1 well at the southern fringe of the Salton Sea KGRA is considerably higher in Li/Ca ratio as compared to other geothermal fluids found in this KGRA. Whether this implies a different source for this fluid or a different subsurface rock matrix that supplies the lithium for this fluid is not known. In any event, recovery of lithium from Mesa L–6–1 fluid would appear to be somewhat easier than from either Sinclair No. 4 or Magmamax No. 1, owing to the relatively higher lithium level with respect to the other salines present.

Recovery of lithium from such naturally occurring geothermal fluids is complicated by several factors: (1) relatively low concentration in the fluid, (2) high temperature of the fluid, and (3) presence of relatively large amounts of other potentially valuable minerals such as iron, manganese, silica, zinc, lead, barium, strontium, and magnesium. In general, geothermal fluids from the

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[1] The data and results presented herein were obtained during the performance of work for the U.S. Bureau of Mines under contracts SO 133084 and HO 144104. The views and conclusions presented herein should not be interpreted as necessarily representing the official policies or recommendations of the Interior Department, Bureau of Mines, or of the U.S. Government.

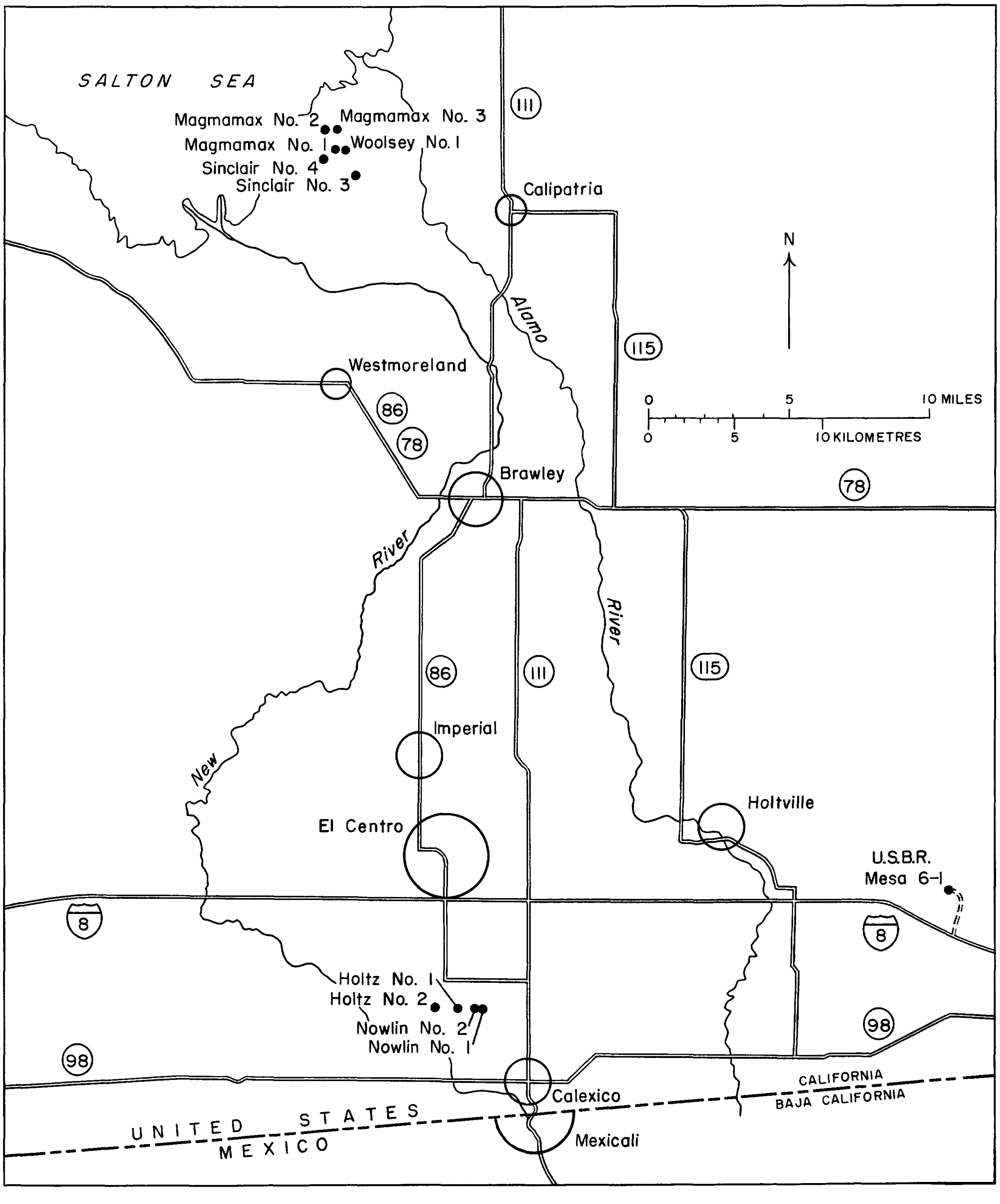

FIGURE 22.—Imperial Valley geothermal area showing location of geothermal wells, highways, and cities.

Salton Sea KGRA require clean-up, or removal and perhaps recovery, of the silica, iron, manganese, lead, zinc, and magnesium therefrom prior to recovery of the lithium values.

RECOVERY METHOD

Recovery methods for lithium contained in solution can be broadly categorized into two general schemes: (1)

TABLE 23.—*Analyses, in ppm, of geothermal fluids*

Sample	Br	Cl	Na	Ca	K	Mg	NH_4	Li	F	SO_4	Li/Na	Li/Ca
Mesa L-6-1	35	18,000	11,000	1,370	1,430	22	39	55	1.5	16	0.005	0.04
Sinclair No. 4	162	186,000	71,000	35,000	18,000	152	611	238	5.8	42	.003	.007
Magmamax No. 1	109	102,000	44,000	21,000	8,300	100	504	143	4.6	50	.003	.007
Clayton Valley, Nev.											.0045	.6
Searles Lake, Calif.											.007	No Ca present

direct recovery from the brine via liquid (Baniel and Blumberg, 1963; Fletcher and Wilson, 1961; Grinstead and Davis, 1970; Morris and Short, 1963; Morrison and Freiser, 1962; various patents[2] and written communications[3]) or solid ion exchange (Kennedy, 1961) and (2) removal of the lithium by precipitation as an insoluble compound or double salt.

In discussing methods of lithium recovery from geothermal fluids, it should be kept in mind that such recovery processes are secondary to the original intent behind the development of geothermal resources, namely power generation and production of freshwater.

Whatever method or methods are used to recover lithium from such resources must be adaptable to the constraints imposed upon geothermal wells. These are:

1. The almost universally accepted belief that waste geothermal fluids must be reinjected back into the producing structure to maintain hydraulic balance and prevent ground surface subsidence. Alternatively, fresh or brackish water, if available, could be used as a substitute fluid, thus allowing some concentration of the geothermal fluid, if this would aid in recovering some of the constituents from the geothermal fluid.
2. Whatever methods or means used for lithium recovery must be compatible with the need for geothermal fluid reinjection. That is, no material should be present that might precipitate out in the subsurface structure, thereby leading to plugging-off of the aquifer(s). The presence of organic compounds, such as might result from liquid ion-exchange methods of lithium recovery, constitutes yet another unknown if reinjected back into the producing zone.

Keeping these constraints in mind, a series of laboratory studies on lithium recovery was started, using Sinclair No. 4 geothermal fluid as the raw material.

Post-flash Sinclair No. 4 geothermal fluid required a "clean up" treatment to remove soluble silica, iron, manganese, zinc, and lead prior to lithium removal. This was achieved by adjusting pH to a nominal value of 7.5 to 8.0 and removing the precipitated hydroxides, together with adsorbed zinc and lead values. At this point, the purified Sinclair No. 4 fluid can be used directly for lithium recovery or else concentrated (using steam evaporation or solar evaporation), if such concentration is deemed necessary and/or desirable.

Our studies utilized both types of Sinclair No. 4 geothermal fluid, post-flash and concentrated. Figure 22A illustrates the behavior of lithium in post-flash Sinclair No. 4 fluid, during the course of concentration by simulated solar evaporation. Using magnesium as a tracer element to follow the course of evaporation, it appears that no lithium is lost from solution up to a concentration ratio in excess of 5.

The limiting factor in degree of solution concentration becomes saturation with respect to the calcium chloride content of the geothermal fluid. Further concentration of Sinclair No. 4 fluid results in crystallization of large quantities of calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) which entrains significant quantities of the valuable, concentrated, lithium-bearing fluid.

While much has been published in the literature and in the patent files regarding recovery of lithium values from solution, our studies have indicated that precipitation of lithium values as the aluminate complex to be the most effective.

Organic solvents such as butyl and amyl alcohols, have been used to selectively dissolve away lithium chloride from mixtures of alkali metal chlorides (Lindal, 1970; Morrison and Freiser, 1962). Alcohol-ketone mixtures have been used to extract lithium from brines, but urea or ammonia additions are required to prevent calcium interference[4]. Lithium Corporation of America has patented a process[5] where lithium is extracted as a complex lithium tetrachloroferrate, but this scheme requires pretreatment of the lithium-containing fluid with both hydrochloric acid and ferric chloride to establish proper operating conditions.

In addition, the application of liquid or solid ion-exchange techniques to such hot saline fluids ($T \geq 110°C$)

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[2] Israel patent 16017, and U.S. patents numbered 3,307,922; 2,964,381; 3,306,700, U.S. Department of Commerce, Patent and Trademark Office, Washington, D.C.

[3] C. Hanson, 1970 written commun., "Extraction of magnesium chloride from brines using mixed ionic extractants," University of Bradford, Bradford, York. W. C. Keder, 1970, written commun., from Kedder and others, "Separation of alkali metals by solvent extraction with mixtures of organic-soluble acids and phenols," Battelle Pacific Northwest Laboratory, Richland, Washington. R. L. Focht and others, 1961, oral commun., "Separation of lithium aluminate" paper presented at the Pittsburgh Conference on analytical chemistry, Pittsburgh, Penn., 1961.

[4] U.S. patent, 3,307,922, U.S. Department of Commerce, Patent and Trademark Office, Washington, D.C.

[5] U.S. patent, 3,537,813, U.S. Department of Commerce, Patent and Trademark Office, Washington, D.C.

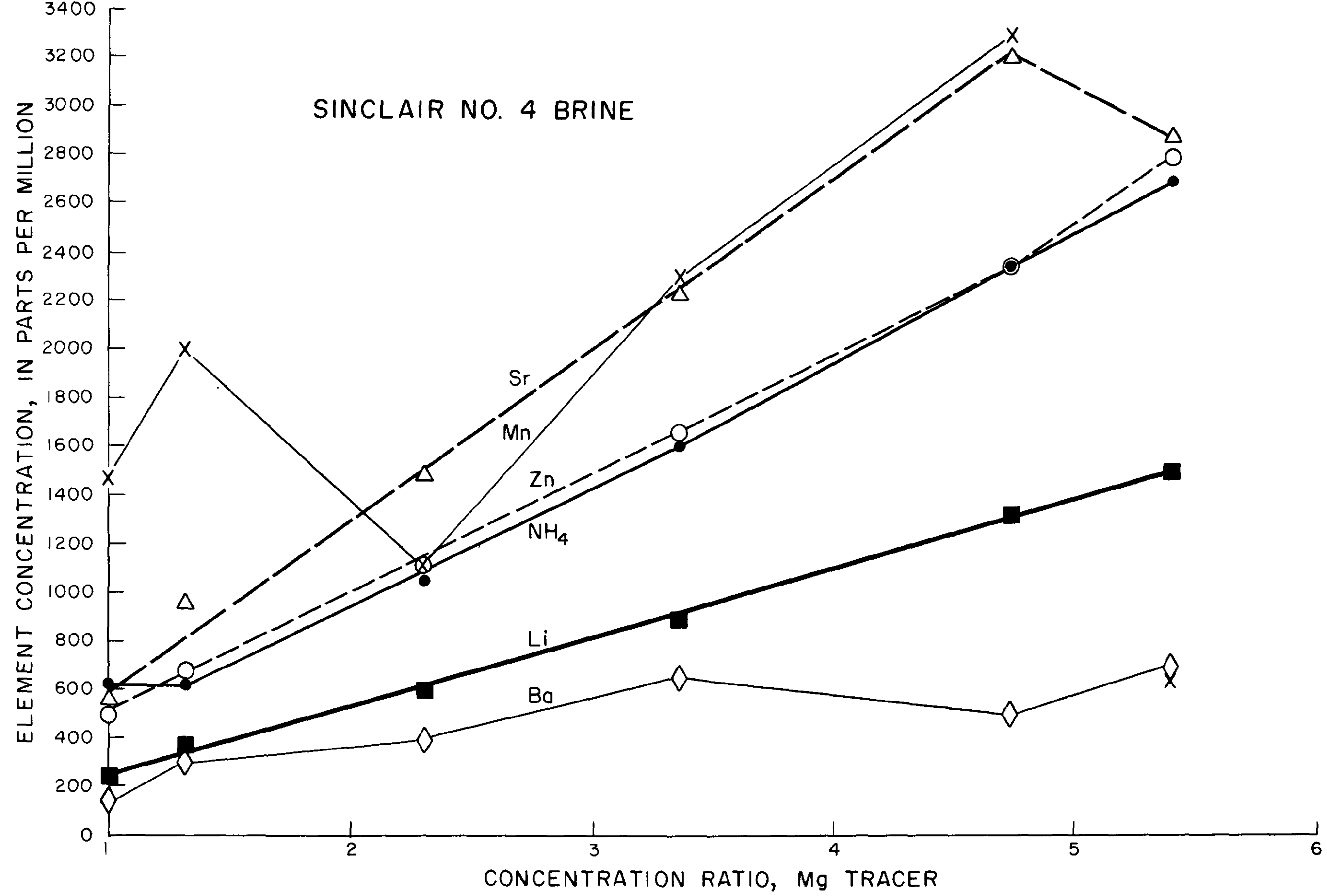

FIGURE 22A.—Behavior of lithium and other elements during concentration by evaporation.

leads to problems regarding solvent degradation and losses due to evaporation of the carrier solvent, while ion-exchange resins are subject to dehydration and shrink-swell fracturing with consequent destruction of the resin beads.

The preferred method for lithium recovery from Sinclair No. 4 geothermal fluid is the precipitation as a complex lithium aluminate using either freshly precipitated aluminum hydroxide or in-situ precipitation of aluminum hydroxide via aluminum chloride with pH control.

Ratios of concentration in excess of 150 have been obtained by this method with lithium recoveries in excess of 98 percent. Figure 23 presents data on lithium recovery versus mole ratio of aluminum to lithium used to effect the precipitation. Apparently the optimum Al/Li ratio for 98+ percent lithium recovery is about 2.75/1. Precipitation temperature for these results was in the 75°C–85°C range.

Control of pH is critical to achieve maximum lithium recovery, with a range of 5.5 to 8.2 appearing to be optimum for Sinclair No. 4 brine as shown in figure 24. This pH range is somewhat different than that called for in the literature and is probably dependent to some degree on the composition of the fluid used. For example, R. L. Focht (1961, oral commun.) recommends a pH range of 10 to 12.5 as being optimum for maximum lithium extraction.

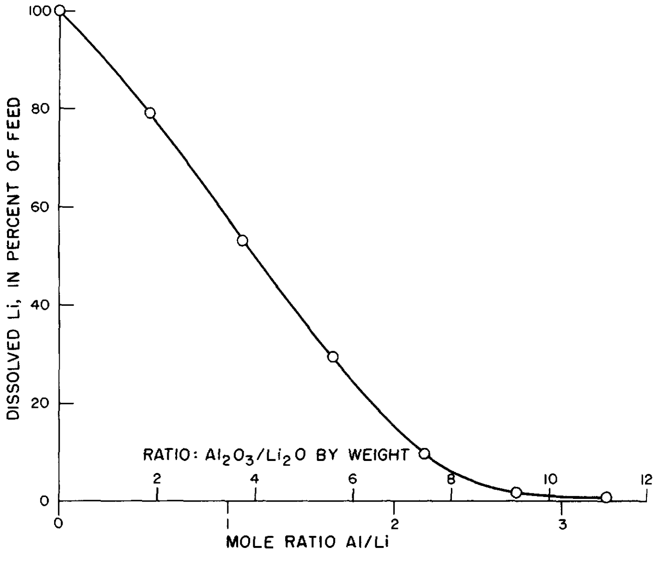

FIGURE 23.—Effect of Al:Li ratios on lithium recovery.

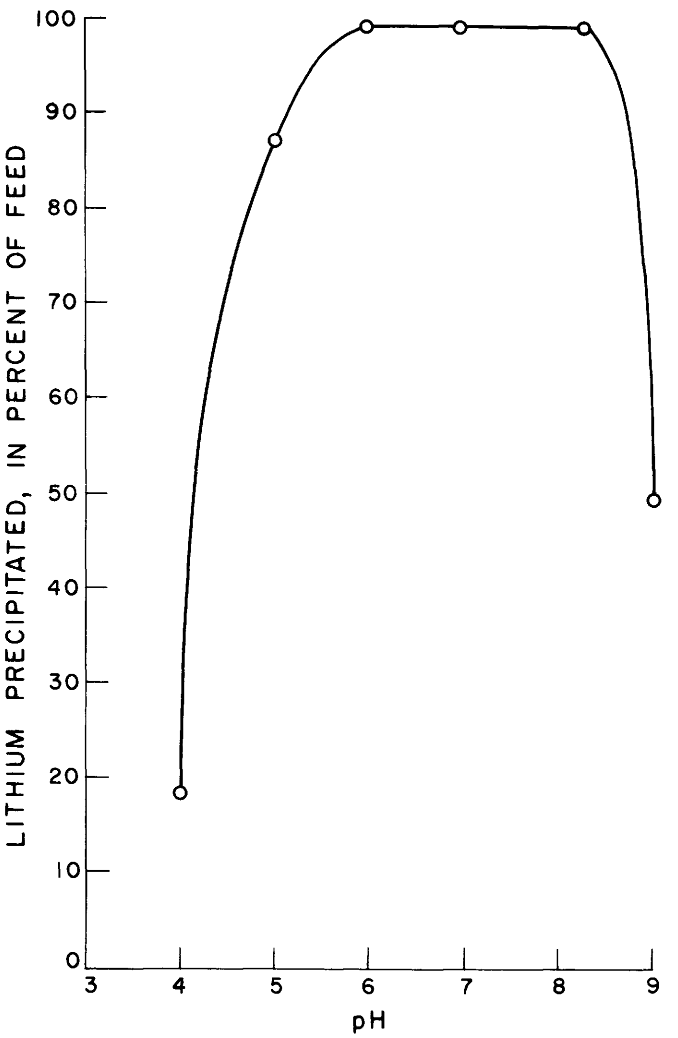

FIGURE 24.—Effect of pH on precipitation of lithium with aluminum hydroxide.

A major difficulty associated with the aluminate method of lithium recovery is the gelatinous nature of the precipitate formed. This is probably due to the high mole ratio of aluminum to lithium used in previous work. In addition, pH of precipitation exerts a profound effect on the settling characteristics of the precipitate as shown in figure 25.

Optimum pH of precipitation for maximum settling rate appears to be about 8.3, using an Al/Li ratio of 4/1. However, a pH of 8.3 is just outside the optimum pH range for maximum lithium recovery.

Using an aluminum to lithium ratio of 3/1 and a precipitation pH of 7.5 resulted in both maximum lithium recovery and a reasonably rapid settling precipitate as shown in figure 26.

In conclusion, it should be noted that the conditions outlined for maximum lithium recovery from Sinclair No. 4 geothermal fluid may not be optimum for other geothermal fluids. A properly planned experimental program should enable one to determine optimum lithium recovery conditions for each type of lithium-containing fluid.

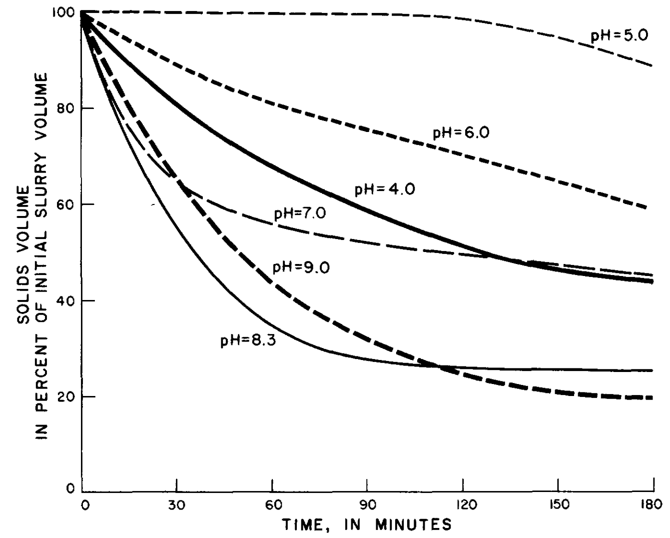

FIGURE 25.—Settling data for aluminum (lithium) hydroxides.

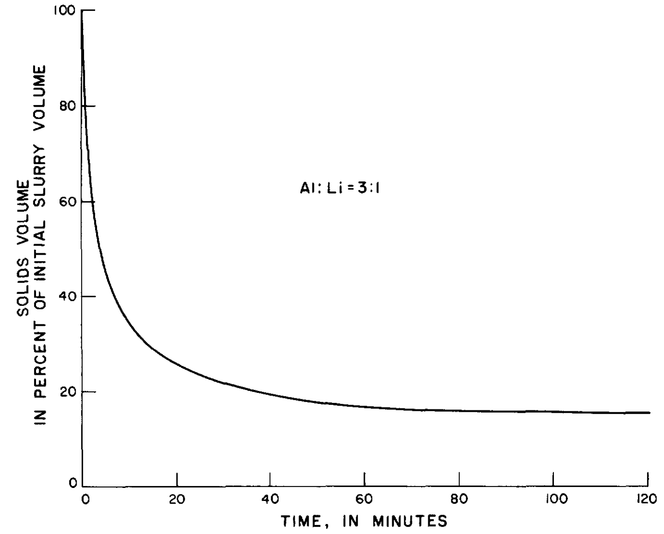

FIGURE 26.—Settling curve—aluminum (lithium) hydroxide at pH=7.5.

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LITHIUM RESOURCES OF SALARS IN THE CENTRAL ANDES

By George E. Ericksen, U.S. Geological Survey, Reston, VA;
Guillermo Chong D., Universidad del Norte, Antofagasta, Chile;
and Tomás Vila G., Instituto de Investigaciones Geológicas,
Santiago, Chile.

ABSTRACT

Lithium occurs in potentially commercial concentrations in salars of the central Andean region of northern Chile, western Bolivia, and northwestern Argentina, and in the nitrate deposits of northern Chile. Preliminary exploration of the salars indicates that Salar de Atacama, one of the largest in the region, contains large amounts of brine that average between about 2,000 and 4,000 mg/l lithium, so that this one salar may contain several million tonnes of recoverable lithium. Brines from several smaller salars in the Chilean Andes were found to contain as much as 200 mg/l lithium. Information about the lithium content of brines in the many other salars of the Andean Highlands is lacking, although some, such as Salar de Uyuni in Bolivia, appear favorable for accumulation of large amounts of lithium-rich brine. Lithium is concentrated locally in brines and saline crusts of salars in the coastal desert of northern Chile in amounts of several hundred to a few thousand parts per million, but potential resources of material averaging more than 100 mg/l lithium are small. Nitrate ore generally contains 20–50 ppm lithium, which is recoverable as a byproduct.

INTRODUCTION

Saline-encrusted playas, locally known as salars, and associated brines[1] that have accumulated in closed basins in the central Andean region contain huge amounts of saline materials. Recent exploration has shown that some of the salars contain relatively high concentrations of lithium, and it seems likely that this region has potentially large lithium resources. Associated saline resources include sodium chloride, sodium sulfate, potassium, boron, and magnesium. Some lithium-rich brines contain small but potentially recoverable amounts of cesium and rubidium.

The salars are in a region of internal drainage in northern Chile, western Bolivia, and northwestern Argentina, an area of more than 1 million km^2 (fig. 27). The region has more than 100 closed basins in which are found at least 75 salars ranging in size from about 1 km^2 to several thousand square kilometres. Salar Uyuni in Bolivia, the largest of the salars, has an area of about 9,000 km^2. Saline lakes occur in several of the basins, and lakes formerly existed in many others that are now occupied by salars. Lake Titicaca, the largest freshwater lake in South America, is at the border between Bolivia and Peru and in the northern part of the region of interior drainage.

The region has an arid climate, and precipitation is now more or less balanced by evaporation so that lake levels and ground-water levels are relatively stable, though during the last several thousand years evaporation has tended to exceed precipitation in the region as a whole. Precipitation is in part dependent upon altitude, ranging from less than 10 mm per year in the Atacama Desert of coastal Chile, at altitudes below 2,000 m, to a maximum of about 300 mm in the Andean Highlands of Chile and nearby parts of Bolivia and Argentina.

Most of the region of internal drainage in the Andean Highlands is underlain by volcanic rocks of Pliocene and Quaternary age, which are considered to be a major source of salines in the region (Ericksen, 1963). Thick rhyolitic ash-flow tuffs, chiefly of Pliocene age, are present throughout the area, representing one of the greatest known accumulations of rocks of this type. Superimposed on this rhyolitic terrane are several hundred volcanoes, most of which are of andesitic composition but a few of which are rhyolitic. Most of these volcanoes are now dead; only a few show fumerolic activity. Ash-flow tuffs from this part of the Andes have been found to contain about 500–3,500 ppm of water-soluble salines (Ericksen, 1961, 1963). Saline thermal springs are found at many places today and probably were widespread during former times of intense volcanic activity. Several spring deposits of the borate mineral ulexite have been found in northwestern Argen-

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[1] In this report, a brine is defined as a body of water containing more than 35,000 mg/l dissolved solids—the approximate concentration of sea water—and saline water is one containing 10,000-35,000 mg/l.

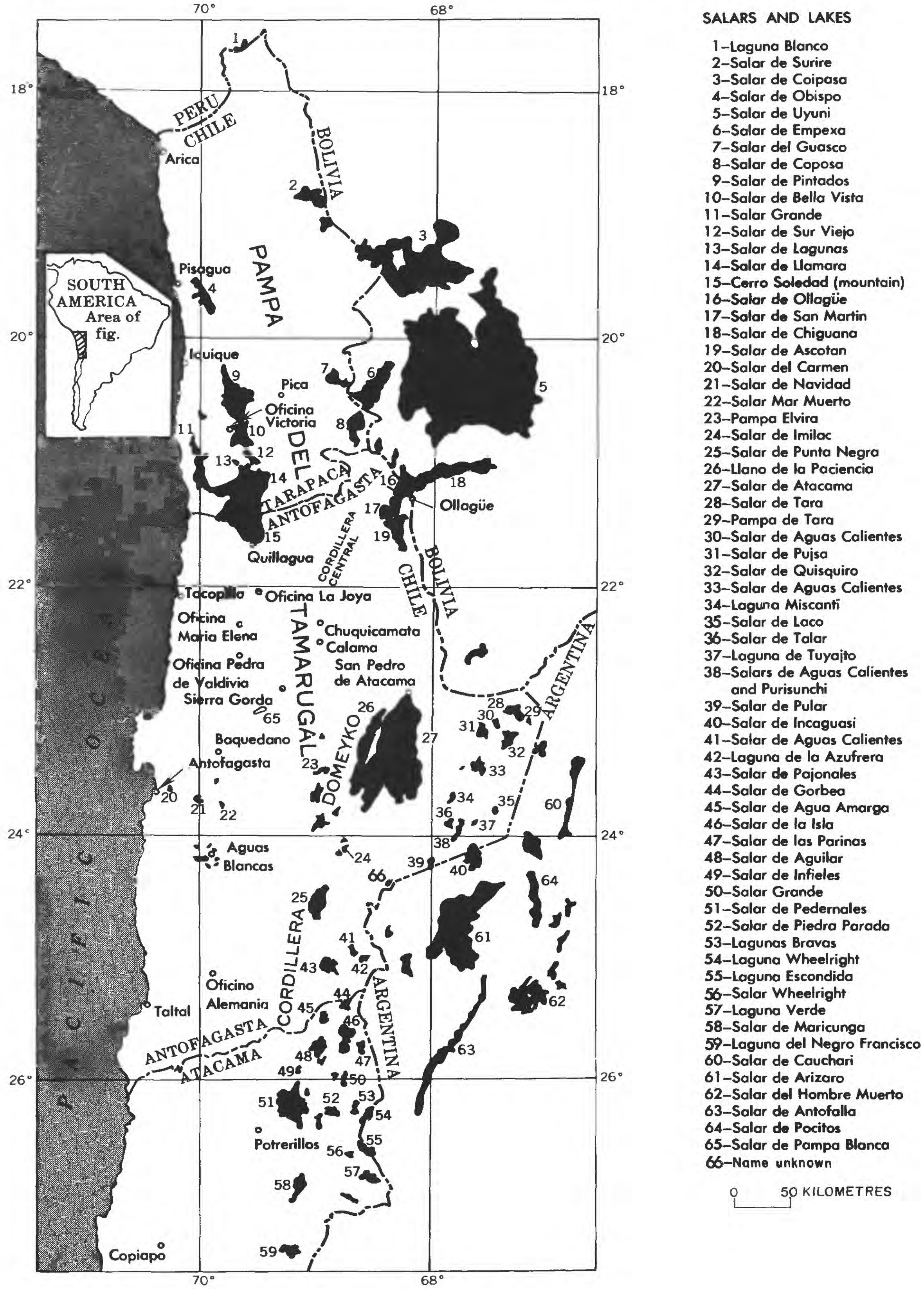

Figure 27.—Index map of the central Andean region showing location of salars and saline lakes. (Modified from Stoertz and Ericksen, 1974).

tina, some of which are associated with present-day thermal springs (Muessig, 1966, p. 153–154).

In contrast to the Andean Highlands, the Atacama Desert to the west is underlain chiefly by sedimentary, volcanic, and plutonic rocks of Jurassic to early Tertiary age. Except for the salines in continental sedimentary rocks of Jurassic to Tertiary age in the region of Salar de Atacama, the rocks of the Atacama Desert lack salt-bearing strata and have contributed a relatively minor portion of the widespread and abundant salines here. A considerable portion of the salines of the Atacama Desert is probably of oceanic origin, having been released from the ocean surface as sea spray and bubble spray and transported inland by wind and fog.

GEOLOGY OF THE SALARS

Three types of salars can be recognized as follows: (1) zoned salars of the Andean Highlands and front ranges, (2) dry silty salars of the Atacama Desert, and (3) Salar Grande, which is a mass of recrystallized halite. Zoned salars show lateral changes in crustal type and composition (fig. 28); they generally have a relatively thick, hard, dry interior crust of halite or gypsum and a thin, soft, moist outer crust consisting of mixtures of these minerals with mirabilite, thenardite, and ulexite. The gypsum crust commonly contains layers or abundant nodules of ulexite. The saline minerals in crusts of zoned salars crystallized chiefly from surface and near-surface saline waters and brines. Ponds and lakes, ranging from a few tens of metres to about a kilometre in diameter, now exist perenially at the margins and in interior low areas of many zoned salars, and the low areas are more extensively flooded during the rainy season. The silty-salar crusts in the coastal region of Chile formed by crystallization of saline minerals, chiefly halite, which served as near-surface cementing material in silty playas in the capillary fringe of the ground-water table. The resulting crust generally is a few tens of centimetres to a metre in thickness and consists of a somewhat loosely cemented mass of nodular to platy fragments of silty salt. The fragmental character of the crust is due to the combined processes of desiccation, heaving, and breaking of old crust as new crust forms beneath it and to leaching by infrequent rains. Salar Grande, near the coast in northern Chile (fig. 27), is unique. It is a huge deposit of coarsely crystalline pure halite nearly 50 km long, as much as 8 km wide, and as shown by drill cores, it has a maximum thickness of at least 160 m. The salt is dry, as is the alluvium beneath it, except for abundant fluid inclusions; former brines evidently drained away along recent faults that cut the salar.

As the result of faulting and tilting during their formation, many of the Andean salars are crowded toward one side of their basin and show asymmetrical zoning (fig. 29). Salar surfaces also may be gently inclined. Many of the basins were tilted towards the northwest, as is well shown by three of the four salars in figure 29. Others were tilted towards the west or southwest; one example is Salar del Guasco, also shown in figure 29. In some cases old salar crusts may have been covered with marginal alluvium deposited during and after tilting.

Lacustrine and playa sediments beneath the salar crusts are known only from shallow pits and short drill holes. Layers of saline minerals have not been encountered within these sediments and probably do not exist beneath most of the salar crusts, which may have formed as single-stage drying of a saline lake or by capillary evaporation of near-surface ground water. On the other hand, some of the large salars such as Atacama, which have had a more complex history, may have additional saline layers at depth. Such layers might contain significant quantities of "fossil" lithium-rich brines. The lacustrine sediments of the salars penetrated by drill holes consist of poorly sorted to well-sorted sand, silt, and clay with varying amounts of calcium carbonate-rich mud and sporadic diatom- and ostracod-rich layers. Several drill holes in marginal areas of Salar de Atacama show abundant calcium carbonate mud and ostracodes to depths as great as 43 m (Moraga and others, 1974, p. 47–51), and thin, relatively pure diatomite layers have been found interbedded with clastic sediments at several salars.

CHEMICAL COMPOSITION

Chemical analyses of saline waters of northern Chile show them to be chloride waters (Clark, 1924, p. 202) in which sodium is the dominant cation, as indicated in table 24. The similarity of salar crusts elsewhere in the central Andes suggests that essentially all of them formed from chloride waters. Concentrations of saline components range from several tens of g/l in saline ground water or brine within gypseous salar crusts, to nearly 400 g/l in brine within halite-rich salar crusts. The saline components in brine tend to show relative concentrations as follows:

$$Na^+ > K^+ > Mg^{++} > Ca^{++} > Li^+$$

$$Cl^- > SO_4^= > BO_3^= > HCO_3^-.$$

Spring waters, which generally contain less than 10 g/l dissolved solids, also are chloride waters but have variable relative amounts of K, Ca, and Mg; HCO_3^- is much more abundant than $BO_3^=$ in spring waters and may occur in amounts equal to or greater than $SO_4^=$.

As indicated by the analyses in table 24 and by other analyses of saline waters and brines associated with salars in northern Chile, lithium and potassium both tend to show an increase in concentration as total salinity increases. Potassium is generally 10–15 times more

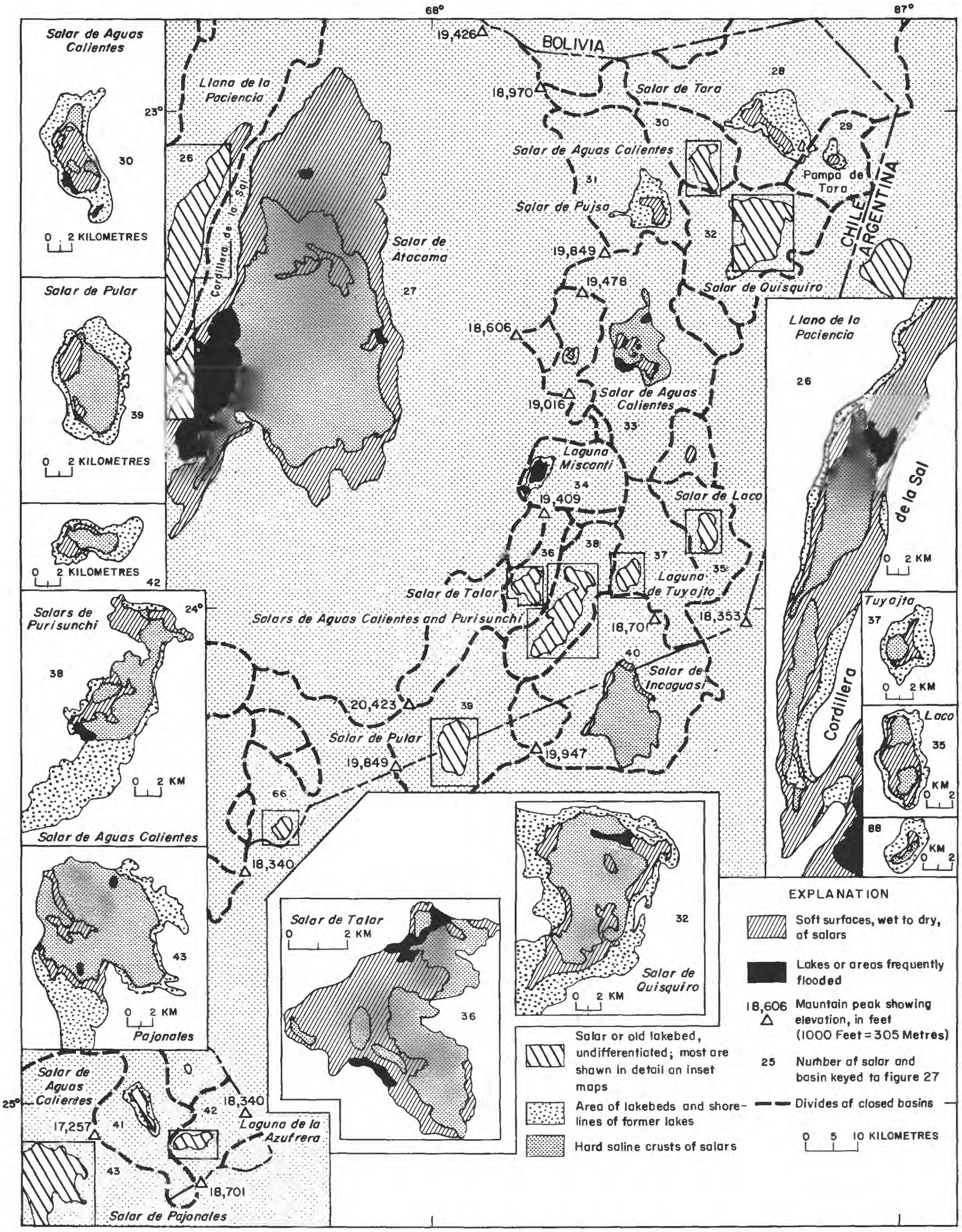

FIGURE 28.—Salars and basins of interior drainage in the eastern central part of Antofagasta Province, Chile. (Modified from Stoertz and Ericksen, 1974).

abundant than lithium, but this relationship is not necessarily linear, nor does it apply to all brines that have been tested for lithium. Figures 30 and 31 show the relation between concentrations of lithium and potas-

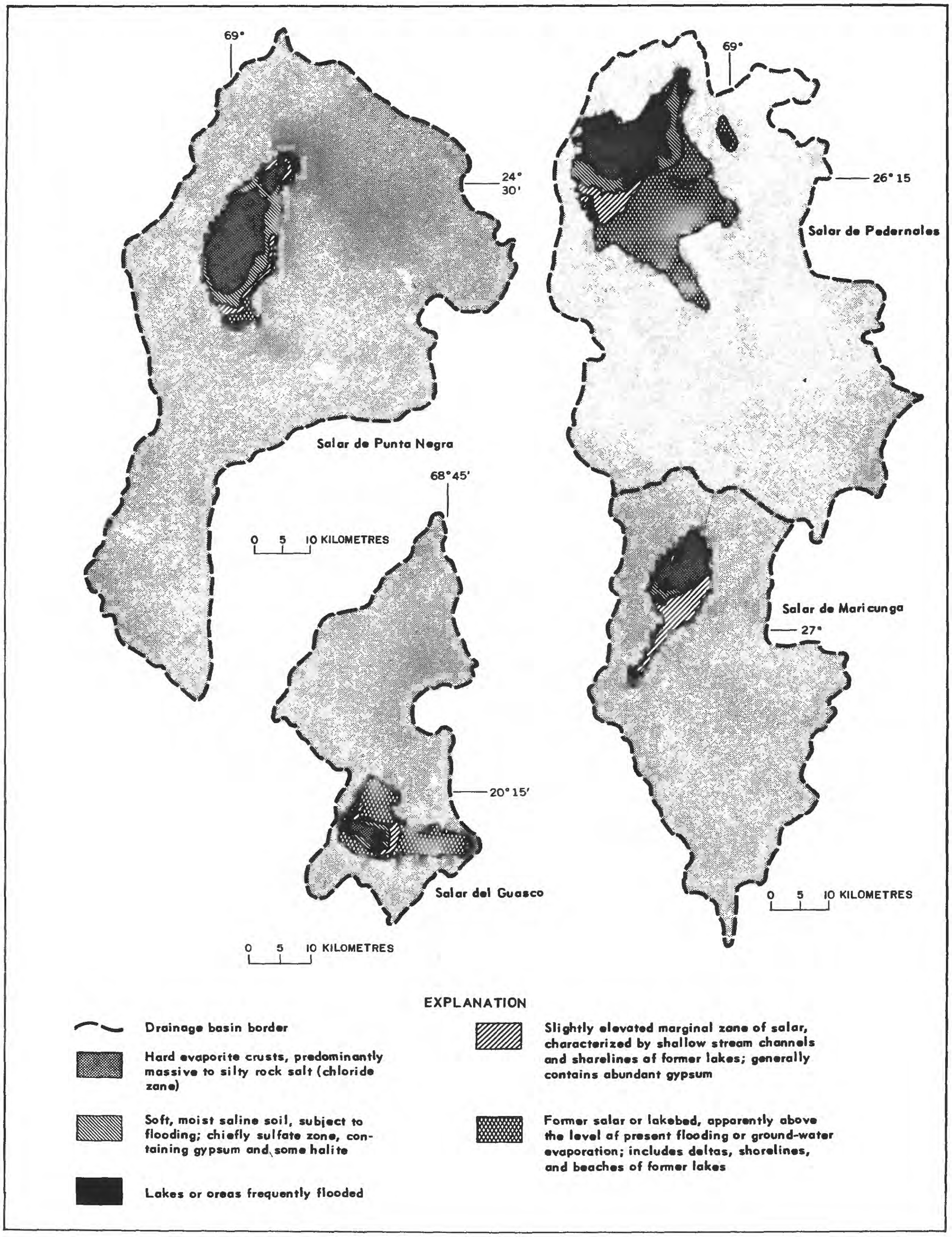

FIGURE 29.—Asymmetrical zoning of salars in basins of interior drainage in northern Chile, attributed in part to faulting and tilting of the basins during late Pleistocene and Holocene time. (Modified from Stoertz and Ericksen, 1974).

TABLE 24.—*Chemical concentrations, in milligrams per liter, in selected lithium-rich brines from northern Chile*

Locality	Dissolved solids[1]	Na	K	Mg	Ca	Li	Cl	SO_4	HCO_3	B
Salar de Atacama[2]	370,000	91,100	23,600	9,650	450	1,570	189,500	15,900	230	440
Do	310,000	85,800	13,000	6,350	1,100	940	163,900	8,540	280	360
Do	190,000	45,100	9,000	5,330	900	520	83,780	18,170	240	360
Do	73,000	18,220	4,220	1,810	360	290	36,750	3,430	320	100
Do	62,000	14,840	2,900	1,930	1,080	190	27,500	7,900	100	88
Do	40,100	10,280	1,690	750	1,160	130	20,300	2,160	92	61
Salar de Ascoton[3]	47,022	13,870	1,670	827	1,195	82	24,000	4,693	0	595
Salar de Pujsa[3]	89,298	28,500	1,295	653	375	137	27,660	28,110	0	675
Salar de Aguas[3] Calientes I	81,436	25,460	1,183	1,361	2,538	152	46,690	3,154	0	474
Salar de San Martin[4]	102,138	28,160	2,614	6,252	1,566	187	60,050	2,490	625	426
Salar de Bellavista[4] Pintados	170,300	50,000	5,403	3,665	5,935	85	100,600	2,720	178	225
Salar de Lagunas[4]	390,000	126,800	14,280	3,630	110	412	176,600	47,770	406	979

[1] By evaporation.
[2] From Moraga and others (1974, table 4).
[3] From Vila (1975, table 6).
[4] Instituto de Investigaciones Geológicas (unpub. data, 1975).

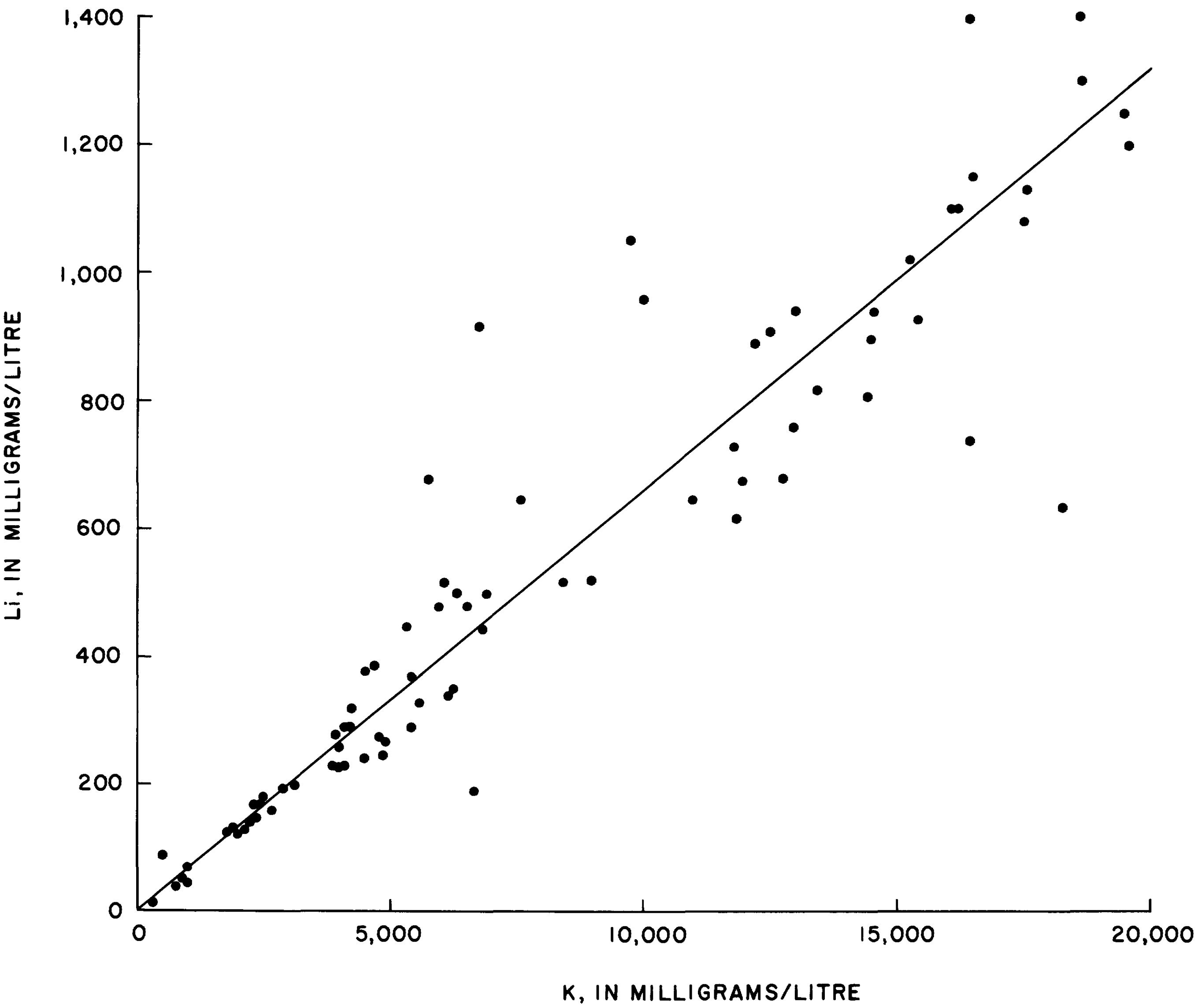

FIGURE 30.—Lithium-potassium ratios (dots) in saline ground water and brine, Salar de Atacama. Average Li:K ratio as indicated by line is 1:15. Analytical data from Moraga and others (1974, table 4).

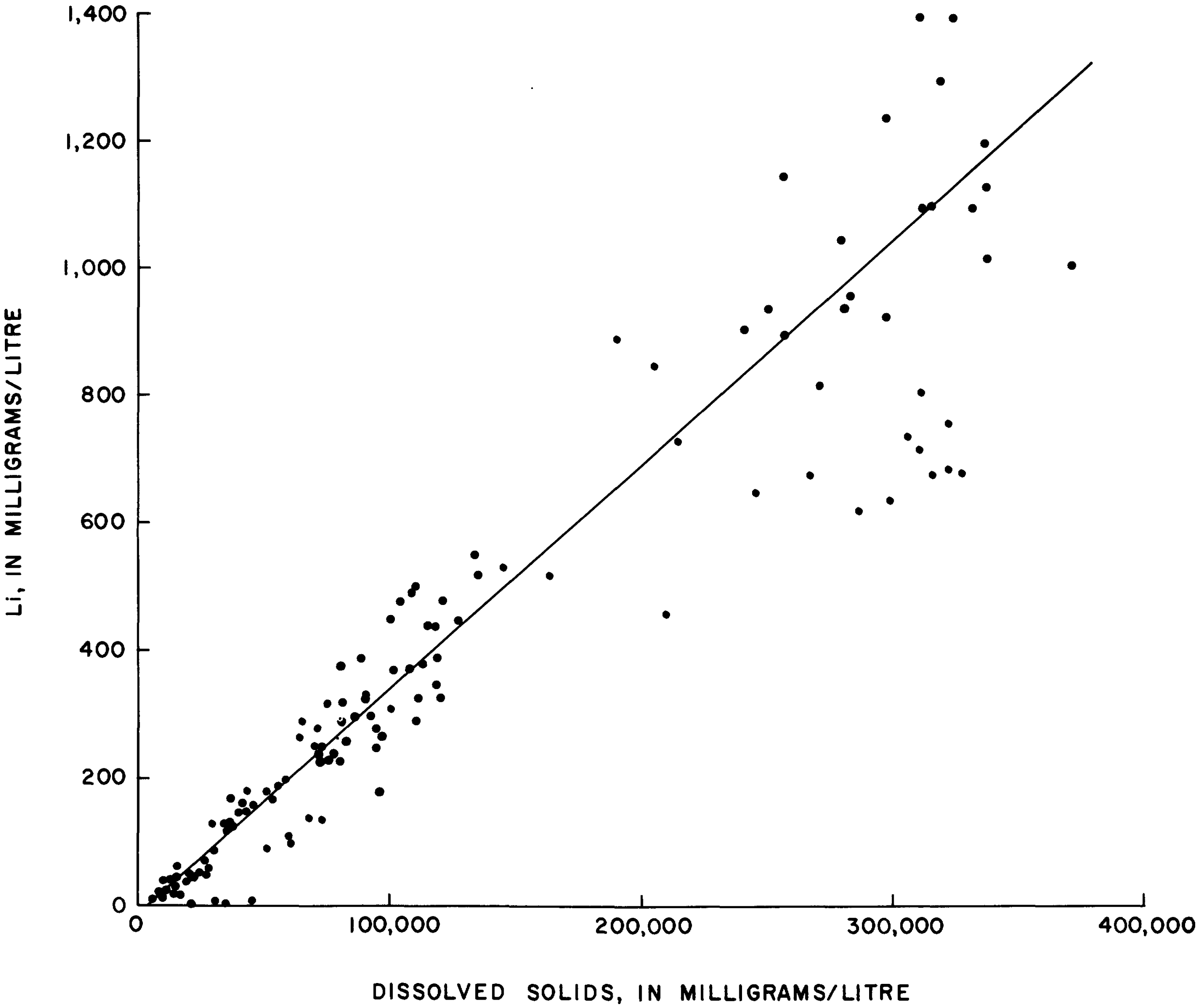

FIGURE 31.—Lithium-salinity ratios (dots) in saline ground water and brine, Salar de Atacama. Average Li:dissolved solids ratio as indicated by line is approximately 1:300. Analytical data from Moraga and others (1974, table 4).

sium and between lithium and total salinity for saline waters and brines from Salar de Atacama.

DISTRIBUTION OF LITHIUM IN SALINE DEPOSITS OF THE CENTRAL ANDES

Lithium is concentrated in brine in salars and saline lakes, in salar crusts, and in the nitrate deposits of the coastal region of northern Chile. Brines associated with salars contain by far the greatest amounts of lithium and offer the greatest potential for future production. Some salar crusts may prove to be exploitable, but the amount of recoverable lithium is relatively small. The nitrate deposits contain lithium that is recoverable as a byproduct. The few saline lakes tested for lithium show concentrations of 20–40 mg/l (Vila, 1975). Other high-salinity lakes, which have not yet been tested for lithium, may have still greater concentrations.

Of the more than 75 salars in the central Andean region, only four—Atacama, Lagunas, Bellavista, and Pintados—have been extensively tested for lithium and potash. More than 200 analyses of saline water and brine from Salar de Atacama have been published (Moraga and others, 1974), and it is evident that this salar contains potentially large lithium resources. Most of these analyses are from shallow pits along the southern and eastern margin of the salar, and relatively few are from the area within the salar that is covered by a thick halite crust. Nine drill holes as much as 43 m deep also were sampled. Moraga and others (1974) show that amounts of both lithium and potassium in brine increase inwards from the salar margin. They reported that the lithium content of brine in a marginal zone (referred to as the zone of efflorescence) averages between 200 and 300 mg/l, whereas an intermediate or transition zone has 500–1,600 mg/l and the marginal interior halite zone has 1,510–6,400 mg/l. Guillermo Chong, co-author of this report, found that brines sampled along a 20-km line within the halite zone in the southern part of the salar averaged 4,100 mg/l lithium and 12,000 mg/l potassium.

Analyses of saline water and brine from another 13 salars in the Andean Highlands of Chile show lithium contents ranging from 3 to 200 mg/l, and potassium contents ranging from 154 to 3,000 mg/l (Vila, 1975, G. E. Erickson, unpub. data, 1975). Total dissolved solids range from 17,000 to 400,000 mg/l. Correlations between lithium, potassium, and salinity in these salars are only fair in comparison to those of Salar de Atacama. Brines containing more than 100 mg/l lithium were found in the salars of Aguas Calientes I, Laco, Pujsa, and San Martin (fig. 27). Brines of Salar de Pedernales, which are known to be high in potassium, may contain more than 100 mg/l lithium.

Because of the lack of chemical analyses from salars in the Andean Highlands of Bolivia and Argentina, it is not possible to estimate their lithium potential. Nevertheless, it can be suggested that the Salars of Coipasa and Uyuni in Bolivia are among the most favorable for accumulation of large quantities of lithium-rich brine.[2] These salars consist chiefly of thick halite crusts that are subject to partial flooding during the annual rainy season. Together with the nearby salars of Empexa and Chiguana (Fig. 27) and Lago Poopo, a large saline lake northeasteast of Salar de Coipasa, they are remnants of the former Lago Minchin, an upper Pleistocene lake that extended over an area of about 40,000 km^2 of the present-day Bolivian Altiplano (Ahlfeld and Branisa, 1960, p. 158–163). Salars Coipasa and Uyuni contain most of the saline materials that accumulated in Lago Minchin and in an earlier Pleistocene lake that existed in the same area.

Chemical compositions of brines and crusts of salars in the Atacama Desert of coastal Chile were reported by Ericksen (1963) and are recorded in unpublished analyses of the Coporación de Fomento de la Producción of Chile (CORFO), the Instituto de Investigaciones Geológicas, and the former nitrate company Cía, Salitrera Tarapacá y Antofagasta. The crust and brine of Salar de Lagunas are unique in that they contain relatively high concentrations of nitrate, perchlorate, and iodate, as well as abundant lithium and potassium. Lithium content of the brine and crust of this salar is as much as 500 ppm. The presence of unusual saline components in Salar de Lagunas indicates that the brines were enriched, at least in part, by rainwater leaching of nearby nitrate deposits. Local concentrations also may be due to contamination by leach solutions from waste dumps at three nitrate beneficiation plants that once operated here.

Salar de Bellavista and Salar de Pintados at the western side of the Central Valley in northern Chile have silty saline crusts relatively rich in potassium and perhaps also in lithium. Ericksen (1963, p. 128–132) reported that 1,700,000 tonnes of salar crust averaging 2.87 percent K was mined from the southern part of Salar de Bellavista. A pit was opened in this area to test the rate of regeneration of new potassium-bearing salt crust, and two samples of new crust which formed in the pit were found to contain 350 ppm and 3,100 ppm lithium, and 3 percent and 10 percent potassium. Brine from this same pit was found to contain 2,130 mg/l potassium, but lithium was not determined.

The nitrate deposits of Chile contain anomalous amounts of lithium in the water-soluble salines from which the nitrate is recovered. The amount of lithium present in this form is generally in the range of 20–50 ppm but locally is as much as 250 ppm, as indicated by about 50 analyses we performed on nitrate ore samples. This lithium becomes concentrated in the recycled brines utilized to extract the nitrate from the ore. The former owner of the two largest nitrate beneficiation plants, the Anglo-Lautaro Nitrate Corp., determined that the lithium could be recovered by a solar evaporation process integrated with the plants. The calculated annual yield was estimated to be 1,610 tonnes of lithium sulfate (209 tonnes of lithium) from 17,000,000 tonnes of nitrate ore, the annual capacity of the two plants. This is based on a concentration of about 60 ppm lithium in the water soluble portion of the nitrate ore, which is about a third of the ore.

SOURCES AND FACTORS FAVORING LITHIUM CONCENTRATION IN ANDEAN SALARS

Information about chemical composition of salars and associated saline waters is too scanty to allow a precise evaluation of the sources of lithium and of the causes for its occurrence in relatively high concentrations in certain salars and not in others. However, a volcanic source of lithium is suggested, because Pliocene and Quaternary volcanic rocks and their erosion products cover large areas in the Andean Highlands where salars are most numerous and are virtually the only rocks exposed in many of the closed basins. Furthermore, it seems likely that thermal spring waters associated with these volcanic rocks were major sources of the lithium. White, Thompson, and Fournier (this report) point out that high-temperature geothermal systems are generally enriched in lithium and that moderately saline waters

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[2] The first known lithium analyses of brine from Saler de Uyuni were made by Shirley L. Rettig, U.S. Geological Survey, on two samples collected in April 1976 by William D. Carter, U.S. Geological Survey, and Paul Ballon, Servicio Geológico de Bolivia, at the request of the senior author of this report. These analyses show 490 and 1,510 ppm lithium, respectively.

above 200°C associated with silicic volcanic rocks contain 1–50 ppm Li. They conclude that these high-temperature waters selectively leach lithium from the volcanic rocks. Ellis (1975) reported that high-temperature thermal water from the El Tatio geyser field, which is in a drainage basin to the north of the Salar de Atacama basin, contains 47.5 ppm lithium.

Conditions that would favor concentration of lithium in the salars are as follows: (1) the relatively old age of basins—some may have been in existence since middle or even early Pleistocene; (2) the large basin/salar ratio, which might contribute to the high degree of concentration of saline waters; (3) the high degree of basin closure so that water loss by either surface or underground flow was minimal; and (4) abundant saline-rich rhyolite ash-flow tuff subject to leaching and widespread fumarolic activity and saline thermal springs associated with volcanic activity. Salar de Atacama, which has the greatest lithium concentrations yet known in the region, has three of these attributes. It has a relatively small basin/salar ratio as is indicated in figure 27. On the other hand, this basin is unique in having Jurassic, Cretaceous, and Tertiary saline continental sedimentary rocks (Dingman, 1967) that furnished a considerable amount of saline material to the salar. These rocks may have been a major source of the lithium.

POTENTIAL LITHIUM RESOURCES

Salars in the central Andean region have large potential resources of lithium chiefly in brines and to a lesser degree in saline crusts. Of the few salars that have been tested for lithium—all in northern Chile—Salar de Atacama appears to have the greatest quantity of lithium-rich brine. Moraga and others (1974) estimate that the brine in a 400-km^2 area of Salar de Atacama contains 40,000 tonnes of lithium per metre depth. (Their calculation was based on an average lithium content of 2,000 mg/l and a brine recovery of 100 l/m^3; this gave an estimate of 80,000 tonnes, which the authors reduced by half to be conservative.) This estimate was made for an area within the central part of the salar where several drill holes show the halite crust ranges from 50 to 335 m in thickness and where brines sampled along a 20-km line (see paragraph 2, "Distribution of Lithium in Saline Deposits of the Central Andes") were found to average 4,100 mg/l lithium. Consequently, total lithium resources may be very large, perhaps amounting to several million tonnes. The potential lithium resources in brines of other salars in northern Chile would be far less. Lithium contents generally are not greater than 200 ppm, and the amounts of brines are such that a comparable-sized area in most salars would yield less than 1,000 tonnes of lithium per metre depth.

The lithium potential of salars in the Andean Highlands of Bolivia and Argentina cannot be estimated because of the lack of lithium analyses. However, Salars Coipasa and Uyuni in Bolivia appear to be most favorable for accumulation of large amounts of lithium-rich brine.

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LITHIUM RESOURCES OF UTAH[1]

By J. A. Whelan, University of Utah, Salt Lake City, UT and
Carol A. Petersen, Utah Geological and Mineral Survey, Salt Lake City, UT

ABSTRACT

Known lithium resources of Utah consist of Great Salt Lake brines, subsurface brines of the Great Salt Lake Desert and Sevier Lake, and Spor Mountain beryllium ores.

The total metric tonnage of lithium in Great Salt Lake is 526,000, of which perhaps half is recoverable. Extraction of lithium from Great Salt Lake will be as a byproduct of magnesium-metal or salt recovery.

The Bonneville-Salt-Flats part of the Great Salt Lake Desert has a recoverable resource of from 1,300 to 2,000 tonnes. This amount could be increased from 1,700 to 2,700 tonnes by recharging a shallow brine aquifer now being utilized to produce potassium and magnesium salts with brines from existing deep wells.

Sevier Lake contains a shallow subsurface brine containing 450 to 540 tonnes of recoverable lithium.

The beryllium ores contain 1,400 to 18,000 tonnes of lithium.

The average lithium content of brines from 58 oil wells in Utah is 7.1 mg per liter. Brines from three oil wells contain over 39 mg/l lithium.

The mean lithium content of 35 hot springs in Utah was 2.33 ppm.

The total lithium resources of Utah are between 200,000 and 240,000 tonnes. No lithium is produced in Utah at present. Plants to recover lithium as a byproduct from existing brine-processing or beryllium-extraction plants could recover from 160 to 600 tonnes of lithium per year.

INTRODUCTION

Only nonpegmatite sources need to be considered in evaluating the lithium resources of Utah, because neither spodumene nor other lithium minerals are reported from the few pegmatites of Utah (Bullock, 1967). Evaluating nonpegmatite lithium resources is a new endeavor for most geologists, and some of the various types of occurrences are discussed by Vine (1975). Lithium in the following occurrences will be considered in this paper: Great Salt Lake brines, subsurface brines, volcanic rocks, and miscellaneous lithium-bearing mineral localities. Location of the occurrences are shown in figure 32.

GREAT SALT LAKE BRINES

The brines of Great Salt Lake constitute the largest lithium resource of Utah. The lake contains three distinct brine types: (1) a nearly saturated brine (320 g/l total dissolved solids) in the area north of a semipermeable railroad causeway, (2) a relatively fresh (117 g/l) brine in the south part of the lake at depths less than about 7 m, and (3) a brine of intermediate concentration (222 g/l) in the south part at depths greater than 7 m. The three brine types have formed because Great Salt Lake is cut in two by an east-west-trending railroad causeway built of gravel armored with rip-rap. Over 90 percent of the surface inflow enters the lake south of the causeway. Flow through the causeway into the north arm is restricted, and high evaporation there forms a concentrated brine. The shallow south-arm brine is becoming fresher each year. The deep south-arm brine represents return flow from the north arm. The north-arm brine contains 64 ppm lithium, the shallow south-arm brine contains 22 ppm lithium, and the deep south-arm brine contains 43 ppm lithium. This amounts to tonnages of 214,000 tonnes, 203,000 tonnes, and 109,000 tonnes of lithium, respectively, in each of the brines; the total tonnage is 526,000 tonnes.

Because lithium follows magnesium during processing of the brines, and because of the low lithium content of the brines, economic recovery of lithium from

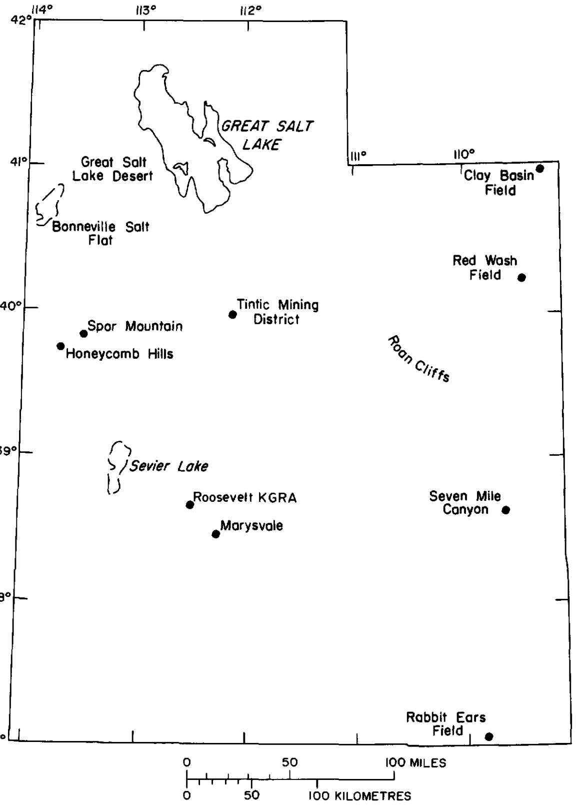

Figure 32.—Locations of lithium resources and mineral occurrences in Utah.

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[1] Permission to publish granted by Director, Utah Geological and Mineral Survey.

Great Salt Lake depends on a viable magnesium industry. NL Industries has a magnesium plant at Rowley, on the west side of the lake, that uses shallow south-arm brines. Design capacity is 41,000 tonnes of magnesium per year; but, to date, the plant has had start-up difficulties and has only produced at a maximum rate of about 14,000 tonnes per year. About 5 kg of lithium can be produced per tonne of magnesium, so the NL plant has the potential to produce 70–200 tonnes of lithium per year.

Great Salt Lake Mineral and Chemical Corporation, located west of Ogden uses north-arm brines. It has a design capacity of 220,000 tonnes of potassium sulfate annually. Although production figures are not available, the plant has been operating successfully. When the Great Salt Lake Mineral and Chemical Corporation project was started, Dow Chemical Company contracted to buy 90,000 tonnes per year of bischofite ($MgCl_2 \cdot 6H_2O$). In 1970, with the magnesium plant nearly complete, Dow cancelled the contract. The partially completed plant is now in standby status. Ninety thousand tonnes per year of bischofite would represent about 8,020 tonnes of magnesium and a potential lithium production of 41 tonnes.

Thus, if all the magnesium-production facilities on Great Salt Lake should become operative, the lake could provide feed for lithium plants capable of producing 241 tonnes of lithium per year. Of the lithium resources in Utah, Great Salt Lake brines probably could be most easily developed.

SUBSURFACE BRINES

Subsurface brines considered to be possible sources of lithium in Utah include (1) subsurface brines of Bonneville Salt Flats in the Great Salt Lake Desert, (2) subsurface brines of Sevier Lake, (3) oil-field brines, and (4) brine that may be produced incidental to geothermal development.

SUBSURFACE BRINES OF THE BONNEVILLE SALT FLATS

The high-potash, shallow subsurface brines in the western part of the Great Salt Lake Desert were first discussed by Nolan (1927). Later studies include those of Turk (1973) and Lindenberg (1974).

Turk (1973) discussed the hydrology of the Bonneville Salt Flats, the part of the desert now being exploited for potassium and magnesium salts by Kaiser Chemicals. He described a shallow brine aquifer, which provides brine for potassium and magnesium chloride production, and a deep brine aquifer at depths greater than about 325 metres. Lindenberg (1974) provided additional geochemical data on the shallow brines, which he sampled over a considerably larger area than that described by Turk (1973). Typical analyses of the shallow brines are given in table 25.

Turk (1973, p. 17) predicted that the current production rate from the shallow brine aquifer can be maintained for 25–40 years before the brine quality deteriorates from slightly less than 1 percent KCl to 0.5 percent KCl. Assuming the same proportional decline, lithium would decrease from about 0.03 g/l to 0.015 g/l. If the decrease were linear, the average lithium content during this time period would be 0.0225 g/l. The assumption of linear decline in brine quality is not valid, as Turk (1973, p. 17) noted, but was made by us to simplify calculations. Turk assumed a discharge of 700 acre-feet (8.6×10^5 m^3) per year. This represents some 19 tonnes of lithium per year. On the basis of a field life of 25–40 years, a potential production of 475–760 tonnes of lithium would be reasonable.

Lindenberg's study (1974) increased the known area of shallow brine by 2.8 times, so the estimated potential production of lithium should be increased to between 1,300 and 2,000 tonnes.

The deep brine aquifer is penetrated by 13 wells. Typical analyses of the brine from two wells are given in table 26. Turk noted that by using the deep brine for

TABLE 25.—*Analyses of shallow aquifer brines, Great Salt Lake Desert, in grams per liter*

[N.D., not determined]

Ion	Nolan (1927, p. 39)	Turk (1973)[1]	Lindenberg (1974)[2]	Overall[3]
Cl^-	96.15	139.63	122.37	119.38
Br^-	.00	.038	N.D.	N.D.
I^-	.00	N.D.	N.D.	N.D.
$SO_4^=$	4.08	4.24	5.75	5.69
$CO_3^=$	.00	.00	N.D.	N.D.
$BO_3^\equiv$	.00	.023	N.D.	N.D.
$Na+$	57.30	76.7	74.71	69.57
$K+$	2.94	4.43	3.49	3.62
$Li+$	.002	.003	.003	.003
$Ca++$	1.51	1.25	1.39	1.38
$Sr++$	.00	.057	N.D.	N.D.
$Mg++$	1.91	1.73	1.84	1.83
SiO_2	N.D.	0087	N.D.	N.D.
HCO_3^-	N.D.	.041	N.D.	N.D.
$Al+++$	N.D.	.0018	N.D.	N.D.
F^-	N.D.	.0013	N.D.	N.D.
NO_3^-	N.D.	.0048	N.D.	N.D.
Total dissolved solids	164.7 @180°C	228.28	209.55	N.D.
Specific gravity	1.11 @ 25°C	[4]1.150 [6]1.145	[5]1.140 [6]1.136	N.D.
pH	N.D.	7.1 @ 25°C not detected: Fe, Mn, As, PO_4	N.D.	N.D.

[1] Average of 15 analyses given in Turk (1973, p. 13).

[2] Average of 65 analyses given in Lindenberg (1974, p. 22–28).

[3] Arithmetic mean of first three columns.

[4] Extrapolated from table, specific gravity versus total dissolved solids, given in Levorsen (1958, p. 663).

[5] Interpolated from table, specific gravity versus total dissolved solids, given in Levorsen (1958, p. 663).

[6] From graph, total dissolved solids versus specific gravity, given in Whelan (1973, p. 19).

TABLE 26.—*Chemical analyses of brine from deep brine aquifer in parts per million*

[Analyses by Kaiser Chemicals, San Leandro, California; from Turk, 1973, p. 9]

Well number	Ca	Mg	Na	Li	K	SO_4	Cl
DBW8	1,600	1,400	41,400	16	1,800	6,000	70,000
DBW13	1,500	1,400	46,000	17	2,000	6,200	72,800

recharge, the life of the project could be extended some 30–40 percent, indicating a total potential lithium production from the Great Salt Lake Desert of 1,700–2,700 tonnes. The deep brines are also a possible geothermal resource (Whelan and Petersen, 1975).

SEVIER LAKE

Lithium-bearing brines are found at shallow depths in the sediments of Sevier Lake, a playa lake in southwestern Utah (Whelan, 1969). The mean of 10 brine analyses, all samples from sites in the southern half of the playa, is given in table 27.

Assuming that the hydrologic characteristics of Sevier Lake sediments are similar to those of the Great Salt Lake Desert sediments and calculating the possible production for relative sampled areas and brine concentrations, one would obtain a potential of about 450–540 tonnes lithium. Because all of the sampled points are in the south half of the lake, the resource may be double the value given. At present, there is no development of saline industries on Sevier Lake.

OILFIELD BRINES

Another possible source of lithium in Utah is oilfield brines. The mean of 58 available lithium analyses of Utah oilfield brines is 7.1 mg/l lithium, with a standard deviation of 14.1 mg/l. Oil production in Utah during 1974 was about 39,400,000 bbl, with a water production of about 107,500,000 bbl. Thus, some 17 tonnes of lithium are brought to the surface each year in oilfield brines. Because of the low lithium content of the brines and the fact that brines are produced in varying quantities from scattered fields. Production of lithium from most oilfield brines in the near future is doubtful.

Certain oilfield brines, however, are of interest and should possibly be investigated further. A sodium chloride-type brine from a well (SE¼NW¼ sec. 22, T. 3 N., R. 24 E., Salt Lake Basin and Meridian) in the Clay Basin field contained 85 mg/l lithium and 50,200 mg/l total dissolved solids. This field is reported to have no water production.

TABLE 27.—*Mean analysis of 10 shallow subsurface brines, southern half of Sevier Lake, Utah*

Ion	Value in grams per liter
Cl^-	92.40
Mg^{++}	3.44
Ca^{++}	.60
Na^+	64.37
K^+	2.54
$SO_4^=$	21.66
Br^-	.054
Li^+	.0225
Boron	035
Total dissolved solids (g/l)	185.14
Specific gravity	1.126

A well (SE¼NE¼ sec. 19, T. 43 S., R. 22 E.) in the Rabbit Ears field produced a sodium chloride-type brine containing 72,830 mg/l total dissolved solids and 58 mg/l lithium. This is a one-well field which, in 1974, produced 3,413 bbl of oil and 60,390 bbl of water.

One deep well (SE¼SE¼ sec. 21, T. 7 S., R. 24 E.) in the Red Wash field of Uintah County produced a sodium-calcium chloride brine containing 144,104 mg/l total dissolved solids and 39 mg/l lithium. This was a dry hole, but it indicates that potential for lithium-bearing brines may exist at depth in this field.

GEOTHERMAL BRINES

Brine produced from hot-water geothermal systems has been considered as a potential lithium resource. Thirty-five analyses of hot-spring water in Utah (Mundorff, 1970, p. 12–19) give a mean lithium content of 2.33 ppm lithium. The highest reported lithium value for a Utah hot spring is 2.7 ppm from Roosevelt Hot Springs, near Milford, Utah (White and others, 1963). White (oral commun., 1976) noted that this same lithium analysis was incorrectly reported as 0.27 ppm by Mundorff (1970, p. 17).

Most of the hot-spring analyses indicate little potential for lithium production as a byproduct of future geothermal development. However, using an estimated potential energy production of 33 MWe-centuries from the Roosevelt Known Geothermal Resource Area (Nathenson and Muffler, 1975, p. 110) and assuming that all the water produced contains 27 ppm lithium, about 40,000 tonnes of lithium could be brought to the surface in this area.

The possibility that lithium-bearing clays exist in the hydrothermally altered rocks associated with geothermal resources should not be overlooked.

VOLCANIC ROCKS

Mineralized rhyolitic crystal-lithic tuffs are mined for beryllium in the Spor Mountain district northwest of Delta, Utah. The ore-grade tuffs contain anomalous amounts of lithium. Lindsey, Ganow, and Mountjoy (1973) discussed the area and reported 75 ppm lithium in unmineralized vitric tuff and 55 ppm lithium in unmineralized zeolitic tuffs. They described hydrothermally altered argillic tuffs containing 105 ppm beryllium and 230 ppm lithium. Hydrothermally altered feldspathic tuffs contained an average of 14 ppm beryllium and 315 ppm lithium. J. A. Whelan (written commun., 1962) reported that a sample from the Hogsback ore body contained 1.25 percent beryllium oxide and 0.10 percent Li_2O (420 ppm lithium). A section of the Rainbow open pit that averaged 0.19 percent BeO also averaged 4,231 ppm lithium (Park, 1968, p. 93–94).

Williams (1963, p. 58) reported 3,175,000 tonnes of blocked-out beryllium ore, with an anticipated tonnage greatly in excess of 4,500,000 tonnes. Thus, the lithium resource of ores of the Spor Mountain beryllium district is probably between 1,400 and 18,000 tonnes of lithium. At present, about 90,000 tonnes of beryllium ore are processed yearly, carrying between 35 and 350 tonnes of lithium.

Similar rhyolitic tuffaceous beryllium-bearing rocks occur in the Honeycomb Hills, west of the Spor Mountain beryllium deposits. An average beryllium value of three analyses (Park, 1968, p. 72) from this area is 0.24 percent beryllium oxide. Unfortunately, the tuffs were not analyzed for lithium. Bullock (1967, p. 167) reported spodumene from these tuffs.

The beryllium occurrences of Utah and other silicic volcanic rocks should be prospected for lithium. Other beryllium occurrences besides Spor Mountain and the Honeycomb Hills that might contain anamalous amounts of lithium are found in the Deep Creek Mountains (pegmatitic), Granite Peak (pegmatitic), Sheeprock Mountains (beryl disseminated in granite), and Mineral Range (skarns).

MISCELLANEOUS LITHIUM MINERAL OCCURRENCES IN UTAH

Lithiophorite, a wad containing about 1 percent Li_2O, has been reported by Bullock (1967, p. 137) from the following localities: Seven Mile Canyon and Shinarump Nos. 1–3 claims, Grand County; Marysvale district, Buddy, Bullion Monarch, Freedom No. 1, and Prospector No. 1 and 3 mines, Piute County. He also reported (p. 163) that the lithium iron manganese phosphate, sicklerite, occurs in the Tintic district, Juab County.

Dyni (1973) reported a trioctahedral smectite from the Roan Cliffs, Uinta Basin, that might be similar to the lithium-bearing montmorillonite, hectorite.

These reported occurrences of lithium minerals have yet to be evaluated.

CONCLUSIONS

The known lithium resources of Utah include Great Salt Lake brines, subsurface brines of the Great Salt Lake Desert and Sevier (dry) Lake, and the beryllium ores of Spor Mountain. Probable recoverable tonnages of the resources are given in table 28. Production could be started with minimum delay by adding lithium-recovery plants to the brine-processing plants on Great Salt Lake and the Great Salt Lake Desert and to the beryllium mill of Brush-Wellman, near Delta, Utah. Probable annual outputs from additions to these plants are given in table 28.

TABLE 28.—*Estimated recoverable lithium resources of Utah and estimated annual recovery possible by adding lithium-recovery plants to existing facilities*

[Leaders (------) indicate no existing facilities]

Source	Probable recoverable resource (tonnes)	Probable annual production obtainable using additions to existing plants (tonnes)
Great Salt Lake brines	260,000	110–240
Great Salt Lake Desert brines	1,000–3,000	10
Sevier Lake brines	500	--------
Geothermal brines	0–40,000	--------
Beryllium ores	1,000–20,000	35–350
Approximate total	262,500–283,500	158–600

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PRELIMINARY DESIGN AND ANALYSIS OF A PROCESS FOR THE EXTRACTION OF LITHIUM FROM SEAWATER[1]

By MEYER STEINBERG and VI-DUONG DANG,
DEPARTMENT OF APPLIED SCIENCE, BROOKHAVEN NATIONAL LABORATORY, UPTON, NY

ABSTRACT

The U.S. demand for lithium by the industrial sector is estimated to increase from 2.7×10^6 kg (3,000 short tons) in 1968 to 1.2×10^7 kg (13,200 tons) in the year 2000. Projections of the demand for lithium by a fusion power economy are subject to uncertainties in the future power demands of the United States and the wide range of requirements for various designs of controlled thermonuclear reactors (CTR). For a one million MWe CTR (D-T fuel cycle) economy, growing into the beginning of the next century (the years 2000 to 2030), the cumulative demand for lithium is estimated to range from $(0.55\sim4.7)\times10^7$ to 1.0×10^9 kg $((0.6\sim5.1)\times10^4$ to 10^6 tons). The present estimates of the available U.S. supply are 6.9×10^8 kg (7.6×10^5 tons) of lithium from mineral resources and 4.0×10^9 kg (4.4×10^6 tons) of lithium from concentrated natural brines. With this kind of demand approaching supply, there is concern for lithium availability in a growing CTR (D-T fuel cycle) economy. There is, however, a vast supply of lithium in seawater. Although the concentration of lithium in seawater is dilute (170 ppb), the total quantity available is large—estimated to be 2.5×10^{14} kg (2.8×10^{11} tons)—thus insuring an unlimited resource for a long-term fusion economy. These estimates provide the incentive for devising an economical process for the extraction of lithium from the sea.

A preliminary process design for the extraction of lithium from seawater is presented on the basis of the literature data. The essential features of the process are that seawater is first evaporated by solar energy to increase the concentration of lithium and to decrease the concentration of other cations in the bittern which then passes into a Dowex-50[2] ion exchange bed for cation adsorption. Lithium ions are then eluted with dilute hydrochloric acid, forming an aqueous lithium chloride which is subsequently concentrated. Lithium metal is then formed by electrolysis of lithium chloride. The energy requirement for lithium extraction varies between 0.08 and 2.46 KWh(e)/g for a range of production rates varying between 10^4 and 10^8 kg/yr. This energy requirement is relatively small when compared to the energy produced from the use of lithium in a CTR having a value of 3,400 kWh(e)/g Li. Production cost of the process is estimated to be in the range of 2.2 to 3.2 cents/g Li.

To obtain a more definitive basis for the process design, it is recommended that a thorough phase equilibria study of the solid-liquid crystallization processes of seawater be conducted. Uncertainties exist in the operation of large solar ponds for concentrating large quantities of seawater. A continued thorough search for a highly selective adsorbent or extractant for Li from low concentration aqueous solutions should be made. Investigation of other physical separation processes such as the use of membranes should be investigated.

INTRODUCTION

The lithium industry was a small industry before World War II. During the war, it was necessary to develop a hydrogen storage means for the warships to lift equipment by balloon in case of emergency. Lithium hydride was developed for that purpose. A small amount of lithium hydride can react with seawater to release a large quantity of hydrogen (Hader and others, 1951). After the war, lithium requirement for nuclear purposes stimulated the production of lithium for some years during 1954–1960. Excess lithium produced in those years required more commercial end use after the need for lithium by the Atomic Energy Commission (AEC) decreased in 1960.

Commerical uses of lithium and its compounds are in the following categories (Cummings, 1968; Shreve, 1967). Lithium itself is mainly used for ceramics, glass, and multipurpose greases. Other commercial uses of lithium and its compounds are for automotive, metallurgy, air conditioning, batteries, and so forth. Besides the commercial use of lithium, it is anticipated that lithium can be used as blanket material in the fusion reactor. Lithium has been proposed for the blanket material of the first wall of a fusion reactor (Controlled Thermonuclear Research Division, 1973) because its nuclear properties are ideal, its thermal conductivity is high, it is a desirable coolant, and above all, it is tritium breeding material. A major difficulty with lithium as a controlled thermonuclear reactor (CTR) coolant is its high electrical conductivity which leads to excessive pressure drop and pumping power in circulating it as coolant in the vicinity of the strong magnetic field of the plasma. To overcome this difficulty, Sze and Stewart (1974) proposed a method of electrical insulation. Other alternative methods (El-Wakil, 1971) are the use of lithium compounds which may be one of the following four materials: (1) molten salts such as $LiF\text{-}BeF_2$ eutectic called flibe, (2) lithium nitrates along with other nitrates, (3) mixtures of liquid metals and molten salts such as lithium and flibe, and (4) LiAl compound (Lazareth and others, 1975).

Use of lithium for blanket or coolant material can be viewed from an energy point of view (Holdren, 1971). The basic deuterium-tritium reaction will release a neutron, an alpha particle, and an energy of 17.6 MeV carried by the neutron and alpha particle. Deuterium is available in seawater but natural tritium is scarce. Bom-

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[1] This work was performed under the auspices of the Controlled Thermonuclear Reactor Division (CTR) of the U.S. Energy Research and Development Administration.

[2] Any use of trade names is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

barded by a neutron, lithium can be used as a breeder for tritium in the fusion reactor. Because of this characteristic, lithium becomes one of the unique elements in the fusion reactions. The energy value of one gram of lithium can be increased by increasing the breeding ratio (tritons produced/tritons consumed) or increasing the amount of energy per fusion. Lee (1969) estimated that the effective energy content of natural Li ranges from about 8.5×10^3 kWh (normal) per gram to 2.7×10^4 kWh (thermal) per gram of natural lithium. Natural lithium consists of 7.5 percent Li^6 and 92.5 percent Li^7.

SUPPLY AND DEMAND OF LITHIUM

Production of lithium for various commercial end uses has been described previously. Fusion power should be available at the turn of the century. Natural lithium demand for fusion reactors varies depending on the reactor type as is shown in table 29. For a solid lithium blanket, the quantity required is about 5.5~46.8 kg/MWe of natural lithium or 0.46~3.9 kg/MWe of 90 percent enriched in Li^6 depending on the first wall load and thermal conversion efficiency. For a liquid lithium blanket, the quantity required may be as high as about 1,000 kg/MWe. It should be noted that the minimum activity solid blanket is 90 percent enriched in Li^6, while the liquid coolant blanket is natural lithium (7.5 percent Li^6). In the following, all the quantities of lithium expressed are in terms of the amount of natural lithium. The total lithium demand consists of both use in the blanket inventory and burning on a continuing basis as to form tritium. Tritium is thus part of the fuel cycle. With the present state of knowledge of the technology, an order of magnitude estimate rather than exact values can only be made at this time. Figure 33 shows the production and demand of lithium as a function of time. This chart indicates the slow growth of the industry prior to World War II and shows the influence of wartime demands, especially in the peak production year of 1944. Projection of future production for conventional use is obtained by a linear regression based on the production rate of previous years. Production of lithium in 1968 was about 3,000 short tons (2.7×10^6 kg, Cummings, 1968). With an annual increase in the rate of about 5 percent, the lithium production in 2000 is estimated to be 1.2×10^7 kg/year. When the requirement of fusion power in the United States reaches about 10^6 MWe beyond 2030, the quantity of natural lithium inventory required ranges from about 0.55×10^7~4.7×10^7 kg (Powell, 1975) for enriched solid CTR blankets to as high as 10^9 kg for liquid lithium coolant blankets. Superimposing these quantities on the previous one for commercial use, the total quantity of lithium required lies between 4.3×10^7 and 10^9 kg beyond the year 2030 (the Energy Advisory Panel, 1973). Figure 33 gives the general trend of lithium production and demand for various time periods. Future projections of these curves may change with respect to the time scale, but the shape of the curve should remain the same.

TABLE 29.—*Lithium requirement per megawatt for various kinds of fusion reactors inventory*

Reactor type	ORMAK[a]	Tokamak[a]	θPinch[a]	ORNL[a] laser	LLL DT[a] mirror	BNL minimum activity[b]
Lithium required per megawatt (kg/MW)	804	454	377	325	182	5.5~46.8

[a] Controlled Thermonuclear Research Division (1973).
[b] Powell, J. R. (1975).

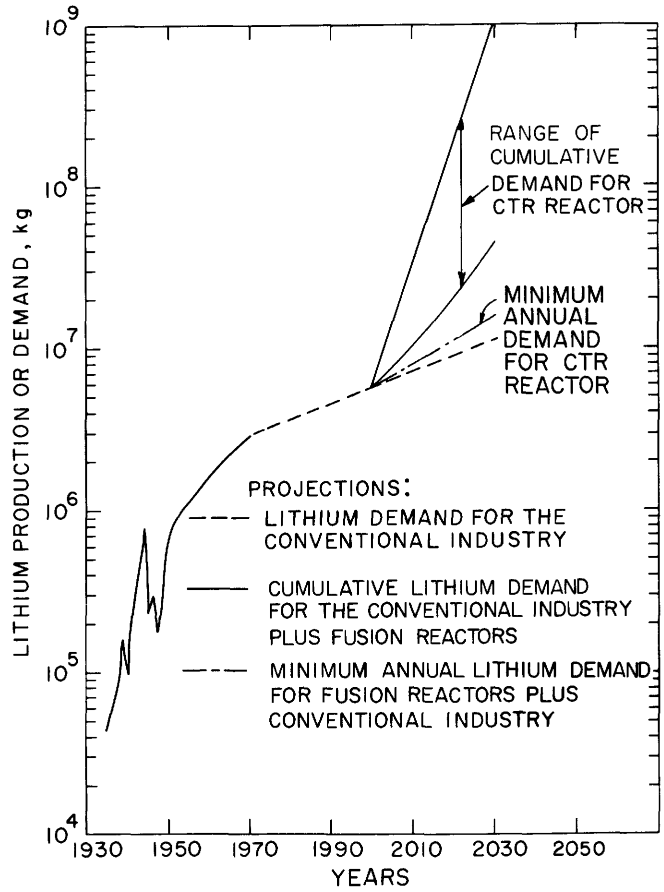

FIGURE 33.—Lithium production rate and demand projections.

Conventional lithium sources are minerals and brines. In the United States most of the lithium minerals come from Kings Mountain, North Carolina. Mainly spodumene and some amblygonite are mined in North Carolina. South Dakota also has some reserves which consist of spodumene, amblygonite, and lepidolite. Elemental composition of these minerals is shown in table 30. Spodumene has the highest lithium composition as compared to the other minerals listed in the table, and more than half of the Free World's output of lithium oxide came from this source in 1963. Estimation of the total quantity of resources from these materials is about 6.89×10^8 kg, as can be seen in table 30.

In order to produce more lithium and to reduce mining operations which rely on relatively expensive mining and conventional hydrometallurgical processing, brine has been investigated for an alternative source for lithium. Lithium has been found in brines in several places such as Silver Peak, Nevada; Great Salt Lake, Utah; Searles Lake, California; and Bonneville, Utah. Of these locations, lithium concentration is highest in Silver Peak, Nevada, as can be seen in table 30 (Brennan, 1966). Commercial production has been carried out in Nevada, Utah, and California. Estimates of the content of two of the richest lithium brines are 3.45×10^9 kg in Silver Peak, Nevada, and 5.91×10^8 kg in the Great Salt Lake in Utah, as is shown in table 30.

The total estimated supply of lithium from brine and mineral reserves is thus about 4.73×10^9 kg, which comes close to the maximum cummulative quantity demanded for fusion reactors after 2030, estimated to be as high as 10^9 kg. If there is any additional large demand for lithium, such as for lithium sulfur batteries and for Li^7 as water conditioner in fission reactors, the reserves will not be sufficient to sustain a long term fusion economy. To remedy this situation, a large new lithium source of supply should be explored in conjunction with a reduction of fusion reactor lithium demand.

In this report, seawater is examined as an alternate large source for Li. The concentration of lithium in seawater has been determined to be 0.17 ppm (Riley and Tongudai, 1964; Riley and Skirrow, 1965; Chow and Goldberg, 1962). Although the lithium concentration in the sea is very dilute, its quantity is tremendous—estimated to be about 2.5×10^{14} kg. If annual requirement for lithium is a maximum of 4.32×10^6 kg/yr after 2030 (Powell, 1975) for solid blanket or even about twenty times larger than the above quantity for liquid blanket, the supply of lithium from the sea can last a million years or more. Thus the presence of an unlimited fuel resource as promised for a deuterium economy becomes possible. Obviously this is possible only if the technology for extraction of lithium from seawater becomes economically feasible.

The objective of the present paper is to outline a process for the extraction of lithium from seawater and to determine in a preliminary manner the mass, energy balance, and economics of such a process.

PROCESS CONCEPT FOR EXTRACTION OF LITHIUM FROM SEAWATER

Regardless of which process scheme is considered, the minimum theoretical energy requirement for extraction of lithium from seawater can be determined from the equation of minimum free energy change, $\Delta F = RT \ln (\gamma N)$, where ΔF is computed to be 0.07 kWh (thermal)/gmLi; ΔF is the difference in free energy, R is the thermodynamic gas constant, I is absolute temperature in degrees Kelvin, and γN is the activity of the dilute species.

Several possible routes for lithium extraction were considered mainly based on a study of the literature. The various processes considered for the concentration of dilute species included adsorption, solvent extraction, ion exchange, evaporation, precipitation, and electrochemical separation. Ideally, it would be most advantageous to have a specific selective adsorbent for lithium. Although this is technically possible our literature survey did not reveal such an agent. As a result, preliminary calculations indicated that an extraction process involving concentration by solar evaporation followed by ion exchange and finally electrolytic separation may be a reasonable process approach. This process has been determined to be a more economical one than a process using solar energy alone for salt separation. The plant can be located either by the seashore or on an offshore island. The ion exchange beds may be built in the strait so that power required to pump seawater to the beds may be eliminated.

TABLE 30.—*Mineral contents and sources of lithium*
[weight percent]

Mineral	Silver Peak, Nevada[a]	Great Salt Lake, Utah[a]	Sea water[b]	Spodumene[c,d*]	Petalite[c,d*]	Lepidolite[c,d*]	Amblygonite[c,d*]
Sodium	7.5	7.0	1.08	0.36	0.68	0.50	0.88
Magnesium	.06	.8	.13	.60	----	----	----
Calcium	.05	.03	.04	.34	----	----	----
Lithium	.04	.006	.000017	2.80	1.58	2.26	.85
Potassium	1.0	.4	.04	.60	.17	10.18	----
Silicon	----	.0004	.0003	29.7	36.2	23.63	----
Aluminum	----	------	--------	13.9	8.81	13.30	17.87
Iron	----	------	--------	.95	.14	.29	----
Sulfate	.75	1.5	.27	----	----	----	----
Chloride	11.7	14.0	1.94	----	----	----	----
Bromide	.0	.0	.0004	----	----	----	----
Total lithium estimated (kg)	3.45×10^9	5.91×10^8	2.5×10^{14}	6.89×10^8			

*All the metals are in oxide forms. Another major element in amblygonite is phosphorus.
[a] Brennan (1966).
[b] Riley and Skirrow (1965, p. 164).
[c] Cummings (1968).
[d] Mellor (1946, p. 425).

Extraction of sodium chloride and magnesium from seawater by solar evaporation has been practiced on a commercial scale for many years (Shrier, 1952; Schambra, 1945). Extraction of uranium from seawater by an ion exchange method was proposed by Davies and others (1964). The concentration of lithium in seawater lies between that of sodium and uranium. The application of solar evaporation alone can hardly produce pure lithium without subsequent chemical treatment, because of its dilute concentration. Application of ion exchange beds alone will require a large quantity of ion exchange resins and therefore become uneconomical. Hence, a method of combination of solar evaporation and ion exchange is proposed for extraction of lithium from the sea. The separation and quantitative determination of lithium in seawater have been carried out by several investigators (Chow and Goldberg, 1962; Riley and Tongudai, 1964; Leont'eva and Vol'khin, 1973) using ion exchange methods. Table 31 lists a survey of these methods. Strelow and others (1974) separated lithium from sodium, beryllium, and many other elements by eluting lithium with 1 molar nitric acid in 80 percent methanol from a column of sulphonated polystyrene cation-exchange resin. This method is similar to that of Riley and Tongudai (1964) and may be used for separation of lithium from seawater. The proposed large-scale engineering process design is based on the laboratory results of Riley and Tongudai (1964).

A schematic flow diagram of the process is shown in figure 34. Seawater flows in the solar pond by tidal waves. Ponds can be built according to the topography of the seashore. The concentration ponds should be built at a higher elevation and the crystallization pond will be built at a lower elevation so that concentrated brine can flow from the concentration pond to crystallization pond by gravity. In the concentration areas, water is evaporated successively to different concentrations of lithium in ponds of various sizes. In the process of fractional crystallization of seawater, sodium chloride, calcium sulfate, and magnesium chloride will precipitate first because of their much higher concentration and thus will reach their solubility limit first. Assuming the salts precipitated out in the order with calcium sulfate first, followed by sodium chloride and magnesium chloride, it is found that when the seawater is concentrated to 10^6 parts of original seawater by evaporation, then lithium chloride will begin to precipitate. The solar pond systems can be designed to be big enough so that two parts in 10^6 parts of water is left after solar evaporation. In this manner, the size and capital investment of the ion exchange bed can be greatly reduced.

The concentrated lithium brine is passed into the precleaned ion exchange bed of Dowex 50–X16 (polymer beads of polystyrene crosslinked with 16 percent polyvinylbenzene). The characteristic of the Dowex resin is selective for exchange of its hydrogen ion with the cations in the seawater in the order of potassium, sodium, and lithium followed by magnesium. After lithium ions are adsorbed, the remaining seawater will be concentrated in a smaller solar pond to concentrate the chloride ions in solution to a stronger hydrochloric acid. One can design the size of the bed to be big enough so that it can be operated 24 hours before the bed is saturated. In order to maintain continuous operations, a second bed is needed so that while one bed is functioning for the adsorption mode, the other bed can operate in the elution mode. Lithium ions are first eluted from the pregnant bed with 0.2–0.5 normal hydrochloric acid. The eluted lithium chloride solution from the bed can flow in the evaporator to obtain concentrated lithium chloride or recycle back to the bed in order to elute more lithium ions. The lithium chloride then flows

TABLE 31.—*Literature on separation and determination of lithium from seawater*

Author	Ocean or sea	Li concentration (μg/l)	Method of separation	Method of determination
(1) Marchand (1899)	English Channel	200		Gravimetric as Li_3PO_4.
(2) Thomas and Thompson (1933)	North Sea	100	Precipitate Ca and Mg as carbonates, NaCl precipitated with alcohol or HCl. Residual Mg precipitated. Filtrate evaporated to dryness and residue extracted with alcohol.	Visual flame spectrophotometry.
(3) Goldschmidt and others (1933)	North Sea	72		Spectrographic on sea salts.
(4) Strock (1936)	North Sea	140		Spectrographic on dry salts.
(5) Bardet and others (1937)	North Atlantic	200	Li separated from NaCl by amyl-alcohol extraction. Other elements removed by repeated precipitation and evaporation	Gravimetric as Li_2SO_4.
(6) Ishibashi and Kurata (1939)	Pacific (Japanese coastal waters).	170	Concentrated by evaporation and elements removed by precipitation.	Gravimetric.
(7) Chow and Goldbert (1962)	Pacific	173	Sample enriched with ^{6}Li. Li separated by ion exchange and eluted with HCl.	Isotope dilution.
(8) Kappanna and others (1962)	Indian (coastal waters)	160	Li + residual Mg precipitated as phosphate and weighed. Mg determined titrimetrically with EDTA.	Gravimetric.
(9) Riley and Tongudai (1964)	All oceans	183	Sample enriched with Li. Li separated by ion exchange and then eluted with HCl.	Flame photometry.
(10) Leont'eva and Vol'khin (1973)	High mineral solution	11,000	ISM–1 ion-sieve cation exchange.	Do.

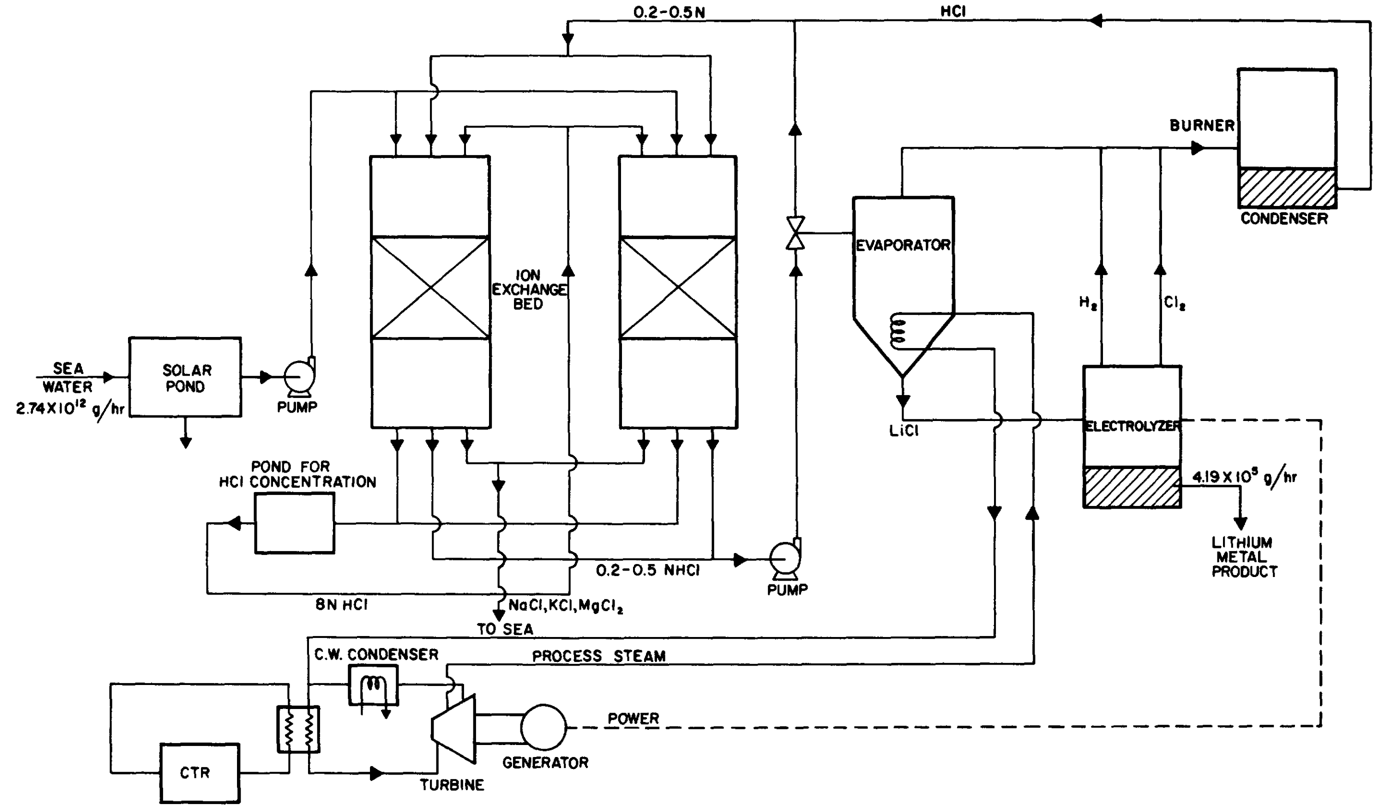

FIGURE 34.—Schematic flow diagram for extraction of lithium from seawater.

into an electrolyzer where lithium is electrolyzed. Hydrogen and chlorine from the electrolyzer react in a burner to form hydrogen chloride which is then dissolved in water from the evaporator to form dilute hydrochloric acid. The dilute hydrochloric acid is recycled back to the ion exchange bed to elute lithium ions. Other cations such as sodium, potassium ions, and so forth will be eluted by concentrated hydrochloric acid (8*N*) from the ion exchange bed after lithium ions are eluted out by dilute hydrochloric acid and before fresh seawater is passed in the bed. The eluted effluent is then passed back to the sea.

Evaporators used are triple-effect backward-feed evaporators. The assumed steam economy (total water evaporated/total steam supplied) is three. Boiling point elevation in each evaporator is neglected. Electrolyzer design follows closely the one described by Hader and others (1951) for electrolysis of lithium chloride.

PROCESS DESIGN AND ECONOMIC ANALYSIS[3]

In the present design calculations, *W* gm/hr of lithium is taken as the production unit throughout and all the design quantities are based on this variable. Once *W* is defined, all other quantities may be computed.

The first major unit to design is the solar pond system. The rate of evaporation of water by solar energy is an important issue here. From a simple energy balance, one can take the heat required for evaporation to be supplied by solar radiation according to the following equation:

$$M\lambda = BAt, \qquad (1)$$

where λ is latent heat of water taken to be 1,000 Btu/lb; *B* is the daily average solar energy received on the ground that varies from a few hundred to 2,500 Btu/ft^2 (Lof, 1966; Pancharatnam, 1972); *t* is the time interval during which the seawater receives solar energy for evaporation; *A* is the pond area in ft^2; and *M* is the mass of water evaporated in pounds. Validity of this equation can be seen from data of Silver Peak (Brennan, 1966) which shows that 10^7 lb/yr of lithium carbonate is produced in a pond of 910 acres. Daily solar energy radiation received on the ground is taken to be 1,500 Btu/ft^2. In order to obtain the number of active days of evaporation from about May to September each year (the period where abundant sunshine is received on ground in the West Coast), a correction factor of 0.5 is needed to validate the results of Silver Peak (Brennan, 1966) in using equation (1) which is a simple and good approximation for large complex solar pond systems. Hence, one can

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[3] The following discussion of the engineering design for a method of extracting lithium from seawater employs English units as the fundamental data for discussion. It involves land area in acres and square miles, equipment size and capacity in standard American sizes, and costs in dollars and cents. Conversion to metric units is not practical. *Editor.*

then apply equation (1) for solar pond design for extraction of *W* gm/hr of lithium from seawater having an initial lithium concentration of 170 ppb. If we select a plant location on the Southwest coast of the country with hourly solar energy intensity of 187.5 Btu/hr ft^2 and time of evaporation to be 8,000 hr/yr, we can calculate the pond area to be $0.288 \times 10^5 W$ ft^2 in order to evaporate 2.36×10^{10} *W* g/yr of seawater. For a production rate of lithium of 10^6 kg/yr which is sufficient for one 1,000 MWe fusion reactor of ORMAK or one hundred 1,000 MWe fusion reactors of Brookhaven National Laboratory (BNL) minimum activity blanket, the area of solar pond required is about 155 square miles. Utilization of waste heat of about 3×10^9 Btu/hr from a 1,000 MWe fusion reactor for part of the heat supply for solar evaporation can also be considered. With the present design, it is found that using the waste heat for solar evaporation can only be reduced by about 0.6 square miles, or about 0.3 percent of the land calculated without using waste heat.

The concentration of cations initially in the seawater which will precipitate in a salt form such as sodium chloride, calcium sulfate, magnesium carbonate, potassium chloride, and so forth, is about 0.0351 g/g seawater. When two parts of the initial 10^6parts of seawater is left from evaporation (lithium chloride will begin to precipitate when 1 part of the initial 10^6 parts of seawater is left), 12.6 *W* g/hr of bittern flows into the ion exchange bed for cation adsorptions. More than 99.9 percent of $CaSO_4$, NaCl, $MgCl_2$, and KCl is precipitated in the crystallization ponds. The flow rate of bitterns that contain cations is 0.568 *W* g-equivalent/hr. The capacity of Dowex-50 is 4.32 meg/g and the design of the ion exchange bed is for a 24-hour operation period before switching over to another bed. Then the total amount of resin required is 6,320 *W* g. The density of the resin is 0.802 g/cm^3, so the volume of each bed is 4.14×10^3 (W/N) cm^3, where *N* is the number of beds. The ratio of height to diameter of the bed is taken to be 15 (Dow Chemical Company, 1958; Chow and Goldberg, 1962; Riley and Tongudai, 1964), so height and diameter of each bed are 93.5 $(W/N)^{1/3}$cm and 6.23 $(W/N)^{1/3}$ cm, respectively.

According to Riley and Tonguadi (1964), 500 ml of 0.5 normal HCL is used to elute 1.17 mg of lithium. Theoretically one equivalent of hydrogen ion can displace one equivalent of lithium so the hydrochloric acid can recycle 1,176 times to elute lithium in the bed before it passes into the evaporator to drive off water from aqueous LiCl. The circulation load of hydrochloric acid is 1.5 *W* gal/min. Riley and Tonguadi reported that one liter of 4 *N* HCl is used to elute other cations such as sodium, potassium, and so forth from the bed. In the present operation, the concentrated hydrochloric acid required is less than that used by Riley and Tonguadi because more than 99.9 percent of the cations are precipitated. With this reduction of cations in the bittern, 25.6 *W* g/hr of 4 *N* hydrochloric acid is needed.

When all the hydrogen ions in 0.2 *N* hydrochloric acid are displaced by lithium ions in the ion exchange bed, LiCl of 8.48 g/l flows into the evaporator at a rate of 746 *W* cm^3/hr.

To obtain a solid lithium chloride in the evaporator, 99.152 percent of the water has to be evaporated. The evaporator type is a triple effect backward feed with a steam economy of three. Process steam at 140 psi and 353°F is used to supply heat of evaporation of water. Using a heat transfer coefficient of 500 Btu/hr ft^2°F, one can estimate the heat transfer area of the evaporator to be $4.62 \times 10^{-3} W$ square feet.

The electrolyzer used is similar to the one described by Hader and others (1951) except larger in scale. A cell with dimensions of 14 ft by 21 ft by 10.5 ft is used and its capacity is 161 lb/hr. Fourteen graphite anodes, 1.25 ft in diameter and 21 ft long, are supported from above the cell and extend downward into the electrolyte bath. The cathode is made of steel. Operating conditions would be the same as in a conventional cell (Hader and others, 1951). Table 32 shows a summary of the dimensions and number of major units. The area of the solar pond is a significant factor in the present process. Table 33 shows the areas of ponds required for various production rates of lithium based on equation (1).

An important aspect of the process is the energy requirement. Mechanical energy is required to transport bittern and hydrochloric acid between the ion exchange bed and other pieces of equipment. The mechanical energy equation for fluid transport in the present system is

$$\frac{g}{g_c} \Delta h + \frac{\Delta u2}{2g_c} + \frac{2fLu}{g_c D} + W_s = 0, \qquad (2)$$

where the first term is for potential energy, the second term is for kinetic energy, the third term is frictional losses in the pipe line, with Fanning friction factor *f*, length of pipe *L*, diameter of pipe *D* and the fourth term is the pumping power required with the pumping efficiency 80 percent. Writing the velocity term in terms of the mass flow rate of liquid and the diameter of pipe, one can rewrite equation (2) as follows:

$$\frac{g}{g} \Delta h + \frac{8G2}{g_c p \; 2 \; 2D4} + \frac{32L \; G2}{g_c p2 \; 2D5} + W_s = 0. \qquad (3)$$

By substituting the mass flow rate for bittern (3.5×10^{-3} *W* lb/hr), 0.5 *N* HCl (6.3 *W* lb/hr), 4 *N* HCl (5.64×10^{-2} *W* lb/hr), height of ion exchange bed and length of transporting line which is taken 7.1 times of the bed height, one can obtain the pumping power required in

TABLE 32.—*Extraction of lithium from seawater—summary of dimensions and numbers of major pieces of equipment*

Equipment	Ion exchange bed	Pumps	Evaporator	Electrolyzer	Solar pond
Dimensions	Height $(h)=3.07\ (W/N)^{1/3}$; diameter $(D)=h/15$.	7,000 gal/min	Total area$=4.62\times10^{-3}W$ ft^2	21 ft by 14 ft by 10.5 ft	Area$=\frac{2\,m\gamma}{Bt}$
Number of units (N)	$N=(153.5/h)^3$	$N=2.14\times10^{-4}$W	$N=3$	$N=\frac{W}{454\times161}$	155 mi^2 or 12.4 mi×12.4 mi
Values are given for $W=1.25\times10^5$g/hr.	$N=17$ when $h=60$ ft $D=4$ ft $N=5$ when $h=90$ ft $D=6$ ft	27	645 ft^2 each	2	

TABLE 33.—*Extraction of lithium from seawater. Solar pond area as a function of lithium production rate*

Lithium production rate (kg/yr)	Solar pond area (square miles)
10^4	1.55
10^5	15.5
10^6	155

Note: for higher production rate, one can have plants located in several sites so that the requirement for solar pond area will not be concentrated in one location.

terms of kWh(e)/lb Li as

$$\frac{0,35\times10^{-9}}{D4}W+1.35\times10-4h+0.61\times10-11\frac{W2h}{D5}.$$

The thermal energy required in the evaporation is 73.1 kwh(thermal)/lb Li. With 80 percent cell efficiency, energy required in the electrolyzer is 8.15 kWh(e)/lb Li; so, total energy required for extraction of lithium from seawater by the present process in terms of kWh(e)/lb Li is then

$$\frac{0.35\times10^{-9}}{D4}W+1.35\times10^{-4}h+0.61\times0.61\times10^{-11}\frac{W2h}{D5}+37.39.$$

Table 34 shows a summary of energy requirements calculated from the above expression for various lithium production rates, pipe sizes for liquid transport, and heights of ion exchange bed. When the lithium production rate is less than 10^5 kg/yr, the energy requirement for the present process is mainly for thermal energy in the evaporation and electrical energy for the electrolyzer. At a higher production rate, pumping energy becomes more important. When the lithium production rate is less than 10^6 kg/yr, energy requirement for lithium extraction is less than 0.2 kWh(e)/g Li. Energy requirement increases with increase in lithium production rate and the height of the ion exchange bed mainly due to increase in pumping power for liquid transport in the pipe line. However, increased pipe size will decrease energy requirements, as can be seen in a decrease from 1.667 to 0.719 kWh(e)/g for a pipe size increase from 2.5 to 3.0 foot diameter at lithium production rates of 10^8kg/yr and bed height of 60 feet. Even using the most energy intensive case in our study (2.46 kWh(e)/g) for production of lithium of 10^8kg/yr which is sufficient to build 124 ORMAK or 10^4BNL minimum activity blanket fusion reactors of 1,000 MW(e), one can see that the present process is still an energy efficient one compared to the minimum natural lithium energy content estimated by Lee (1969) for fusion reactor as 3,400 kWh(e)/g Li.

TABLE 34.—*Summary of energy requirements for lithium extraction from seawater at various lithium production rates, pipe size for liquid transport, and height of ion exchange bed*

Lithium production rate	Diameter of pipe	Height of ion exchange bed	Energy requirement for Li Production*	
(kg/yr)	$(D(\text{ft}))$	$(h(\text{ft}))$	kWh(e)/gd	(kWh(e)/lb)
10^4	1	60	0.082	(37.39)
	1	90	0.082	(37.39)
	2	60	0.082	(37.39)
10^5	1	60	0.083	(37.46)
	1	90	0.165	(37.50)
	2	60	0.082	(37.39)
10^6	1	60	0.098	(44.46)
	1	90	0.106	(48.00)
	2	60	0.083	(37.61)
10^7	1	60	1.642	(745.39)
	1	90	2.422	(1,099.39)
	2	60	0.131	(59.52)
10^8	2.5	60	1.667	(761.5)
	2.5	90	2.460	(1,123.6)
	3	60	0.719	(328.4)

*Energy requirements include pumping energy, evaporator energy, and energy for electrolysis.

A preliminary economic assignment of the process has also been studied. A solar pond is made of a dike surrounding an area holding seawater and can be constructed at a negligible cost compared to the other major items such as equipment and ion exchange beds. The cost of ion exchange resins was obtained from Dow

Chemical Company (1974, written commun.). The cost of the pump is obtained from Peters and Timmerhaus (1968, p. 466). The cost of the electrolyzer is evaluated from its basic material cost such as steel and graphite. The cost of the evaporator and burner for HCl is obtained from Popper (1970, p. 145 and p. 87). Table 35 lists the capital investment of the present process for extraction of lithium from seawater in terms of W g/hr of lithium production rate in 1970 dollars. Results of the capital investment for three different lithium production rates (10^4–10^6kg/yr) are exhibited in table 36. Table 37 gives the production cost of the process. The cost of steam is reasonably taken to be 0.249 cents/1,000 g ($1.15/1,000 lb) (Peters and Timmerhaus, 1968, p. 772) or 0.07 cents/g Li, and a small cost is taken for HCl in the recycling elution process. Table 36 and figure 35 shows the lithium production cost versus lithium production rate. The production costs range from 2.2 cents to 3.2 cents/g. It is seen that the production cost (1974 value) is competitive with the cost of lithium at 2 cents/g (Holdren, 1971. The costs are somewhat higher than the selling price of lithium at 2 cents/g (Holdren, 1971). In terms of use in fusion reactors the per kWh(e) cost is no more than 0.01 mill/kWh(e), which thus insures a negligible cost. Of main importance is the resource availability which is insured by the sea.

CONCLUSION

A process for the separation of lithium from seawater is designed based on solar evaporation and ion exchange sorption/desorption followed by electrolytic recovery for metal. The preliminary analysis shows that the process appears to be technically feasible. Uncertainties exist in the practical operation of large ponds. The energy requirement for lithium extraction by this process can be as low as 0.082 to as high as 2.46 kWh(e)/g Li depending on lithium production rate. Compared to the equivalent minimum nuclear energy content of natural lithium of 3,400 kWh(e)/g, the energy requirement for this process is relatively small. A preliminary economic analysis shows that the production cost of lithium for the present process is in the range of 2.2 to 3.2 cents/g (1974 values) which is slightly above present selling price of about 2.0 cents/g from conventional mineral resources. The point is that it should be possible to insure an unlimited resource for lithium for the long term fusion economy at a reasonable cost. To remove the uncertainties in the process technology, it is recommended that a phase study of the salts in the sea be undertaken to determine the liquid-solid equilibrium during solar evaporation. It is further recommended that a laboratory search for a highly selective absorbent or adsorbent for extraction of lithium from seawater be undertaken on a continuing experimental effort so as to insure the technology when it will be needed.

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TABLE 35.—*Capital investment for a plant for the extraction of lithium from seawater in terms of* W *gm/hr lithium production rate*

	Item	Capital cost ($)			
(1)	Resin beds	$70W$			
	Pumps			$221.9W^{0.489}$	
	Evaporator				$2.1W^{0.8}$
	Electrolyzer	$0.3W$			
	Burner		$184.6W^{0.85}$		
(2)	Land for solar pond, 4.6 percent of item (1)[a]	$3.23W$ +	$8.49W^{0.85}$ +	$10.2W^{0.489}$ +	$0.1W^{0.8}$
(3)	Piping, 29 percent of item (1)[a]	$20.4W$ +	$53.5W^{0.85}$ +	$64.4W^{0.489}$ +	$0.6W^{0.8}$
(4)	Service facilities, 56 percent of item (1)[a]	$39.4W$ +	$103.4W^{0.85}$ +	$124.3W^{0.489}$ +	$1.2W^{0.8}$
(5)	Unlisted equipment and miscellaneous, 10 percent of above[b]	$13W$ +	$34.2W^{0.85}$ +	$41.1W^{0.489}$ +	$0.4W^{0.8}$
(6)	Installation of equipment, 35 percent of above[a]	$45.5W$ +	$119.7W^{0.85}$ +	$143.9W^{0.489}$ +	$1.4W^{0.8}$
	Subtotal (lines 1–6)	$191.9W$ +	$503.9W^{0.85}$ +	$605.8W^{0.489}$ +	$5.8W^{0.8}$
(7)	Site preparations, buildings, 20 percent of above[b]	$38.3W$ +	$101W^{0.85}$ +	$121.2W^{0.489}$ +	$1.2W^{0.8}$
(8)	Electrical and instrumentation, 20 percent of above[b]	$38.3W$ +	$101W^{0.85}$ +	$121.2W^{0.489}$ +	$1.2W^{0.8}$
	Subtotal (lines 1–8)	$268.5W$ +	$705.9W^{0.85}$ +	$848.2W^{0.489}$ +	$8.2W^{0.8}$
	Total, two times[c] to include engineering construction overhead and contingency	$537W$ +	$1411.8W^{0.85}$ +	$1696.4W^{0.489}$	+ $16.4W^{0.8}$

[a] Peters and Timmerhaus (1968, p. 104).

[b] Harrington and others (1966, p. 36).

[c] Page (1963, p. 124–127).

TABLE 36.—*Capital investment for plants for the extraction of lithium from seawater*
[Capacity range $=10^4$–10^6kg/yr plants (1974 dollars)]

Item	Capital cost ($$10^6$)			Percentage of total		
	10^4kg/yr	10^5kg/yr	10^6kg/yr	10^4kg/yr	10^5kg/yr	10^6kg/yr
(1) Resin beds	0.09	0.88	8.75	7.2	8.4	9.4
Pumps	.00	.01	.04	.2	.1	.0
Evaporators	.00	.00	.02	.0	.0	.0
Electrolyzers	.00	.00	.04	.0	.0	.0
Burner	.07	.46	3.31	5.4	4.5	3.5
(2) Land for solar ponds	.00	.06	.56	.5	.6	.6
(3) Piping	.04	.39	3.52	3.7	3.8	3.8
(4) Service facilities	.09	.76	6.80	7.2	7.3	7.3
(5) Unlisted equipment and miscellaneous	.03	.26	2.31	2.5	2.5	2.5
(6) Installation of equipment	.11	.90	8.07	8.9	8.6	8.6
(7) Site preparations, buildings	.09	.74	6.68	7.2	7.1	7.1
(8) Electrical and instrumentation	.09	.74	6.68	7.2	7.1	7.1
Subtotal	0.60	5.13	46.78	50.0	50.0	50.0
(9) Engineering, construction overhead, and contingency	.60	5.13	46.78	50.0	50.0	50.0
Total	1.21	10.43	93.56	100.0	100.0	100.0

TABLE 37.—*Production cost for extraction of lithium from seawater in terms of* W *g/hr lithium production rate (1974 dollars)*

Items	Production cost (cents/m I	Cents/m Li				Percentage of total			
Lithium production rate		10^4kg/yr	10^5kg/yr	10^6kg/yr	10^7kg/yr	10^4kg/yr	10^5kg/yr	10^6kg/yr	10^7kg/yr
Yearly charge, 13 percent[a]	$0.85+2.25W^{-0.15}+2.71W^{-0.511}+0.03W^{-0.2}$	1.70	1.42	1.25	1.12	54.0	53.4	53.2	51.4
Electrical energy cost (for pumping and electrolysis), 1.5 cents kWhe		.03	.03	.04	.05	.9	1.1	1.7	2.31
Steam cost, 0.249 cents/1,000 g		.07	.07	.07	.07	2.6	2.6	3.0	3.21
Raw material	0	.00	.00	.00	.00	.0	.0	.0	.00
Chemical (HCl)	.07	.07	.07	.07	.07	2.2	2.6	3.0	3.21
Maintenance, labor and so forth, 10 percent[b]	$.66+1.73W^{-0.15}+2.08W^{-0.51}.02W^{-0.2}$	1.31	1.10	.96	.87	41.6	41.4	40.8	39.9
Total	$1.65+3.98W^{-0.15}+4.8W^{-0.50}+.05W^{-0.2}$	3.18	2.69	2.34	2.18	100.0	100.0	100.0	----

[a] Harrington and others (1966, p. 37).
[b] Kunin (1958, p. 396).

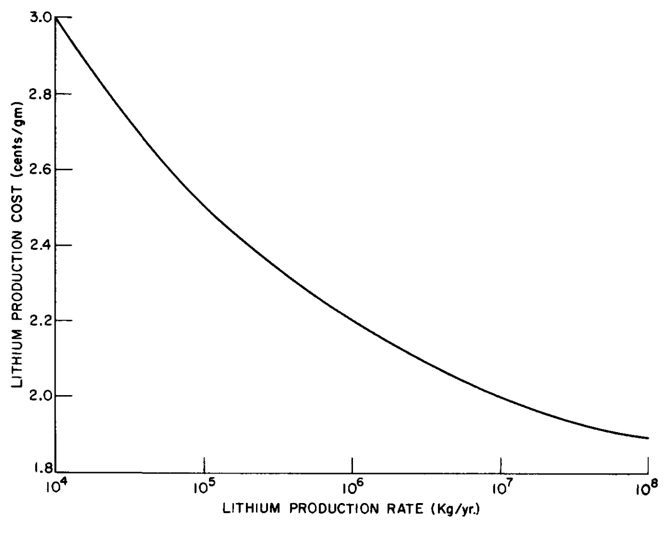

FIGURE 35.—Lithium production cost versus lithium production rate.

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LITHIUM BRINES ASSOCIATED WITH NONMARINE EVAPORITES

By Richard K. Glanzman and A. L. Meier,
U.S. Geological Survey, Denver, CO

Lithium is enriched in brines resulting from the evaporation of ground and surface water in the arid regions in the western United States. Most of the world's total supply of lithium is in the continental crust (Ronov and others, 1970). Chemical and mass weathering constantly redistribute lithium on the continental surfaces where runoff in the form of both ground and surface water from the continental highlands transports lithium to valleys from which there is no surface drainage (closed basins), and continuous evaportation of the water results in brines and the precipitation of the less soluble salts. Lithium salts are very soluble; the ions of the salts tend to remain in the brine and are among the last salts to precipitate. This process was in operation during late Tertiary and Quaternary time in the semi-arid to arid regions of western Utah. The geologic histories of Lake Bonneville in the Pleistocene and the Great Salt Lake in more recent times illustrate this process. The drainage basin of Lake Bonneville, therefore, was investigated to determine the areal distribution and enrichment of lithium resulting from the evaporation process.

The location, areal extent, and major physiographic subdivisions of the Lake Bonneville drainage basin are shown in figure 36. Lake Bonneville was the largest of the Pleistocene Great Basin Lakes with approximately 140,000 km^2 (54,000 mi^2) of drainage basin. Paleozoic marine limestones and dolomites in many of the present mountain ranges formed islands in Lake Bonneville. Weathering of these limestones and dolomites undoubtedly contributed much of the carbonate deposited in the remnant terraces and benches of the lake as the lake water evaporated. Evaporation first exposed Sevier Lake playa, then the Great Salt Lake Desert; finally, the once great lake dwindled to the remnant brine of the Great Salt Lake of today.

The tectonic setting of the eastern Basin and Range province in Utah is shown in figure 37. The north-south fault zone known as the Wasatch line nearly bisects the state. The highlands immediately east of this fault zone form the east boundary of Lake Bonneville and the ancestral drainage basins. The east-west trending mineral belts that were created by the Oligocene-Miocene-

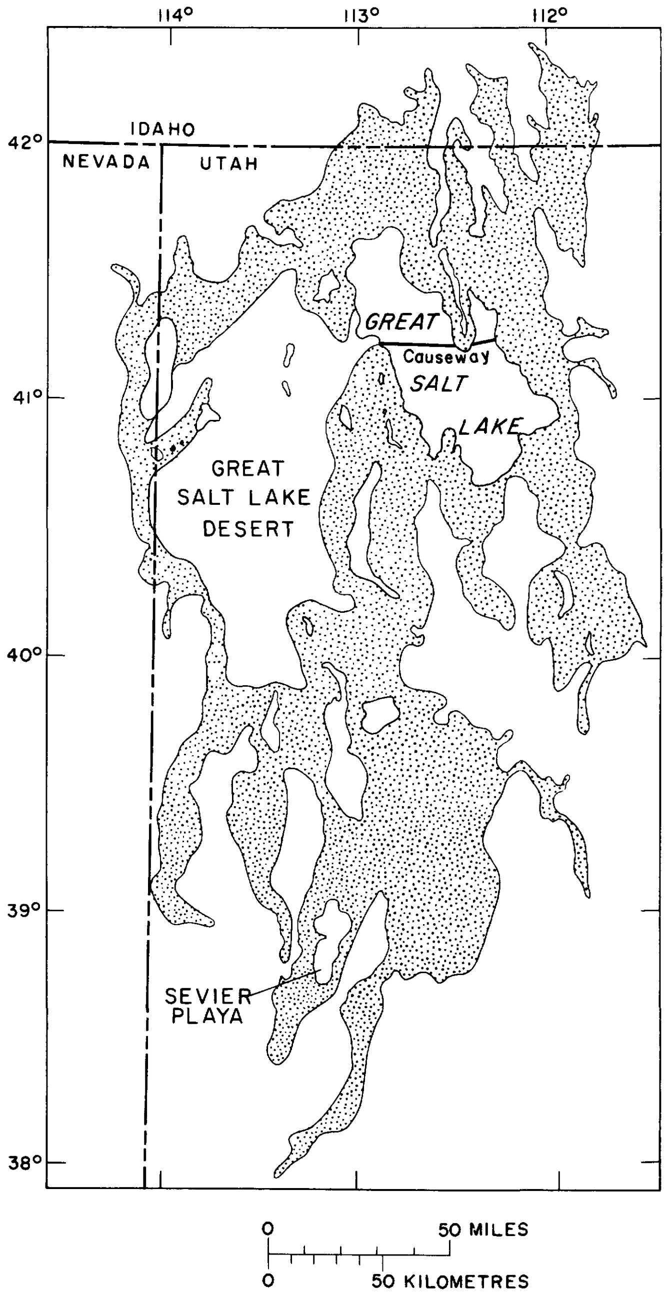

FIGURE 36.—The location, areal extent, and major physiographic subdivisions of the Lake Bonneville drainage basin.

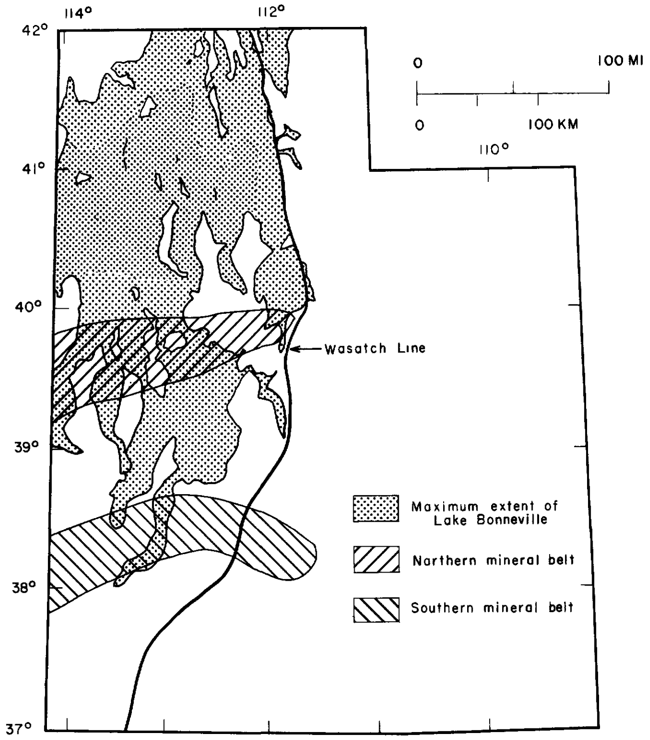

FIGURE 37.—The tectonic setting of the eastern Basin and Range province in Utah.

Pliocene and earlier tectonic activity form not only a structural setting but also contain elements normally associated with lithium. The southern mineral belt (Callaghan, 1973) includes the Marysvale mining district in the area where the belt crosses the Wasatch line. Lithiophorite, a lithium-manganese mineral, is reported to occur in this district (Bullock, 1967). The northern belt is the Nevada-Utah beryllium belt (Shawe, 1966) containing both beryllium and tungsten mineral deposits. Lithium is generally associated with both elements. It has been known for many years that lithium is enriched in the Spor Mountain beryllium district (Shawe and others, 1964; Starkey and Mountjoy, 1973; and Lindsey and others, 1973). Lake Bonneville (outlined in fig. 36) was not the first large lake in Utah.

Large lakes have occurred in Utah at least as early as Eocene time with the Green River Lake (Hunt, 1956) in the Uinta Basin (fig. 38a). The Lake Bonneville drainage basin was a land mass with streams draining across

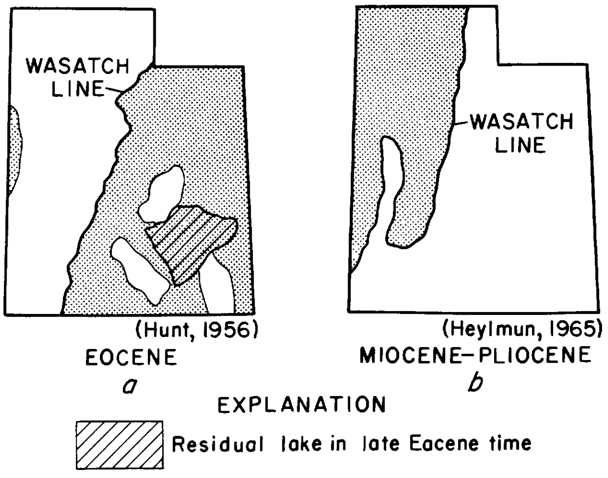

FIGURE 38.—The pre-Bonneville lake and lake-playa distribution in Utah.

the Wasatch line into the Green River Lake. These environmental conditions should have effectively leached any near-surface evaporites along the Wasatch line into the Green River Lake. The lake evaporated to the residual lake in late Eocene time and to dryness in the Oligocene. Tectonic activity along the Wasatch line during the Oligocene and early Miocene resulted in a lowering of the western part of Utah and the formation of a progressively larger lake or series of lakes and playas from the northwest corner of Utah to the extent shown in figure 38b (Heylmun, 1965). Identification of any evaporites formed in these western lake sediments will depend on drilling because of burial by Lake Bonneville sediments. According to Stokes (1973) and Axelrod (1957), during Oligocene-Miocene time the eastern Basin and Range physiographic province had a humid climate which caused deep weathering and supported deciduous hardwood forests. The Pliocene to early Pleistocene climate, however, was one of increasing aridity.

Water associated with volcanic rocks of Oligocene through Pliocene age within the mineral belts transported lithium into Tertiary drainage basins. Because lithium is a very soluble element, water and brine are the most indicative sampling media for lithium exploration. A sampling program was conducted following a literature search for all available lithium data in the eastern Basin and Range physiographic province (essentially Mundorff, 1970; Young and Carpenter, 1965; Nolan, 1927; Turk, 1973; Lindenberg, 1974; and White and others, 1963).

The combination of tectonism with the formation of closed basins and of a climatic sequence of increasing aridity before Lake Bonneville gives favorable conditions for the concentration of lithium. The specific areas of enrichment depend on a structural basin to form the trap and a supply of lithium to be transported into the trap. Two areas within the drainage basin appear to satisfy both conditions—the Sevier–Black Rock desert area and the northern Great Salt Lake Desert area.

The results of the sampling program in combination with other available data for the area between the north and south mineral belts are shown in figure 39. In general, a sample containing more than 1 mg/l (milligram per litre) lithium may indicate an area suitable for further study; more than 10 mg/l in a potable or brackish water certainly is suitable. The lithium concentration in samples along the upper Sevier River valley from Kingston to just below Salina ranges from 2 to 8 mg/l. Marine evaporites near Redmond increase the total dissolved solids but contribute little or no lithium. The Sevier River drains into the Sevier Desert. At the present time, the course of the Sevier River would carry water through the Sevier Desert to Sevier Lake Playa.

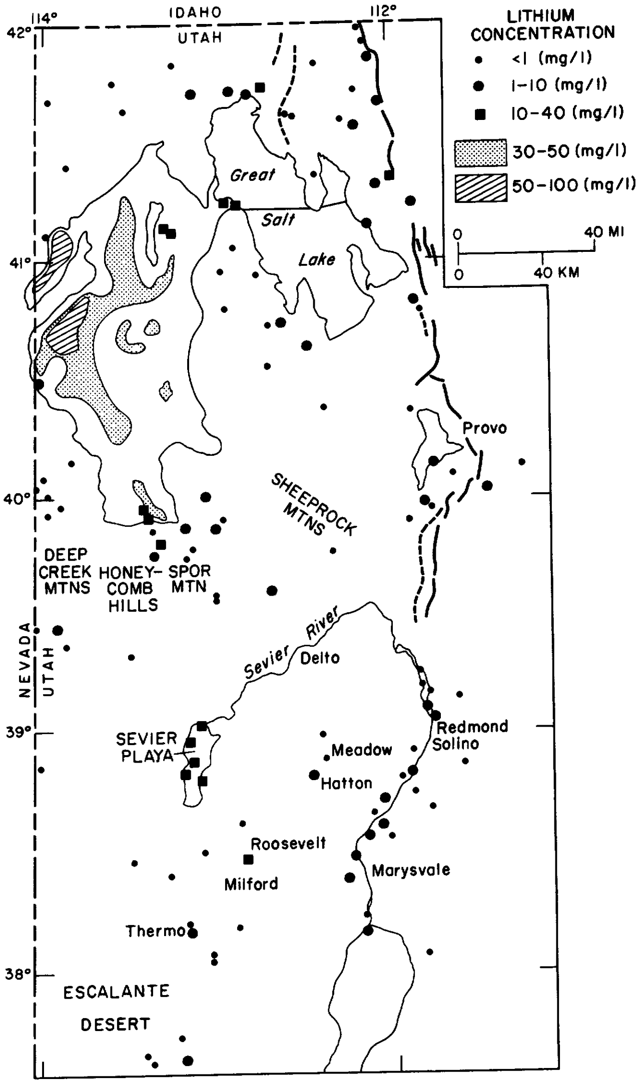

FIGURE 39.—Lithium concentration in water and brine in the Lake Bonneville drainage basin.

Surface water, however, seldom reaches the playa. Near surface brine (within upper 6 ft, approximately 2 m) contains 10 to 40 mg/l lithium (Whelan, 1969). The lithium concentration with depth is unknown.

The northern mineral belt formed a highland from which water containing lithium drained both to the south into the Sevier Desert and to the north into the Great Salt Lake Desert. The mineral deposits within this belt probably contributed as much if not more lithium to the Sevier Desert than those in the southern belt. Rock and sediment samples from the area of beryllium prospects in the Sheeprock Mountains contain 50–300 ppm (parts per million) lithium; beryllium deposits at Spor Mountain 200–1500 ppm; a beryllium prospect in the Honeycomb Hills 100–1000 ppm; and the tungsten-beryllium deposits in the Deep Creek Range 50–500 ppm. Water, in leaching lithium from these sources and the aforementioned sources, deposited at least 1,800 m (6,000 ft) of Tertiary and Quaternary sediments in the Sevier Desert because Gulf Oil No. 1 Gronning Well in sec. 24, T. 16 S., R. 8 W., 13 km (approx. 8 mi) northwest of Delta, Utah, showed this thickness (Heylmun, 1965). Lithium-bearing clay and (or) brine enriched in lithium in the upper Tertiary rocks of the Sevier Desert would appear to be an excellent exploration drilling target.

A line of sample localities with lithium concentrations greater than 1 mg/1 crosses the area diagonally from the southwest corner in the Escalante Desert to the northeast corner in Utah Valley marking the Wasatch line. Thermal springs are the major sources of these higher lithium concentrations. Water from Roosevelt thermal spring contained the highest lithium concentration of any spring sampled with 27 mg/1. Water from Roosevelt as well as Thermo hot springs (1.4 mg/1), hot springs near Meadow and Hatton (3.7 mg/1) all ultimately discharge to the north into the Sevier Desert. These sources and the upper Sevier River valley, however, are not the only sources of lithium draining into the Sevier Desert.

During the time of Lake Bonneville and for an undetermined part of the time of ancestral Lake Bonneville, water crossed the northern mineral belt into the Great Salt Lake Desert through the "Old River Bed" described by Gilbert (1890). Anomalous lithium concentrations are quite evident north of Spor Mountain, and they extend into the Great Salt Lake Desert (fig. 39). The thermal spring at the defunct Wilson Resort, which is approximately 1.61 km (1 mi) from the nearest outcrop, Fish Springs Range, produces water that contains 2.1 mg/l lithium. Near surface brine in the Great Salt Lake Desert containing 30–50 mg/l lithium surrounds the Bonneville Salt Flats near Wendover, Utah. The Bonneville Salt Flats area and a smaller area in Pilot Creek Valley contain near-surface brine with 50–100 mg/l lithium. Whelan and Petersen (1974) have shown that an abnormally high geothermal gradient may exist in the Bonneville Salt Flats area. The lithium concentration in both areas compares very favorably with the Great Salt Lake brine which ranges in concentration from 20 to 65 mg/l.

A comparison of near-surface brines in the Lake Bonneville drainage basin and the Great Salt Lake illustrates the process of enriching lithium through evaporation. Brine in Sevier Lake playa, first isolated by the evaporation of Lake Bonneville, contains 20–40 mg/l lithium; Bonneville Salt Flats and Pilot Creek Valley, 50–100 mg/l; and Great Salt Lake, even with fresh water inflows, contains 20–65 mg/l. Great Salt Lake is a good example of how little time is required for evaporative processes. An approximate 35 percent increase in lithium concentration in brine in the north arm of the lake has occurred since the construction of the causeway in 1959. Eardley (1970), in his discussion of the salt balance in Great Salt Lake, suggested the existence of earlier saline lakes in the Lake Bonneville drainage basin. He further suggested that somewhere in the basin there is a buried deposit enriched in lithium, boron, and potassium. Such a deposit may be a result of late Tertiary volcanic events along the Wasatch line and in the two mineral belts with the formation of lithium enriched brine and clay in several parts of the drainage basin.

Gravity profiles in the northern Great Salt Lake Desert (Cook and others, 1964) indicate a horst and graben structure beneath the playa (fig. 40). Grabens 1.22 km (4,000 ft) deep extend beneath the Bonneville Salt Flats, extend beneath Pilot Creek Valley north to the Raft River Mountains, and extend beneath the playa west of and parallel to the Newfoundland Mountains. Southern Pacific No. 1 Lemay Well, in sec. 29, T. 7 N., R. 14 W., at Lemay siding and north of the graben structure near the Newfoundland Mountains drilled through 93 m (305 ft) of brown limestone at a depth of 422 m (1,385 ft) that Heylmun (1965) assigned to an upper Miocene-lower Pliocene sequence. Paleozoic rocks were reached at a depth of 643 m (2,108 ft). The possibility that the

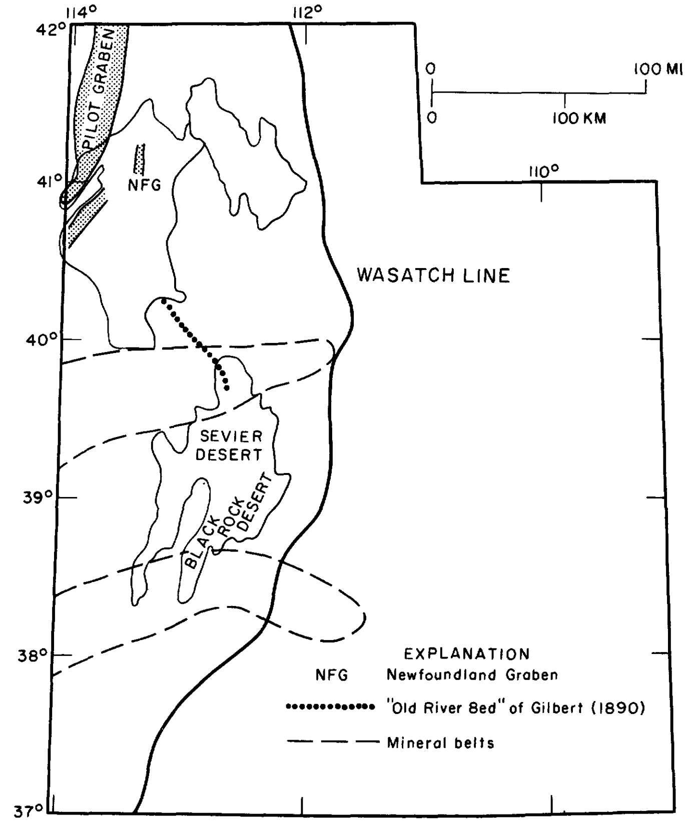

FIGURE 40.—Location of the Sevier Desert, Black Rock Desert, and the gravity-defined grabens in the northern Great Salt Lake Desert.

upper Tertiary section formed on a shoreline or in an ancestral Lake Bonneville that occupied these graben structures is speculative because the subsurface data currently available is meager. The existence, however, of such a lake or lakes appears to be very possible. These graben structures, like the Sevier Desert, appear to be good drilling prospects for lithium.

Summary

The enrichment of lithium by evaporation during the formation of nonmarine brines in Utah probably began with upper Tertiary lakes and playas, continued with Pleistocene Lake Bonneville and is continuing in the Great Salt Lake Desert and Great Salt Lake. The existence of the older lakes and playas is based on late Tertiary geologic history of flora and sedimentation, on the interpretation of near-surface geochemical data, on the interpretation of gravity profiles, on salt balance studies, and on data from a dozen oil wells drilled several years ago. Drilling of oil wells in the near future in the Great Salt Lake will add much more information on which to base the existence, and possibly the locations, of these pre-Lake Bonneville lakes. Lithium-enriched brine and clay may be encountered by drilling in the Sevier Desert, Bonneville Salt Flats, Pilot Creek Valley, and the gravity-defined graben west of the Newfoundland Mountains formed as a result of the evaporation process in late Tertiary and early Pleistocene time.

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ORIGIN OF LITHIUM AND OTHER COMPONENTS IN THE SEARLES LAKE EVAPORITES, CALIFORNIA

By George I. Smith,
U.S. Geological Survey, Menlo Park, CA

ABSTRACT

The lithium and many of the other valuable components in the salt layers of Searles Lake came from thermal springs in the Long Valley area. However, about two-thirds of the sodium, chlorine, and bromine were apparently derived from atmospherically transported sea salts

and by solution of older salt deposits. About one-quarter of the boron may have been derived from thermal springs in the Coso Range, and about 15 percent of the sulfate may have come from solution of gypsum in older lake beds. The components were transported by the Owens River and its pluvial-stage downstream extension via Owens and China Lakes to Searles Lake. Most of the potassium, sulfate, and boron that entered the Owens River reached the salt layers in Searles Lake, but about 95 percent of the lithium was removed prior to crystallization of the salts, and 50 to more than 99 percent of certain other components are not accounted for.

The time required to account for the valuable salts in Searles Lake that came from springs in Long Valley is only about 10 percent of the time that the thermal springs are likely to have been active. Either one or more large deposits remains undiscovered (unlikely), or the springs have had their present chemical characteristics for only the last 30,000 to 40,000 years.

INTRODUCTION

Searles Lake lies near the middle of Searles Valley in the southwest corner of the Great Basin, an area where the surface drainage of all basins flows toward a central lake or playa rather than to the sea. At present, Searles Valley and most of the other valleys within the Great Basin contain playa (dry) lakes or salt flats in their centers; a few valleys contain permanent lakes but most of them are near the east and west edges of the province where they receive drainage from the bordering high mountain ranges.

During the pluvial periods of the Pleistocene, however, most valleys in the Great Basin contained large bodies of water as a result of increased precipitation and runoff and decreased evaporation. Several of these lakes were interconnected to form chains; the evaporation that occurred in each lake caused progressive increases in the downstream concentrations of dissolved solids. Searles Lake was a lake in one of these chains. It was the third (and sometimes fourth) in a chain that included as many as six lakes during the most intensely pluvial periods of the Pleistocene (fig. 41). Owens River, which drains the east side of the southern Sierra Nevada, was the source of most of the water that flowed into this chain of lakes; although, during some periods, Mono Lake and tributaries to that basin added their waters to those of Owens River. Owens River flowed into Owens Lake, spilled out of that lake into China Lake, then into Searles Lake; during the peaks of most pluvial episodes, Searles Lake overflowed into Panamint Lake, and, at times, that lake overflowed into Death Valley. This sequence is shown diagrammatically in cross section in figure 42.

The number of lakes in the chain and the depth of water in the last lake were a function of the amount of runoff versus the cumulative evaporation from their combined surfaces. Using probable evaporation rates and measured lake areas, calculations show that when Searles Lake received water from upstream sources, Owens River had to flow at a rate approximately four times more than that of the present. For Searles Lake to overflow, Owens River and other sources had to contribute about seven times more than the present river flow. Water overflowing from Mono Lake was included in these volumes part of the time, but present runoff patterns suggest that less than 20 percent of the total flow

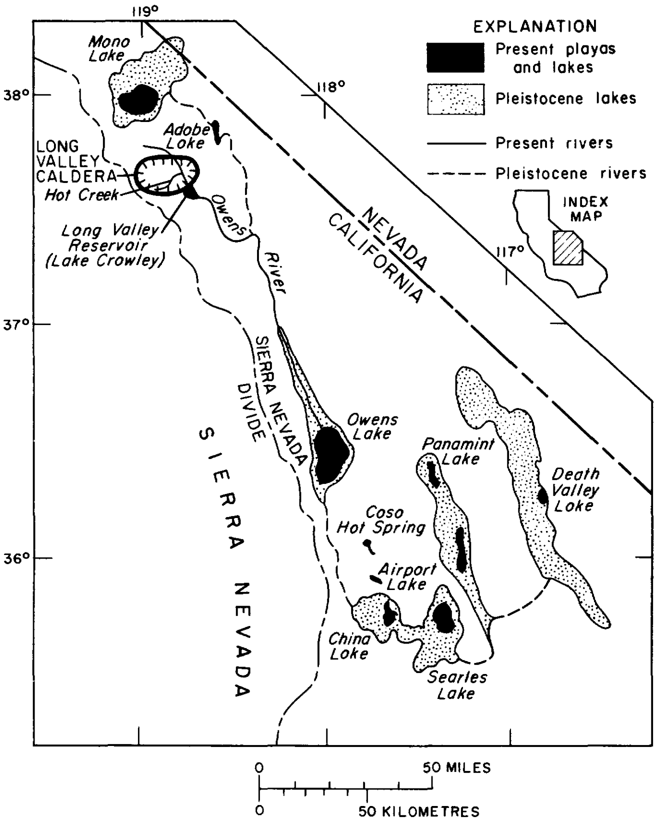

FIGURE 41.—Index map showing relations between present lakes and rivers, and between those features during pluvial maxima of the Pleistocene. Locations of the Long Valley caldera (from Bailey and others, 1976), Long Valley Reservoir (Lake Crowley), Coso Hot Springs, and Airport Lake also shown.

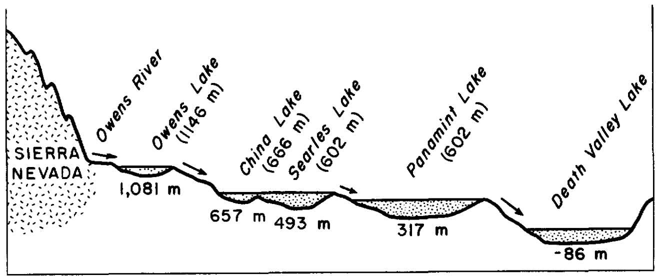

FIGURE 42.—Diagram showing relation between Pleistocene lakes in the chain that includes Searles Lake; Mono Lake is omitted. Elevations of the present valley floors (and spillways) are shown in parentheses. From Gale (1914).

was added by that basin. When the pluvial periods of the Pleistocene ended, major concentrations of salts that were trapped in the basins crystallized as layers on the valley floor. Drilling has shown that no layers of salts accumulated in the upper several hundred metres of Owens Lake and China Lake, that only halite and gypsum accumulated in Panamint Lake, and that major quantities of rare elements and salts accumulated only in Searles Lake (Smith and Pratt, 1957).

Searles Lake now is a nearly dry salt flat with a surface area of approximately 100 km^2. Two distinct salt bodies lie within 50 m of the surface; these are informally named the Upper Salt and the Lower Salt. The volume of the Upper Salt body is approximately 1 km^3 and the volume of the Lower Salt is about half that amount. Two chemical plants are operated by the Kerr-McGee Chemical Corp. on the west side of Searles Lake, one at Westend and one at Trona. One or both of them extract sodium carbonate and sulfate, potassium chloride and sulfate, lithium carbonate, sodium borate, phosphoric acid, and bromine from the interstitial brines pumped from the Upper Salt and Lower Salt. The brine which is pumped from the interstitial fluids in the Upper Salt body contains approximately 80 ppm Li, and this is processed by the plant at Trona. Brine from the peripheral parts of the body contain 10–70 ppm Li. Lithium is precipitated from the brine as Li_2NaPO_4 and converted to Li_2CO_3. The value of all components produced annually by the two plants is in excess of $30 million. Total production from the deposit since 1926 exceeds $1 billion.

GEOLOGIC HISTORY OF SEARLES LAKE

The sequence of muds and salts now found beneath the surface of Searles Lake is shown in figure 43. The mud layers are mostly composed of calcium, magnesium, and sodium carbonate minerals, but clastic and organic components are also present. The salt layers, which represent the economically valuable part of the deposit, are composed of a large number of minerals, which are given in table 38. No minerals in the salt layers contain lithium, and all production of lithium (as well as of bromine and phosphate) comes from components that are present only in dissolved form.

The history of the fluctuations of Searles Lake during the last 150,000 years is shown in figure 44. Most of the time is represented by mud layers, and only small parts of the total time are represented by salts. The climatic history represented by this curve is representative of other parts of the Great Basin, and most of the hundred or more closed basins of this area can be considered to have had enlarged lakes for about 100,000 of the last 150,000 years. During the intervening dry periods, saline layers were deposited in some basins.

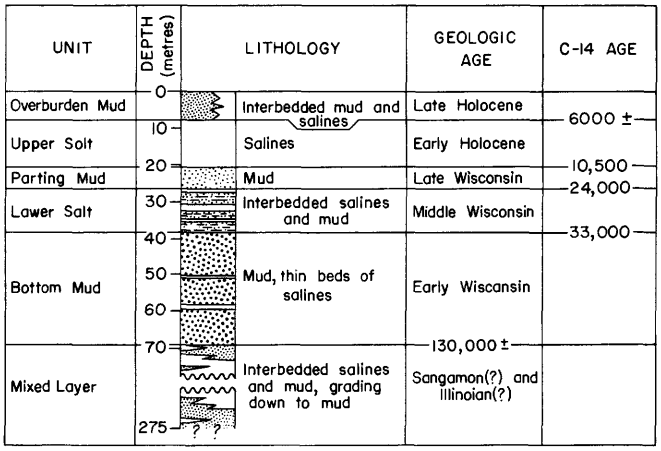

FIGURE 43.—Generalized subsurface stratigraphy of upper Quaternary units in Searles Lake. Patterns represent marl ("mud") layers; clear areas represent salts. The names of the units are informal terms used locally; the indicated geologic ages are based on correlations with glacial deposits in the central parts of North America.

TABLE 38.—*List of minerals found in the saline layers of Searles Lake and of their compositions*

Aphthitalite	$K_3Na(SO_4)_2$
Borax	$Na_2B_4O_7 \cdot 10H_2O$
Burkeite	$2Na_2SO_4 \cdot Na_2CO_3$
Halite	$NaCl$
Hanksite	$9Na_2SO_4 \cdot 2Na_2CO_3 \cdot KCl$
Mirabilite	$Na_2SO_4 \cdot 10H_2O$
Nahcolite	$NaHCO_3$
Northupite	$Na_2CO_3 \cdot MgCO_3 \cdot NaCl$
Sulfohalite	$2Na_2SO_4 \cdot NaCl \cdot NaF$
Teepleite	$Na_2B_2O_4 \cdot 2NaCl \cdot 4H_2O$
Thenardite	Na_2SO_4
Tincalconite	$Na_2B_4O_7 \cdot 5H_2O$
Trona	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$
Tychite	$2Na_2CO_3 \cdot 2MgCO_3 \cdot Na_2SO_4$

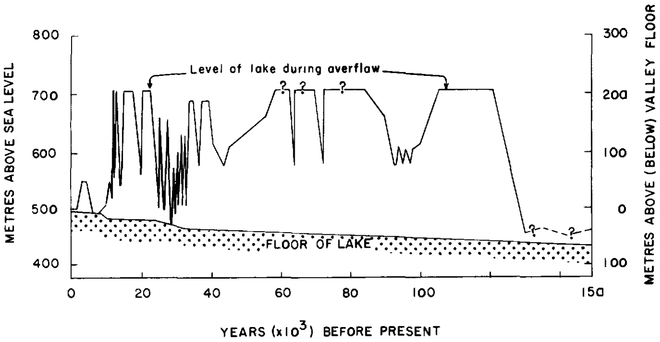

FIGURE 44.—Diagram showing the fluctuations in Searles Lake during the last 150,000 years.

Since the original deposition of the salts and brines in Searles Lake, dilution by surface water has reduced the concentration of the original brine. The total volume of brine has apparently remained the same, so some of the original components that were concentrated in the brine—like lithium—were lost. The displaced brine presumably migrated toward Panamint and Death

Valleys—both of which have floors at lower elevations—but this has not been confirmed. Evidence of dilution is found in three forms: (1) Large crystal cavities are numerous in certain horizons of the salt layers, and such features are rarely (if ever) formed during natural crystallization of salt layers; cavities of these sizes virtually require the removal of some original components (Smith and Haines, 1964, fig. 8). (2) The phase chemistry applicable to these saline bodies shows that the present brine compositions are those produced by partial solution of existing solids and not those produced as bitterns at the close of normal crystallization (G. I. Smith, unpub. data, 1976). (3) Data from the deuterium-hydrogen ratios in the salts and brines show that about half of the water in the present brines has been derived from local rainwater and runoff (G. I. Smith, Sadao Matsuo, and Irving Friedman, unpub. data, 1976). The hydrogen-deuterium ratio in the parent brine is represented by the ratio of these isotopes in the primary mineral borax (Matsuo and others, 1972), but the present brines in Searles Lake have values that are intermediate between the values indicated by borax (approximately 0 permil relative to SMOW, Standard Mean Ocean Water) and the values found in present-day rains and runoff in the valley, which average about −80 permil SMOW. The replacement of original brine with local surface waters has resulted in a proportional loss and lower concentrations of components found only in the original brines, but components found in both minerals and brines (potassium, borates, chlorides, carbonates, sulfates, etc.) have concentrations that are only slightly lower, because the lost quantities were mostly replaced by partial solution of the crystal body.

SOURCES OF COMPONENTS IN THE BRINES

The components in the salts and brines of the Searles Lake deposit were apparently derived from at least three sources: the atmosphere, rocks, and thermal springs. Much or most of the carbonate probably came from atmospheric CO_2 which was dissolved in the river and lake waters. About 20 percent of the sodium chloride and other seawater components were probably carried into the Owens Valley by air masses moved inland from the sea (Holser, 1970, table 3). Some of the sodium, potassium, and magnesium, and the balance of the carbonate were derived from the solution of those components in rocks that crop out within the drainage area of the extended chain of lakes; and evidence described later shows that halite and gypsum were also dissolved and contributed Cl and SO_4 to the total. The substances that make Searles Lake a valuable resource and virtually unique, however, were mostly derived from hot springs that lie at the head of the Owens River drainage. Lithium was among these components.

Figure 41 shows the location of the Long Valley caldera, which is now an area containing geysers, thermal springs, and saline marshes. Analyses of the waters issuing from these areas are cited by the California Department of Water Resources (1967), Mariner and Willey (1976), Eccles (1976), and from an unpublished administrative report by L. V. Wilcox (1946) that is based on work done cooperatively by the U.S. Salinity Laboratory (U.S. Department of Agriculture) and the Los Angeles Department of Water and Power. This report is published here with the written permission of both agencies. The first line of evidence that this source contributed many of the uncommon elements now found in Searles Lake is provided by the abundance of these elements in such waters. Table 39 lists the concentration of selected ions, and table 40 lists the concentrations and monthly tonnages of chloride and boron contained in the measured discharge above and below a major thermal spring in the area, as well as in the Owens River. Table 39 also lists the ratios between certain elements that will be related to the dissolved components in the Owens River and Searles Lake. These data make it clear that the quantities of the unusual components are large enough, given geologic units of time, for major deposits to form.

A second line of evidence that the thermal springs in the Long Valley area contributed most of the uncom-

TABLE 39.—*Concentrations of selected components in waters from Long Valley area and ratios of selected ions*

[All values in mg/l; leaders (----) indicate no data]

Station (listed in order of downstream position)	Concentrations								Ratios					
	Na	K	SO_4	Cl	F	B	As	Li	Na/K	Cl/B	Cl/SO_4	K/B	B/Li	F/Li
Casa Diablo hot spring[1]	390	45	130	280	12	15	2.2	2.8	8.7	18.7	2.2	3.0	5.4	4.3
Mammoth Creek, below Casa Diablo; average of three analyses[2]	6.6	1.3	6.8	.5	.1	.05	.01	----	5.1	10.0	.07	26	----	----
Hot Creek, in gorge at hot springs[1]	400	24	100	225	9.6	10.5	----	2.3	16.7	21.4	2.2	2.3	4.6	4.2
Little Hot Creek[1]	410	30	96	200	8.4	10.6	.74	2.8	13.7	18.9	2.1	2.8	3.8	3.0
Hot Creek, below most springs; average of six analyses[2]	83	7.0	26	43	1.8	2.0	.20	----	11.9	21.5	1.6	3.5	----	----
Owens River, Benton Crossing[2]	24	2.8	11	11	.6	.47	.05	----	8.6	23.4	1.0	6.0	----	----
Lake Crowley, outlet[3]	34	4	13	18	.6	.66	.03	.13	8.5	27.3	1.4	6.1	5.1	4.6

[1] Mariner and Willey, 1976, table 1.

[2] Eccles, 1976, table 9.

[3] California Department of Water Resources, 1967, appendices E and F; Li values obtained by spectrographic analysis, average of six analyses, 1957–64.

TABLE 40.—*Monthly boron and chlorine contents of Hot Creek and Owens River*

[Data from Wilcox, 1946, tables 1 and 8. Data expressed as parts per million (ppm) and tonnes per month (t/mo)]

Date	[1]Station 2					[2]Station 4					Owens River at Aqueduct Intake[3] (t/mo)
	Discharge (t/mo×10^6)	Boron		Chlorine		Discharge (t/mo×10^6)	Boron		Chlorine		
		ppm	t/mo	ppm	t/mo		ppm	t/mo	ppm	t/mo	
1933:											
August	2.41	0.37	0.89	0.33	0.80	3.15	2.34	7.37	1.52	4.79	17.54
September	1.98	.42	.83	.32	.63	2.65	2.57	6.81	1.72	4.56	9.82
October	1.75	.39	.68	.38	.67	2.51	2.86	7.18	1.81	4.54	5.17
November	1.58	.40	.63	.29	.46	2.37	2.98	7.06	1.90	4.50	36.34
December	1.54	.39	.60	.33	.51	2.42	2.88	6.97	1.81	4.38	27.12
1934:											
March	2.13	.34	.72	.29	.62	3.03	2.47	7.48	1.67	5.06	25.05
April	1.96	.34	.66	.33	.65	2.83	2.53	7.16	1.77	5.01	34.86
May	2.35	.49	1.2	.28	.66	3.17	2.35	7.45	1.46	4.63	24.87
June	2.37	.39	.92	.29	.69	2.85	2.31	6.58	1.55	4.42	25.92
September	1.24	.43	.53	.29	.36	2.06	3.38	6.96	2.11	4.35	11.11
Mean ($\bar{x}$)	1.93	.40	.77	.31	.60	2.70	2.66	7.10	1.73	4.62	21.78
Standard deviation (s)	.39	.04	.20	.03	.13	.37	.34	.29	.19	.25	10.54
$s/\bar{x}$	.20	.10	.26	.10	.21	.14	.13	.04	.11	.05	.48

[1]Hot Creek, in canyon, approximately 200 m upstream from thermal springs (lat 37°39.8′N., long 117°49.5′W.).
[2]Hot Creek, about 200 m downstream from thermal springs.
[3]At Aberdeen (lat 36°58.5′N., long 118°12.6′ W), about 60 km north-northwest of Owens Lake; waters include all sources of boron in northern Owens Valley.

mon elements comes from the apparent balance between the tonnages of certain elements contributed by the springs of this area to the Owens River each year, and the tonnages of those components now found in the Upper Salt of Searles Lake, which represents a known number of years. Discrepancies arise in the balance between several other elements, but they are in expected directions.

The balance between the source and the salt body requires two assumptions. One is that the present Owens River carries approximately the same tonnages of these components each year as it did during pluvial periods of the Pleistocene, even though the volumes of water increased greatly during those periods; data supporting this proposal are given in a later section. The second assumption is that virtually all the dissolved solids carried by the Owens River during the last 50,000 years are now found as salts in either Owens or Searles Lake. Dissolved solids carried during that period must be in one or more of the downstream basins, yet China Lake contains no salt layers and Owens Lake contains salts only in the 1–3-m surface layer formed during this century. Searles Lake overflowed into Panamint Valley part of this time (fig. 44); and the dissolved solids that reached Searles Lake must have been in waters that overflowed into Panamint Valley. However, no known sodium borate or sodium carbonate minerals are found in that valley, and the brines apparently do not contain abnormal amounts of potassium, bromine, lithium, or tungsten (Smith and Pratt, 1957). The lack of uncommon elements in Panamint Valley suggests that the quantities of salts lost during those periods of overflow were small. It appears, therefore, that Searles Lake contains the vast bulk of the materials that were contributed by the Owens River during this time. A period extending from 24,000 years ago to the present is chosen because that represents the period during which the Parting Mud, Upper Salt, and Overburden Mud (fig. 43) accumulated; the salts and brines of the Upper Salt contain most of the uncommon elements.

Analyses of the present Owens River water are listed in table 41. The data in the first column summarize, over a 17-year period (1929–45), a large number of analyses for boron and chlorine and a smaller number of analyses for other components. These analyses were accompanied by discharge data, thus allowing calculation of absolute quantities of those substances over the same period of time. The first 11 years of that period also predate the completion of the Long Valley Dam and the Mono Basin Tunnel; those structures make interpretations of seasonal variations in more recent chemical data more difficult. The data in the second column mostly represent one sample of water collected from the inlet to Haiwee Reservoir, but the values for

TABLE 41.—*Dissolved solids in waters of the Owens River or its equivalent*

[Values in mg/l; leaders (----) indicate no data]

Component	Owens River at aqueduct intake, range includes years from 1928 to 1946[1]	Los Angeles aqueduct at Haiwee Reservoir[2]	Los Angeles aqueduct average for 1975[3]
Na	23–100	26	29
K	7–13	3.4	2.9
Ca	21–42	----	23
Mg	5–33	----	5.1
CO_3	----	10	105
HCO_3	----	130	
SO_4	15–72	17	23
Cl	11–93	14	12
B	.3–2.4	----	.33
F	.5–1.0	2	.53
Li	----	.11, .08	----
PO_4	----	.4	.11
As	----	----	.02
Br	----	----	.02
I	----	----	.04
W	----	----	.07
pH	7.6–8.4	8.4	8.18
Total dissolved solids	187–691	221	181

[1]Wilcox, 1946, table 1; sample point is at Aberdeen, about 45 km southeast of Bishop.
[2]Friedman, Smith, and Hardcastle (1976). All components except Li and PO_4 found in water sampled in June 1965 at point where aqueduct enters Reservoir, about 135 km south of Bishop; Li and PO_4 determined from water collected at point where California Highway 136 crosses the Owens River.
[3]Los Angeles Department of Water and Power, Sanitary Engineering Division records; sample point where aqueduct empties into Van Norman Reservoir, San Fernando, Calif.

lithium and phosphate are for two water samples collected in 1969 at the point where the Owens River entered Owens Lake during a year when Owens River runoff exceeded the capacity of the aqueduct. Two values for lithium are listed—0.11 and 0.08 mg/l suggesting an average of approximately 0.1 mg/l at the time those samples were collected. The data in the third column represent the average composition of the water in the Owens Valley aqueduct, during 1975, as it flowed into Van Norman reservoir in Los Angeles. Waters carried by the Los Angeles aqueduct are presumed to be the compositional equivalent of the Owens River.

Table 42 gives a sample calculation of the amounts of seven components, whose concentrations and abundances are known for Owens River, Owens Lake, and Searles Lake. The amounts of potassium, sulfate, and boron in the two salt lakes are quite close to the amounts calculated to have been carried by Owens River in 24,000 years. The amounts of sodium and chlorine in the two lakes are too large, and the amounts of carbonate and lithium are too small. Similar calculations can be made for bromine, phosphate, arsenic, iodine, tungsten, and fluorine by assuming that the quantities of those elements now trapped in Owens Lake form a minor part of the total. With the exception of fluorine, these elements are found in Searles Lake only in the brine phase, which makes calculations of their abundance more reliable.

The balance between the quantities of these components carried by the Ownes River over a period of 24,000 years and the amounts now present in the Upper Salt of Searles Lake is plotted in figure 45. The values from table 42 are used for those seven components; the values for other components in the Owens River are calculated from table 41, and in Searles Lake, from data cited by Smith (1973, tables 14 and 15). The amounts of components now found in the Lower Salt of Searles Lake (fig. 43), compared to the amounts that would be contributed by 8,000 years of flow by the present Owens River, are also plotted; these are discussed later. Points that lie on the diagonal line represent perfect agreement between the predicted and observed amounts. Points above the line represent a greater amount of that component in Searles Lake than predicted, and points below the line represent a deficiency or loss. The two points for chlorine represent the two values derived for the Owens River in table 42; the four points for boron rep-

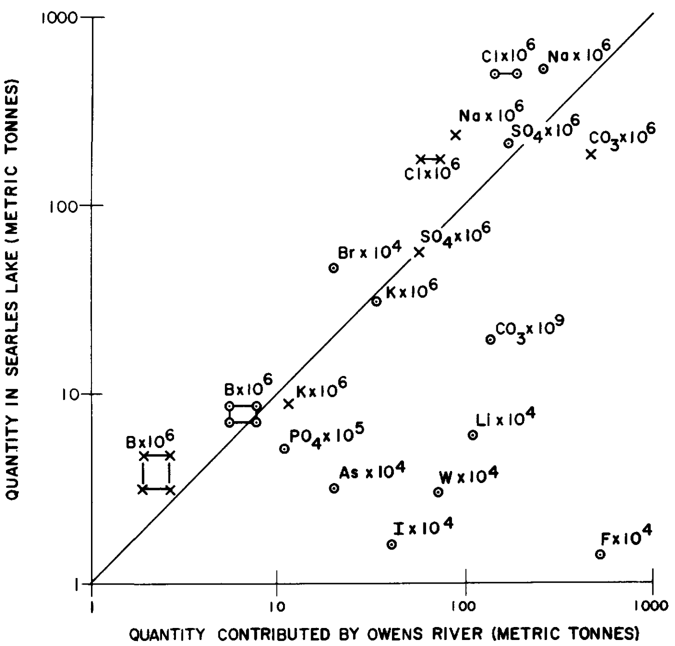

FIGURE 45.—Diagram showing the relations between tonnages of selected components carried by the present Owens River in 24,000 years versus tonnages in the Upper Salt of Searles Lake (circles), and the tonnages carried by the river in 8,000 years versus tonnages in the Lower Salt (X). Plotted on three-cycle log scale; quantities expressed as tonnes multiplied by indicated exponent. Diagonal line indicates 1:1 relation. Multiple points connected by lines represent independent determination.

TABLE 42.—*Comparison of amount of selected components carried by Owens River in 24,000 years with amount now in Owens Lake and Upper Salt of Searles Lake*

[Quantities expressed as parts per million (ppm) and tonnes (t)]

Component	Present concentration in Owens River[1] (ppm)	Amount carried annually[2] by Owens River (× 10^3 t)	Amount carried by Owens River in 24,000 years (× 10^6 t)	Amount now in Upper Salt, Searles Lake (× 10^6 t)[3]	Amount in Owens Lake in 1912 (× 10^6 t)[4]	Total amount now found in Searles and Owens Lakes (× 10^6 t)
Na	26	10.9	262	462	54	516
K	3.4	1.4	34	28	3	31
Total CO_3	137	57.5	1,380	163	30	193
SO_4	17	7.1	170	192	15	207
Cl	14	5.9	142	448	38	486
	----	[6]7.8	187	----	----	----
B	[6].77	.32	7.7	7.9	.8	8.7
	----	[6].23	5.5	[7]6.4	----	7.2
Li	.11	.046	1.1	[5].06	[1].005	.06+

[1] Friedman, Smith, and Hardcastle (1976) except value for B.

[2] Average annual flow of river, 4.2×10^{14} g/yr (calculated for period before irrigation in Owens Valley, using data of Gale, 1914, p. 254–261).

[3] Values from Smith (1973, table 15), except as indicated.

[4] Recalculated from Gale (1914, p. 259); he incorrectly calculated quantities in this report, but he corrected them in later reports.

[5] Calculation assumes average values of 60 ppm Li in brine and 20 ppm in salts.

[6] Data from Wilcox (1946); value for concentration, from his table 12, is mean for the years 1929–45 at the inlet to the aqueduct near Aberdeen. Values of amounts of Cl and B carried annually compiled by methods described in footnote 3, this chapter.

[7] D. V. Haines, unpub. data, 1956.

resent the two values for that substance in the river and two independently determined values for the lake (Smith, 1973, p. 112), plotted in the four possible combinations. The spread among them probably indicates about the level of uncertainty in the data.

As shown in figure 45, the predicted and observed quantities of boron, sulfate, and potassium in the Upper Salt are close to the diagonal line that indicates equality. The quantity of potassium in Searles and Owens Lakes is about 90 percent of that predicted. This close balance results in part from compensating errors, because some potassium must have been added downstream, where additional drainage from bedrock sources joined the system, and some potassium is normally lost from natural solutions owing to adsorption by clay. The quantity of boron now found in the two lakes may be a few percent less or 60 percent more than predicted, depending on which combination of the estimates listed in table 42 is used; the "best" values (5.5 versus 7.2×10^6 tonnes) suggest that the lake contains about 30 percent more boron than predicted. An even greater discrepancy may exist because additional quantities of boron are contained in ulexite that occurs in small quantities in lake sediments exposed around the edges of Searles Valley, and boron also may be adsorbed by clays. Some increase in the amount of boron flowing from the Long Valley area may have occurred during pluvial periods, and some boron was probably contributed to China Lake and downstream basins by the Quaternary volcanic rocks in the Coso Range (fig. 41) and the Coso Hot Springs,[1] which lie along the north side of China Lake. The observed quantity of sulfate in the Upper Salt of Searles Lake is about 20 percent greater than predicted, suggesting that greater quantities of sulfate were contributed during pluvial periods by drainage from upper Cenozoic lake beds in Owens Valley and from the gypsiferous sediments and fault gouge zones of the Slate Range that forms the east edge of Searles Valley.

In the upper salt, only about 15 percent of the predicted amount of carbonate and 5 percent of the lithium are accounted for. Large quantities of carbonate are known to have been precipitated in Owens and China Lakes as calcite in calcareous silt and clay (Smith and Pratt, 1957), and the large quantities of calcite, aragonite, dolomite, gaylussite, and pirssonite in the mud layers in Searles Lake account for major additional quantities. Some of the carbonate lost during transit was probably restored as the lakes and streams dissolved atmospheric CO_2, but because of the slowness of this process and the rising pH of the lake waters, the original quantities were never fully replaced. The amount of lithium now found in Searles Lake indicates even more loss. The calculations assumed the following: (1) an average of 30 ppm Li in the salts of the Upper Salt (the average of 54 unpublished analyses of water-soluble lithium in cores GS–1, GS–4, and GS–10, obtained and described by the Geological Survey (Haines, 1959)); (2) an average of 60 ppm Li in the brine (intermediate between the richest (80 ppm) brines, from the center of the deposit, and the brines present around the edge (10–40 ppm)); (3) a brine:salt ratio of 40:60; (4) salt and brine densities of 2.1 and 1.3; and (5) the volume of the Upper Salt to be 1.05×10^9 m^3. Reasonable variations in these assumptions are possible, but none alter the fact that much of the lithium in the Owens River disappeared before the salts in Searles Lake were crystallized.

The amounts of sodium and chlorine now in Searles Lake are two to three times greater than the present Owens River seems likely to have supplied. The excess of sodium in the Upper Salt is somewhat less, because major quantities reacted after burial to form gaylussite and pirssonite in the interbedded mud layers. The excess of chlorine was noted by Holser (1970). It tends to confirm his suggestion, based on both the absolute amounts of chlorine and the Cl/Br ratios in the Upper Salt of Searles Lake, that Searles received chlorine and bromine from erosion of older lake beds as well as from springs and atmospheric sources. The erosion of older lake beds also accounts for excess sodium. Lake beds are included in the Waucoba (of Hopper, 1947) and Coso (of Schultz, 1937) Formations, of late Cenozoic age. These areas drain into Owens Valley, and although little surface runoff from these areas occurs under present climatic conditions, substantially greater amounts probably occurred during pluvial maxima. According to the data plotted in figure 45, the Cl/Br ratio of the Owens River is 710 (or 935), and the ratio in the Upper Salt of Searles Lake is 975; Holser (1970), using slightly different data and assumptions, estimated these ratios as 520 (his table 4) and 860 (his table 2). All estimates of Cl/Br ratios for the Owens River and Searles Lake lie between that of sea water (about 200) and that of primary marine evaporites (greater than 1,000). As noted by Holser (p. 308–9, table 4), neither thermal springs nor atmospheric salts normally contribute these elements in this ratio, and contributions from recycled salts (ultimately of marine origin) seem required.

The other components plotted in figure 45, like lithium, suggest loss during transport between the Owens River and Searles Lake. Losses range from one-

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[1] During pluvial periods, the Coso Hot Springs (lat 36°2.8'N., long 117°46.2'W.) probably flowed with the waters draining south via Coso Wash to Airport (dry) Lake. Those waters probably contained large amounts of boron (Austin and others, 1971, table 6). Airport Lake is now separated from China Lake by a gravel divide about 15 m above the lake surface, but shorelines showed that it overflowed during pluvial periods into China Lake (Duffield and Bacon, 1976). That uncommon amounts of boron reached Airport Lake is shown by observations made in 1955 by R. E. von Huene and D. V. Haines of the sediments exposed in a trench in the lake floor (lat 35°54.4'N., long 117°43.7'W.). They noted concentrations of ulexite in three layers that had thicknesses ranging from 0.1 to 0.7 m and were at depths of approximately 1, 2, and 4 m. Four analyses (by H. Kramer) of bulk samples from the ulexite-rich horizons averaged 0.5 percent B and 75 ppm Li.

half order to two orders of magnitude. The postdepositional dilution and loss of brine from Searles basin might account for the observed deficiency of phosphate, but it is inadequate to account for deficiencies of the others. Nothing is known about the concentrations of phosphate, arsenic, iodine, tungsten, and fluorine in the clastic sediments of Owens, China, or Searles Lakes, but those deposits seem most likely to contain the missing elements if they were adsorbed by clays or fixed by biological processes during transport.

The losses of fluorine are most notable. The quantity plotted in figure 45 for the Owens River is calculated from the lower value (0.5 ppm) listed in table 41, and use of the larger value would have further increased the apparent loss. Table 43 lists several analyses for fluorine and other selected components in waters from the Owens River and Hot Creek (Wilcox, 1946). It also lists the ratio of the chemical activity product (AP) to the equilibrium constant (K_T) for the mineral fluorite in solutions having the indicated compositions and estimated temperatures. These data were provided by E. A. Jenne, who used the computer program described by Nordstrom and Jenne (1976).

An AP/KT ratio of 1 indicates fluorite saturation under equilibrium conditions. Although the ratios of waters at the Aqueduct Intake are only 3–5 percent of saturation, evaporative concentration of 20–30 times (assuming no other changes) would theoretically precipitate fluorite. Owens River water (ca. 200 ppm), concentrated by a factor of 30 times, would have a salinity of about 0.6 percent, more than an order of magnitude below levels that produce salts. If the lost fluorine was precipitated as fluorite during transport, it would be upstream from any highly saline lakes. Therefore, large quantities of disseminated fluorite may be present in the upper 50 to 100 m of muds beneath the surfaces of Owens and China Lakes.

Figure 45 also shows the balance between the quantities of major components in the Lower Salt of Searles Lake (Smith, 1973, table 11) and the amounts contributed by the present Owens River over a period of 8,000 years. That period was chosen because it produced the best balance between the boron, potassium, and sulfate, which were apparently transported during the final 24,000 years with the least gain or loss.

The pattern of Lower Salt components is strikingly similar to the pattern determined for the Upper Salt.[2] Potassium and sulfate are again very close to the diagonal line, indicative of equality; boron is a little above it; sodium and chloride are substantially above it, with the excess of chloride being greater than that of sodium; and carbonate is substantially below it (although less so than for the Upper Salt). The detailed similarity of this Lower Salt pattern to that of the Upper Salt adds substantial weight to the likelihood that the source of the dissolved solids was the same for both units, the Owens River.

A major problem, however, is that the quantity of time required to introduce the components in these two salt units—about 32,000 years—is substantially less than

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[2] A very similar pattern also emerges when the amounts of components carried by the Owens River in 2,000 years are plotted against the amounts now found in Owens Lake (table 42, columns 3 and 6). The amounts of sulfate and potassium are almost on the diagonal line, boron is slightly above it, sodium and chlorine are substantially above it (suggesting that outcropping halite beds were being dissolved), and carbonate is well below it. Inasmuch as no deeper beds of salts exist in the upper part of Owens Lake, the exposed salts in Owens Lake appear to be the residue of about 2,000 years of evaporative concentration, and the salts contributed prior to that time were apparently carried downstream. Gale (1914, p. 264) and Antevs (1936, 1938) calculated the quantities of sodium and chlorine in Owens Lake and, from those data, concluded that the time since the last overflow (for saline deposition) was nearer 4,000 years. The evidence in the present paper indicates that sulfate and potassium are more reliable components for this purpose and suggests that the age of 2,000 years is more nearly correct.

TABLE 43.—*Analyses for calcium, fluorine, and other elements in waters from Owens River and Hot Creek, and the ratio of the chemical activity product (AP) of Ca^{++} and F^- in these waters to the equilibrium constant for fluorite (K_T)*

[Analytical data from Wilcox, 1946, tables 1 and 8, values in parts per million; AP/K_T ratios computed by E. A. Jenne using procedures described by Nordstrom and Jenne (1976). Leaders(----) indicate no data]

Station	Year	Date	Sampling discharge (g/d × 10^{10})	pH	Chemical analyses (ppm)								C° (est.± 10°)	AP/KT (fluorite, CaF_2) (1 = saturation under equilibrium conditions)
					Ca	Mg	Na	K	SO_4	Cl	B	F		
Owens River[1]	1935	10/29	80.4	7.9	21.2	6.2	47.59	----	18.73	25.53	0.80	0.6	20	0.035
	1945	10/4	7.1	7.9	33.3	28.1	79.08	11.34	29.30	58.50	1.48	.6	20	.045
			----	----	----	----	----	----	----	----	----	----	25	.038
Station 2 Hot Creek[2]	1933	10/3	5.6	7.7	12.2	7.9	34.48	4.30	12.97	13.48	.39	.4	10	.01
	1933	11/6	5.3	7.7	14.0	10.7	25.75	11.73	15.85	10.28	.40	.5	8	.025
	1934	3/16	6.9	8.1	13.4	9.7	29.43	----	19.69	10.28	.34	.2	7	.004
	1934	4/9	6.5	7.9	13.0	7.1	27.82	6.65	11.05	11.70	.34	.2	7	.004
	1934	5/7	7.6	7.8	13.6	8.5	16.55	----	9.61	9.93	.49	.4	9	.016
	1934	9/17	4.1	7.7	11.6	7.7	32.41	----	9.61	10.28	.43	.2	15	.0027
		----	----	----	----	----	----	----	----	----	----	----	20	.0023
Station 4 Hot Creek[3]	1933	10/3	88.1	6.7	13.2	7.3	125.06	12.12	27.38	64.18	2.86	2.6	10	.52
	1933	11/6	7.9	6.9	16.2	7.7	118.16	12.12	33.14	67.38	2.98	3.0	8	.90
	1934	3/16	9.8	7.2	14.2	9.7	100.92	----	40.83	59.22	2.47	2.2	7	.44
			----	----	----	----	----	----	----	----	----	----	17	.31
	1934	5/7	10.0	6.9	18.2	8.9	93.10	----	15.85	51.77	2.35	2.4	7	.71
	1934	9/17	6.9	7.4	12.2	5.3	132.41	----	35.06	74.82	3.38	3.2	9	.75
		----	----	----	----	----	----	----	----	----	----	----	19	.54

[1] At aqueduct intake.

[2] Station 2 is upstream from the major thermal springs in canyon, but downstream from Casa Diablo hot spring and other thermal areas.

[3] Station 4 is downstream from major thermal springs.

the age of the volcanic rocks involved in the Long Valley caldera. Minimum reasonable estimates of the time at which the associated thermal springs are likely to have been initiated are in excess of 100,000 years, and the best estimates are nearer 300,000 (Bailey and others, 1976). The 32,000 years of spring discharge that can be accounted for by the deposits in Searles Lake leaves about eight times that amount unaccounted for. It seems unlikely that existing subsurface data could have overlooked one or more deposits of this size, although obviously it is not impossible. Alternative explanations that would provide for a smaller mineral discharge from the caldera area during its first 270,000 years of cooling and much more intense discharge thereafter seem worth exploring.

The third line of evidence indicating that streams discharging from the Long Valley area carried most of the valuable components now found in Searles Lake comes from the similarity in the ratios of spring-derived elements in various parts of the Owens River (table 44). Changes occur, but they are mostly small or occur for reasons that can be demonstrated or are plausible. Between Hot Creek and Lake Crowley, as a result of mixing with waters from the upper Owens River and Mono Basin, the Na/K and Cl/SO_4 ratios are reduced by almost half because of the low ratios (5.9 and 0.33) in those waters (Eccles, 1976). The K/B ratio increases because of mixing with waters having ratios near 8. The Cl/B ratio increases for reasons that are unclear because the added water has a ratio near 17; possibly some Cl is added by drainage from other tributaries. Ratios for B/Li and F/Li increase slightly, possibly because some Li is adsorbed by the muds of Lake Crowley.

Between Lake Crowley and Haiwee Reservoir (10 km south of Owens Lake), the Na/K ratio stays nearly the same while the Cl/SO_4 ratio decreases, possibly because gypsum is being dissolved from the upper Cenozoic lake deposits that lie east of this segment of the river. The constant Na/K ratio, combined with small increases in the Cl/B and K/B ratios, suggests that proportional amounts of Na, Cl, and K are added without proportional amounts of B. This, combined with the fact that the F/Li ratio stays about the same while the B/Li ratio decreases, suggests the enroute addition of small amounts of Li and F from springs.

TABLE 44.—*Comparison of ratios of selected ions in waters from Long Valley area, Owens River, and Searles Lake*

Ratio	Hot Creek gorge[1]	Lake Crowley[1]	Owens River and/(or) L.A. aqueduct[2]	Searles Lake Upper Salt[3]
Na/K	16.7	8.5	7.6. 10.0	16.5
Cl/SO_4	2.2	1.4	.8, .5	2.3
Cl/B	21.4	27.3	36.4	56.7
K/B	2.3	6.1	8.8	3.5
B/Li	4.6	5.1	3.0	132
F/Li	4.2	4.6	4.8	.24

[1] Data from table 39.
[2] Data from table 41, columns 2 and 3; both ratios listed where possible.
[3] Data from table 42, and Smith (1973, and unpub. data, 1976).

Data plotted in figure 45 suggests that most of the boron, sulfate, and potassium in the lower Owens River reached Searles Lake. Changes in the ratios that include these elements are explained using this assumption. Increases between the Owens River and Searles Lake in the Na/K, Cl/SO_4, and Cl/B ratios thus suggest that additional sources of NaCl were draining into the river during pluvial periods; this explanation is consistent with the surplus of Na, Cl, and Br indicated by figure 45 and discussed previously. The decrease in the K/B ratio is consistent with the earlier conclusion that a little K was lost and that some B was added, but that the changes in relative total amounts were not large.

The notably large increase in the B/Li ratio indicates a major loss of Li. The change in ratios suggests that about 98 percent of the amount introduced into the first lake of the once-connected chain was lost during transit. (The data in table 42 and fig. 45 suggest that 95 percent was lost.) The decrease in the F/Li shows that even more F than Li was lost and that only about 0.1 percent of the F originally contributed by the Owens River reached Searles Lake. (Fig. 45 suggests that about 0.3 percent of the F reached the salt lake.)

PRESENT RELATION BETWEEN RUNOFF AND BORON AND CHLORINE CONTENTS

The conclusions of this paper depend in part on the likelihood that the annual tonnages of components derived from thermal springs remained nearly constant during times when flow in the Owens River exceeded that of the present by as much as an order of magnitude (Smith, 1976). The evidence of this constancy comes from the low to negative correlation between discharge of both the Owens River and Hot Creek and from the relative long-term constancy in the tonnages of boron and chlorine contained by them.

Table 45 lists the annual discharge of the Owens River and the tonnages of boron and chlorine dissolved in it during the period 1929–45. During the 17 years of sampling (about 350 samples), the daily discharge varied by a factor of about 32; the concentration of boron in water samples varied by a factor of 7, and the estimated boron tonnage per day varied by a factor of almost 40. The tonnages of boron and chlorine carried during a full year, however, varied much less. During the 17-year period, the quantity of boron[3] varied from 150 t/yr to

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[3] These values for annual quantities were derived by plotting each of the samples listed by Wilcox (1946, table 1) at the appropriate point on the horizontal axis of 365-day graph paper, with the vertical axis representing the tons per day on that day. The points were then connected with straight lines, and the area beneath the curve was integrated mechanically using a planimeter. The total area was then converted to total tonnes per year.

TABLE 45—*Annual discharge and tonnages of boron and chlorine in Owens River, 1929–45*

[Data from Wilcox, 1946, tables 1 and 12; sample point at aqueduct intake near Aberdeen; quantities in metric tonnes (t) and parts per million (ppm)]

Year	Discharge (t/yr × 10^8)	Average concentration of boron (ppm)	Total boron (t/yr)	Total chlorine (t/yr)
1929	1.78	0.77	146	4,870
1930	2.78	.57	166	6,040
1931	2.68	.62	178	5,990
1932	2.77	.98	264	8,330
1933	2.94	1.12	274	9,470
1934	2.45	.93	261	8,000
1935	3.02	.76	236	7,360
1936	2.61	.78	227	8,890
1937	3.21	.84	327	11,700
1938	3.82	.72	279	9,510
1939	3.26	.72	232	7,320
1940	2.71	.76	208	[1]6,670
1941	2.83	.78	212	[2]6,950
1942	3.80	.63	268	8,030
1943	3.43	.63	244	9,140
1944	3.18	.78	202	6,810
1945	3.24	.67	206	7,970
Mean (*x*)	2.97	.77	231	7,830
Standard deviation(*s*)	.50	.14	46	1,630
s/x	.17	.18	.20	.21

[1] Waters from Mono Basin added to Owens River after April 1940.

[2] Long Valley Dam completed April 1941; Long Valley Reservoir (Lake Crowley) averages seasonal variations in later years.

330 t/yr, averaged 230 t/yr, and had a standard deviation of 40 t/yr, or about 20 percent of the average. This compares favorably with data compiled by Goudey (1936) who estimated an annual average of 228 tonnes of boron for the years 1928–36 at the San Fernando Powerhouse (at the south end of the aqueduct) and an average boron concentration of 0.71 ppm. During the same period, the annual quantity of chlorine in the river varied from 4,900 t/yr to 11,700 t/yr, averaged 7,800 t/yr, and had a standard deviation of 1,600 t/yr, again about 20 percent of the average.

Variations in the tonnages of boron and chlorine from year to year (table 45) were as much as 50 percent of the average, but their pattern of variations is similar (correlation coefficient=0.92). The relations between the annual quantities of boron and chlorine in a given year and total annual discharge for that year, though, are not especially close. Correlation coefficients for boron and chlorine versus discharge are both near 0.55. After 1941, all the water from the Long Valley area was stored temporarily in the Long Valley Reservoir (Lake Crowley), and most of the seasonal inequalities in dissolved solids were removed. (The Mono Basin Tunnel, put in service in April 1940, does not appear to have introduced significant amounts of additional boron and chlorine; the average amounts of boron and chlorine during the years 1940–45 are 223 and 7,595 metric tons, somewhat less than the 1929–39 averages of 235 and 7,930 tons.) The remaining annual variation of 15 percent (between 1942 and 1945) suggests that some boron was still being added erratically from sources downstream from the reservoir.

The data in table 40 (which shows the monthly amounts of boron and chlorine in Hot Creek) suggest that the amount of boron added by the largest set of thermal springs in the Long Valley caldera area is almost uninfluenced by seasonal variation in runoff, although the chlorine may be slightly affected. Sets of samples taken along Hot Creek (table 40) show that waters issuing from spings that flow into the creek, between Station 2 and Station 4 (of Wilcox, 1946), contribute about 30 percent of the water and most of the boron and chlorine in the creek. Variations in the total discharge of the creek change the element concentrations but do not greatly change the tonnages being carried by it. Table 40 lists the average boron and chlorine concentration for 10 months (spread over a 12-month period) in waters from above and below the thermal springs, and the estimated tonnages carried each month by the creek past each station. It also lists the tonnages of boron carried by the Owens River where it enters the Los Angeles Aqueduct Intake 90 km to the south. About 33 percent of the boron that entered the aqueduct came from Hot Creek, and about 89 percent of that portion came from the interval between Stations 2 and 4 which includes the termal springs.

The standard deviations in the monthly runoff and tonnages of boron and chlorine in waters from above the springs (Station 2) are 20, 26, and 21 percent of the mean values, and the correlation coefficients between these tonnages and discharge are 0.83 and 0.90. This means that the relatively minor sources upstream from this point that contribute these elements are responsive to runoff. (Tonnages in the Owens River vary monthly by larger amounts, and the standard deviation is nearly half the mean value, suggesting that many of the other sources that contribute boron are also seasonal and (or) responsive to discharge.) Variations in the monthly tonnages in the waters at Station 4, just below the springs—even including the variations that affected the upstream waters at Station 2—are less than 5 percent during the sampled year, and correlation coefficients between total discharge and tonnages of boron and chlorine passing Station 2 are subtracted from the amounts passing Station 4 are near 0.50. However, when the tonnages of boron and chloride passing Station 2 are subtracted from the amounts passing Station 4 (which represents the combined thermal-spring discharge and the flow passing Station 2), the remaining quantities represent the amounts coming from the springs themselves. When these quantities are plotted against stream discharge at Station 4, boron has a correlation coefficient of -0.42 and chlorine a coefficient of 0.26. The negative coefficient for boron is probably a result of the fact that the amounts of boron passing Station 2 were proportional to discharge, and when this was subtracted from the relatively constant amounts ($\bar{x}$=6.5 t/mo, s=0.38) issuing from the thermal springs, a negative correlation results. The very low coefficient for chlorine was partly due to the same effect, but the large difference between the numbers for boron and chlorine suggests that although there is no correlation between discharge and the tonnage of boron from the main thermal springs, there may be some correlation between discharge and tonnage of chlorine.

The primary source of almost all the boron in the Owens River is presumably from thermal springs similar to those immediately upstream from Station 4, and this relation suggests that seasonal variations in the tonnages of primary boron are minimal. On this basis and on the basis of relatively small variations in annual amounts, it seems reasonable to suggest that increases in boron output of these thermal springs during pluvial periods were small. Lithium and the other components contributed by these springs are assumed to have also been introduced to the tributary streams at nearly consistent rates.

CONCLUSIONS

The data presented here suggest that most of the lithium and other unusual components in the Upper Salt and Lower Salt of Searles Lake came from thermal springs in the Long Valley area, but that more than 95 percent of that lithium was lost before reaching Searles Valley. If losses of lithium had been reduced to 80 percent, the concentration of lithium in Searles Lake brines would be about 300 ppm—approximately the concentration in the brines in Clayton Valley, Nev., which are exploited solely for lithium. In prospecting for lithium brines that can become resources, therefore, finding an adequate source of lithium in spring waters clearly is only the first step. Important but unanswered questions remain as to what geologic environments are most likely to transport a relatively large percentage of that lithium from the point where it reaches the surface to an area where it can be concentrated.

Most of the boron, sulfate, and potassium in the Owens River reached Searles Valley, but high percentages of most other components were lost enroute. About one-third of the sodium, chlorine, and bromine came from springs in the Long Valley area, but about two-thirds of these substances were derived from sea salts carried by the atmosphere and by erosion of Cenozoic lake deposits in downstream areas.

Economic deposits of lithium-rich clays or brines might exist in Owens and China Lakes, where the missing lithium is most likely to have been trapped; but it seems more likely that the clays in Owens and China Lakes adsorbed the lithium so now the lithium is in a form that is not economic. The amount of fluorine that is contributed by the Owens River annually (140 t/yr) and the large amount that was lost suggest strongly that it precipitated as fluorite in the same basins, possibly in significant concentrations.

A problem arises in reconciling the small amount of time apparently needed to accumulate the valuable salts now found in Searles Valley—about 32,000 years—to the time the thermal springs in Long Valley are likely to have been active. Either large deposits of salts remain undiscovered or only the later stages of spring activity contributed unusual elements to the Owens River.

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USE OF LITHIUM AND CHLORIDE CONCENTRATIONS IN GROUND WATER FOR LITHIUM EXPLORATION

By Cole L. Smith, U.S. Geological Survey, Denver, CO

ABSTRACT

The use of spring-water composition in geochemical exploration for lithium-rich brines was investigated. In arid regions, the ratio of metal ion to chloride ion versus chloride ion yields least-squares straight lines having characteristic slopes. The concentration of chloride ion in spring waters is used as a general indicator of the extent of evaporative concentration of the spring waters. The slopes of the straight lines are related to the solubility of secondary minerals that have formed in the vadose zone. The kinetics of dissolution of these secondary minerals control the amount of a particular ion that reaches the ground-water table. In the case of lithium, hot springs were chosen as the water type whose chemical composition would be the most useful in exploring for subsurface brines. Their deep circulation allows some mixing with fossil ground water and (or) brines. Deviations from the characteristic slopes of the graphs indicate that chemical processes other than those occurring in the vadose zone have influenced the chemical composition of the spring waters. Lithium-rich brines, such as the Salton Sea geothermal system, Clayton Valley, Nev., and Great Salt Lake, have associated hot springs with anomalous compositions.

INTRODUCTION

Since lithium-rich brines were first produced in 1938 at Searles Lake, Calif., lithium from brines has contributed an increasingly larger percentage of the total lithium production of the United States. At the present time, about one-third of the total production is from brine deposits (J. D. Vine, oral commun., 1975). Brine areas from which lithium is currently being produced or could potentially be produced are located in arid regions of the Western United States. Brines currently in production are located at Searles Lake, Calif., and Clayton Valley, Nev. Brines that potentially could produce lithium are located at Great Salt Lake, Utah, and in the Imperial Valley geothermal system in California.

DISCUSSION

This study was conducted to evaluate a near-surface geochemical-exploration technique as a means of locating lithium-rich brines. There is an obvious advantage to using samples that can be collected at or near the surface as opposed to samples that must be collected using more expensive exploration techniques, such as drilling. Because hot springs contain water that has been deeply circulated and consequently has had the opportunity to mix with fossil waters including brines, they were chosen as the sampling media. Also, the chemistry of hot springs has proven useful in estimating reservoir temperature in geothermal exploration, and relatively large amounts of data have been published on their compositions. The hot-springs data used in this paper have been previously published by Mariner, Rapp, Willey, and Presser (1974a), White (1968), Sanders and Miles (1974), Kunasz (1970), and Willey, O'Neil, and Rapp (1974). The data used in this report were restricted largely to hot springs in the arid regions of California, Oregon, Nevada, and Arizona; limited data from Utah were also included.

Lithium data are presented in the graphical form of the logarithm of the lithium- to chloride-concentration ratio times 100 versus the logarithm of the chloride concentration (fig. 46). Chloride ion was chosen as an indicator of the extent of evaporative concentration of the ground water for five reasons: (1) Usually the major source of chloride in ground water is atmospheric precipitaiton. (2) When ground water is evaporatively concentrated, chloride is one of the last ions to precipitate and to form a secondary solid phase. It is also one of the first ions to go back into solution on subsequent wetting of the precipitated phase. (3) Because the chloride ion possesses a single negative charge, it is unlikely to be the ion exchanged in the sediments. (4) Chloride ion usually makes up a large percentage of the total dissolved solids of ground water. (5) It is a relatively easy and inexpensive ion to analyze. By dividing the concentration of the

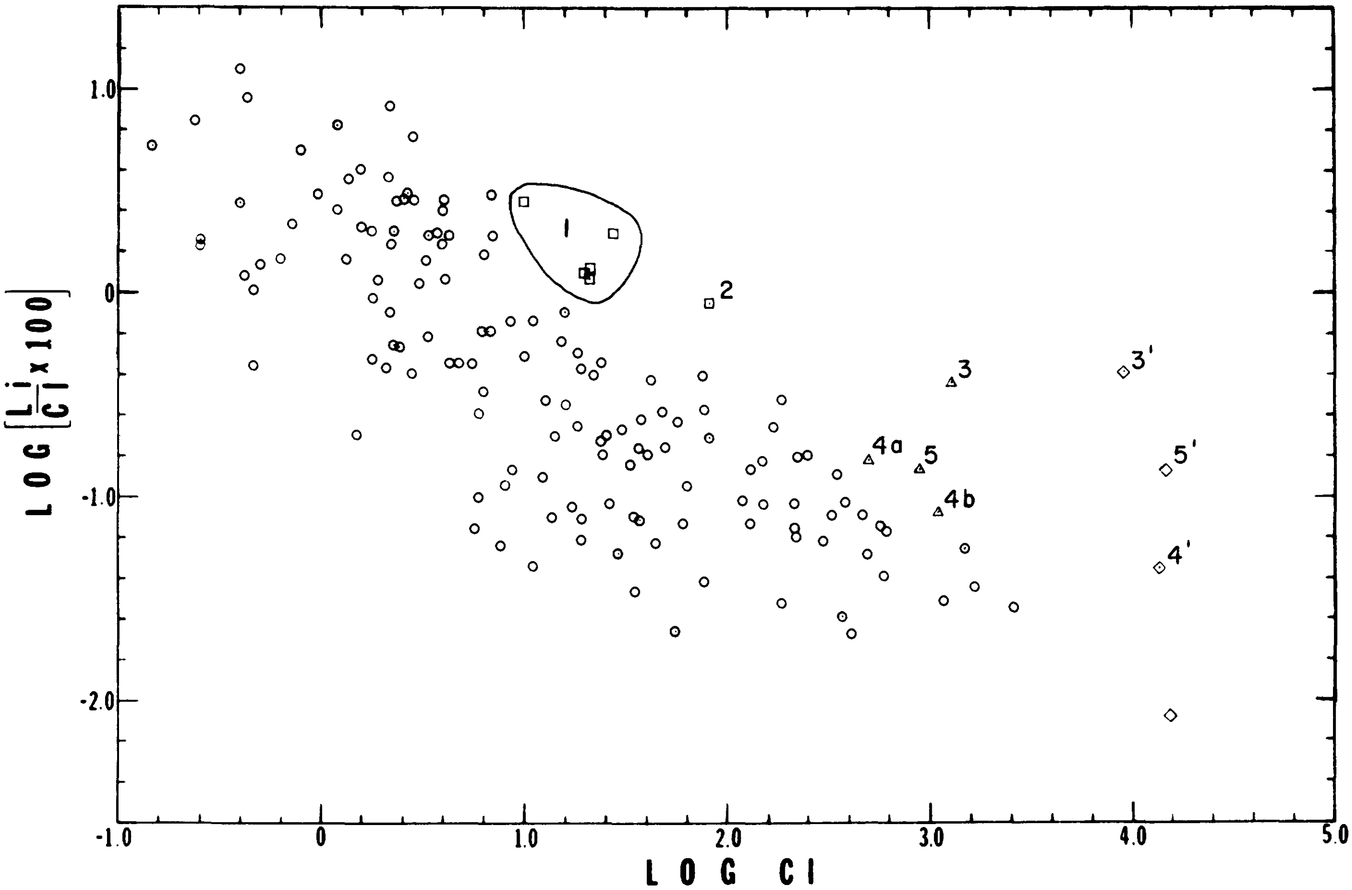

FIGURE 46.—Variation diagram showing the lithium: chloride ratio versus chloride in brines and in waters from hot springs. Squares represent some of the dilute hot springs having high lithium-to-chloride ratios that are not associated with known high-lithium brines. Triangles represent hot springs associated with economic or potentially economic lithium-rich brines. Diamonds represent economic or potentially economic lithium-rich brines. Data points in area 1 are located near Mono Lake, Calif.; 2, Steamboat Springs, Nev.; 3, Clayton Valley, Nev., hot spring; 3', Clayton Valley, Nev. brine; 4a, Ogden hot spring; 4b, Utah hot spring near the Great Salt Lake; 4', Great Salt Lake brine; 5, Sportsman Mud hot spring in Imperial Valley, Calif.; 5', Imperial Valley geothermal brine.

metal ion by the chloride ion and plotting this value against the chloride concentration, the behavior of the metal ion on evaporative concentration of the gound water can be demonstrated. If the metal ion, relative to chloride, is not removed from or added to solution upon evaporative concentration of the ground water, the ratio remains the same and the slope of a straight line fitted through the data points is zero. If the concentration of the metal ion remains relatively constant while the concentration of chloride increases, then the slope of a straight line through the data points is a minus one. This situation might occur if (1) dissolution of salt beds adds chloride without adding the other ion or (2) the concentration of the other ion is controlled by forming a solid phase below the ground-water table. For example, at pH's less than about 9.2, silica concentration has an upper limit of 120 ppm independent of evaporative concentration of the water because amorphous silica forms when the concentration exceeds this value. Another process that would cause a slope of a minus one is the formation of secondary minerals in the vadose zone. When the metal ion forms a relatively insoluble secondary phase in the vadose zone, sufficient rainfall can cause chloride to be carried to the ground-water table while the metal ion remains in the vadose zone. In the case of lithium, some but not all of this ion is immobilized relative to chloride, and a straight line fitted to the logarithm of the data produces a slope between zero and minus one. Logarithms are used because the chloride concentration of spring waters will vary from about 1 ppm to over 100,000 ppm; and the slope of the data—not the correlation between lithium and chloride—is the important quantity. This type of display allows the identification of anomalous concentrations of lithium because background values can be characterized. Even though hot springs are deeply circulated waters, near-surface processes can have a strong influence on the chemistry of these waters. Most hot springs are heated, local meteoric waters of surface origin (Craig and others, 1956; Craig, 1963). In the arid Western United States, evaporation often plays a dominant role in controlling both ground-water and hot-spring chemistry.

The known lithium-rich brines, with the exception of the brine present at Searles Lake, are characterized by associated hot springs having high chloride concentrations and relatively high lithium-to-chloride ratios. The hot spring associated with the Clayton Valley brine is clearly the most anomalous of the group. Utah and Ogden hot springs, which are near the Great Salt Lake, are possibly mixed with a subsurface lithium-rich brine. The association of the Sportsman Mud hot spring with the Imperial Valley geothermal brine has been postulated by White (1968). Additional dilute hot springs have anomalous ratios but are associated with no known brines containing lithium of economic importance. These include hot springs at Steamboat Springs, in Nevada, and near Mono Lake, Calif.

CONCLUSIONS

Most of the known lithium-rich brine deposits have associated hot springs whose lithium-to-chloride ratio is above background. Characteristically, these springs have chloride concentrations over 400 ppm. The ratio of lithium to chloride is of less importance than the behavior of the ratio upon evaporative concentration of the ground water.

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THE INFLUENCE OF DRAINAGE BASIN AREA UPON THE DISTRIBUTION OF LITHIUM IN PLAYA SEDIMENTS

By Joseph R. Davis, U.S. Geological Survey, Denver, CO

ABSTRACT

Sediment samples were collected from 41 playas in the Basin and Range province of the United States and were analyzed for lithium. The influence of drainage basin size upon the distribution of lithium was examined statistically in order to explain a portion of the variance observed in the lithium values. The present-day drainage basin area shows no correlation with lithium concentration, but modifying the drainage basin area to simulate Pleistocene overflow of pluvial lakes or hydrologic underflow produces significant correlation between drainage area and lithium. The linear relationship assumed in this correlation explains about 20 percent of the total variance in the lithium distribution observed in the suite of playa samples.

INTRODUCTION

Brines associated with nonmarine evaporite sequences in desert basins currently constitute the only nonpegmatite resource of lithium in the United States. Very little is known about the behavior of lithium in the sedimentary cycle or about the relationship between the lithium content of the desert basins sediments and the occurrence of economically exploitable lithium-containing brines. Whereas playas represent the topographic low points of desert basins, they therefore should receive the ions weathered from the bedrock and transported by surface and ground waters. Therefore, though other factors are certainly involved, it is conceivable that a relationship exists between the area of the drainage basin and the amount of lithium transported to the playa. The primary objective of this report is to examine the relationship between areal factors and the distribution of lithium in playa sediments.

METHODS

A geochemical reconnaissance of over forty structural basins in the western part of the Basin and Range province was conducted by Robert Bohannon, Cole Smith, James Vine and the author in 1973–75 in order to study the distribution of lithium in the surficial sediments of these basins. Sediment samples were taken from hand dug pits and auger holes which penetrated the playa surface to maximum depths of about two metres. An effort was made to sample the central part of the playas, but access was often limted to the edge of the playa. Samples which contained visible and sand size material or large quantities of evaporite minerals were not included in the sample suite which is summarized in table 46. All analyses were determined by atomic adsorption.

DISTRIBUTION OF LITHIUM IN PLAYA SEDIMENTS

The distributions of most trace-elements are thought to approximate the lognormal distribution (Till, 1974, p. 43). Analytical values are therefore often transformed to logarithms in order to normalize the distribution and to improve the efficiency of the estimates of population parameters such as the mean (μ) and standard deviation (σ). Although the frequency distribution of the 156 lithium analyses summarized in table 46 is skewed to the right and displays a large amount of variation, the hypothesis that the natural logarithms of the analyses are normally distributed is rejected when the chi-square (χ^2) test is employed ($\chi^{2\,(0.05,11)}=19.76$). In this case lithium is considered to display a pseudolognormal distribution. Although Link and Koch (1975) have discussed some of the consequences of making the lognormal transformation on pseudolognormal populations, the analytical values were transformed into natural logarithms in order to facilitate graphic display of the data and to present some of the statistical tests discussed. The reader should be cognizant of the possible bias introduced by this transformation.

TABLE 46.—*Lithium distribution in selected basins of internal drainage*

Area	County and state	Number of samples	Li, mean (ppm)	Li, range (ppm)
Abert and Summer Lakes	Lake Co., Ore	3	60	29–80
Alkali Spring	Esmeralda Co., Nev	2	64	63–64
Alvord Lake	Harney Co., Ore	1	12	------
Amargosa River	Nye Co., Nev	3	267	230–310
Big Smoky, North Valley	do	4	139	130–155
Big Smoky, South Valley	Esmeralda Co., Nev	8	100	42–160
Buffalo Valley	Lander Co., Nev	3	92	37–170
Christmas and Silver Lakes	Lake Co., Ore	1	33	------
Clayton Valley	Esmeralda Co., Nev	5	147	73–220
Columbus Salt Marsh	do	2	150	100–200
Death Valley	Inyo Co., Calif	7	207	87–500
Diamond Valley	Eureka Co., Nev	4	56	46–69
Dixie Valley	Churchill Co., Nev	3	62	35–87
Edwards Creek Valley	Lander Co., Nev	5	58	50–85
Eureka Valley	Inyo Co., Calif	5	162	68–280
Fish Lake Valley	Esmeralda Co., Nev	7	213	63–460
Gabbs Valley	Mineral Co., Nev	3	36	28–40
Goshute Lake	Elko Co., Nev	4	25	15–62
Granite Springs Valley	Pershing Co., Nev	3	102	75–150
Grass Valley	Eureka Co., Nev	5	208	150–270
Harney Lake	Harney Co., Ore	4	43	36–50
Jakes Valley	White Pine Co., Nev	1	60	------
Kumiva Valley	Pershing Co., Nev	3	56	52–59
Lahontan Valley	Churchill Co., Nev	15	107	44–200
Lake Valley	White Pine Co., Nev	1	16	------
Long Valley	Mono Co., Calif	4	250	40–460
Monitor Valley	Nye Co., Nev	3	60	40–75
Newark Lake	White Pine Co., Nev	6	70	61–85
Owens Lake (dry)	Inyo Co., Calif	4	48	34–66
Panamint Valley	do	1	190	------
Railroad Valley	Nye Co., Nev	3	88	63–120
Ralston Valley	do	6	60	25–76
Rhodes Salt Marsh	Mineral Co., Nev	1	31	------
Ruby Valley	Elko Co., Nev	4	64	55–80
Saline Valley	Inyo Co., Calif	3	33	32–36
Smith Creek Valley	Lander Co., Nev	4	61	49–85
Soda Spring Valley	Mineral Co., Nev	4	32	29–37
Spring Valley	White Pine Co., Nev	7	37	10–57
Steptoe Valley	do	1	43	------
Stonewall Flat	Nye Co., Nev	2	65	64–65
Tikaboo Valley	Clark Co., Nev	3	40	38–42

Figure 47 illustrates the frequency distribution of the 156 playa samples, and figure 48 is a similar diagram of the 41 playa mean values. The range in lithium values for the 156 playa samples is 10–460 ppm; the arithmetic mean is 99 ppm; and the mean of the natural logarithms is 74 ppm (table 47). These estimates of the population mean as well as estimates of the standard deviation are frequently used in geochemical exploration to define anomalous values; there is 97.7 percent probability that a random sample from a normally distributed population will be less than $\mu+2\sigma$. Table 48 lists several estimates of this value.

Caution should be exercised in using this type of geochemical reconnaissance as an exploration tool. In addition to the bias introduced by the departure from a normal distribution, a large degree of variation was probably introduced by the lack of control over the location of the sample site and the mineralogical composition of the individual samples. Furthermore, there is as yet no clear understanding of the relationship between the lithium content in playa sediments and the concentration of lithium in subsurface brines. However, the facility with which sediment samples can be collected from playa surfaces relative to the difficulty of sampling

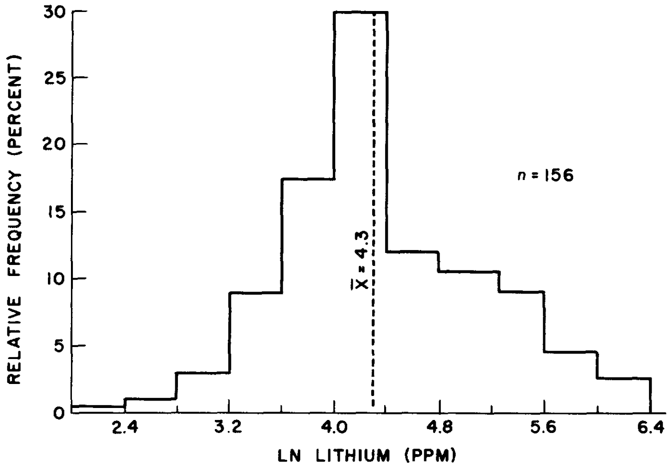

FIGURE 47.—Frequency histogram of the lithium concentration of 156 playa samples.

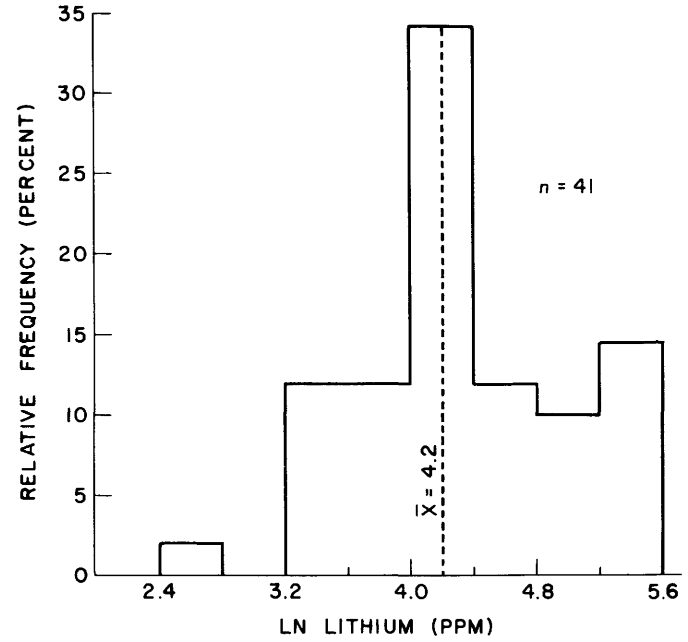

FIGURE 48.—Frequency histogram of the mean values of the lithium samples.

TABLE 47.—*Population statistics of lithium analyses*

Sample population	$\bar{X}$, arithmetic mean (ppm)	s, arithmetic standard deviation (ppm)	$\bar{X}_{ln}$, mean of natural logarithms	S_{ln}, standard deviation of natural logarithms
156 playa samples	99	86	4.31 (74 ppm)	0.75
41 playa means	90	76	4.24 (69 ppm)	.73

TABLE 48.—*Statistical estimates of a lithium anomaly*

Sample population	$\bar{X}+2s$	$\bar{X}_{ln}+2S_{ln}$
156 playa samples	271 ppm	5.81 (334 ppm)
41 playa mean values	242 ppm	5.70 (299 ppm)

interstitial brines somewhat compensates for the disadvantages of the method.

AREAL FACTORS INFLUENCING THE DISTRIBUTION OF LITHIUM

The suite of sediment samples collected in the reconnaissance was examined statistically in order to better understand the distribution of lithium in closed basin sediments. If the size of the drainage basin is an important factor in determining the amount of lithium introduced into the playa by weathering of the bedrock, there may be some relationship between drainage basin area and the lithium concentration in the playa sediments and interstitial waters. To assess this relationship, the natural logarithm of the area of each basin was plotted against the natural logarithm of the mean lithium value for that playa (fig. 49), and Pearson's product-moment coefficient of linear correlation was calculated. The value $r=-0.1788$ indicates no significant correlation at the 95 percent confidence level (Till, 1974, p. 83–87).

The lack of a significant correlation in the relationship between lithium and drainage area does not necessarily preclude the importance of areal factors in the distribution of lithium. Many of the playa basins studied had different drainage areas during Pleistocene pluvial periods; some basins had pluvial lakes which spilled into adjacent basins. The expanded drainage area of basins which received pluvial overflow could be a significant factor in the accumulation of the unusual concentrations of soluble salts found in some of these basins. When the drainage basin areas were modified to allow for pluvial spillover (Snyder and others, 1964) and plotted against the mean lithium values (fig. 50), the correlation coefficient, $r=0.3493$, indicates significant correlation at the 95 percent confidence level; however $r^2=0.12$ indicates that only 12 percent of the total variance observed in the lithium distribution is explained by the

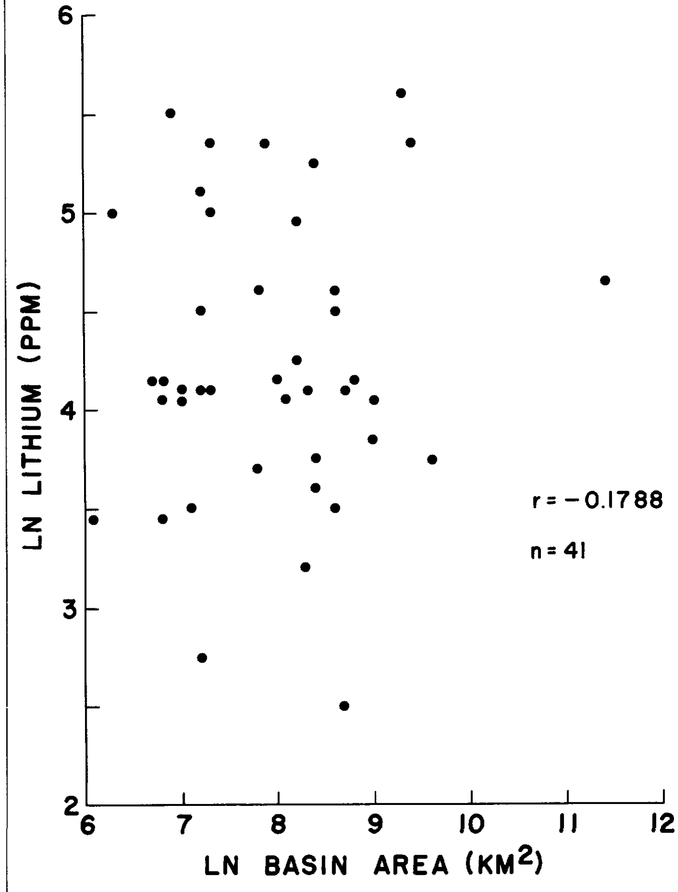

FIGURE 49.—Plot of lithium values versus drainage basin area.

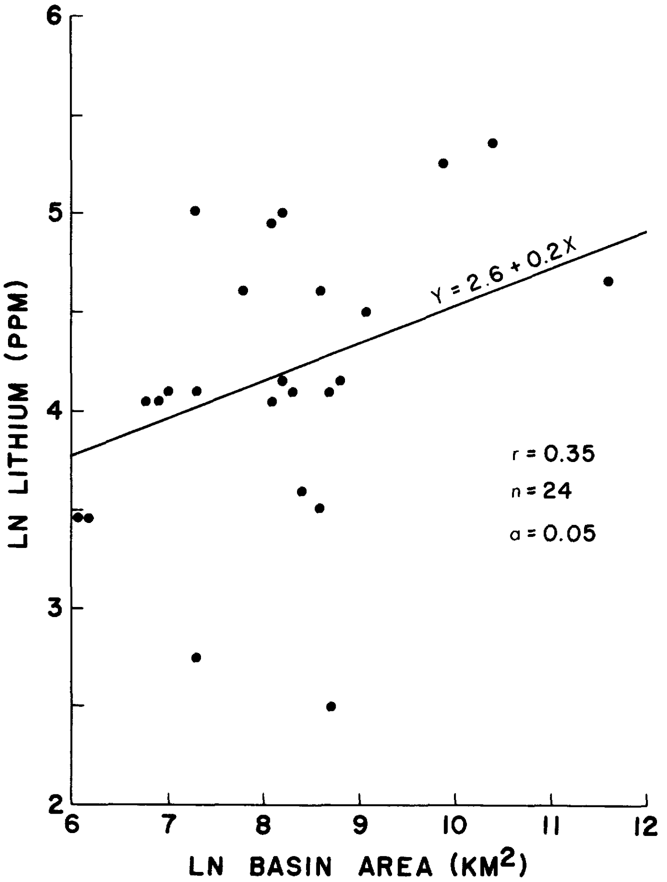

FIGURE 50.—Lithium versus drainage basin area. Area simulates pluvial spillover.

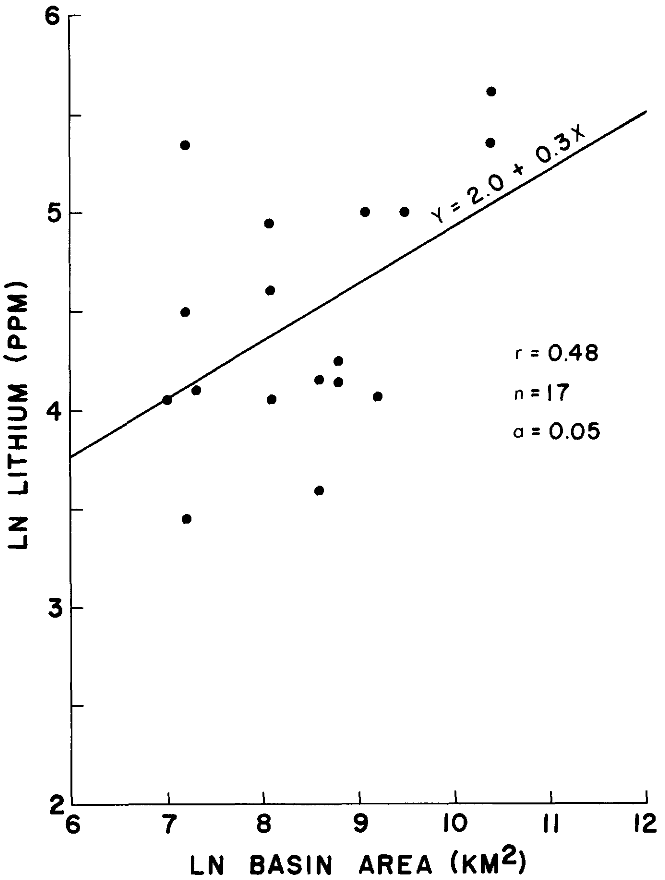

FIGURE 51.—Lithium versus drainage basin area. Area simulates hydrologic underflow.

linear relationship between lithium concentration and area.

In expanding the concept of areal influence on lithium distribution, groundwater movement can also be considered. Some data are available which indicate probable hydrologic underflow in many of the basins studied in this reconnaissance (Hunt and others, 1966; Walker and Eakin, 1963; Rush and others, 1971). When the drainage basin areas were modified to simulate suggested hydrologic underflow and plotted against lithium concentration, the correlation coefficient increased to $r=0.48$ (fig. 51). The coefficient $r^2=0.23$ for this improved correlation indicates that 23 percent of the variance in lithium concentration can be accounted for by the linear relationship between area and lithium concentration.

This rudimentary study was based upon the assumption that drainage basin size is the only factor influencing the weathering of bedrock and the subsequent transportation of ions to the playa. The significant correlation between drainage basin area and lithium concentration in the playa suggests that weathering of bedrock does indeed contribute lithium to the playa sediments. The importance of bedrock weathering as a lithium source might be clarified by considering other factors which could influence the amount of lithium reaching the playa; the chemical composition of the bedrock, as well as factors which influence weathering such as relief, slope, climate and vegetation, and factors influencing surface flow such as flow frequency, runoff, infiltration, and evaporation may significantly affect the amount of lithium reaching the playa. When the role of these factors are more thoroughly understood, it will be possible to evaluate more accurately the importance of regional sources of lithium which are not related to drainage basin morphology or process.

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THE TECTONIC AND SEDIMENTOLOGIC ENVIRONMENT OF LITHIUM OCCURRENCES IN THE MUDDY MOUNTAINS, CLARK COUNTY, NEVADA

By ROBERT G. BOHANNON, U.S. GEOLOGICAL SURVEY, DENVER, CO

ABSTRACT

In the vicinity of the Muddy Mountains of southern Nevada, the Horse Spring Formation of Miocene age and the Muddy Creek Formation of Miocene(?) and Pliocene age contain various saline deposits that are rich in lithium as well as other alkali metals and alkaline earths. The rocks of the Muddy Mountains have been involved in several episodes of deformation. Thrust faulting occurred during Cretaceous time and strike-slip faulting during Tertiary time. However, normal faulting in the Tertiary and Quaternary that is characteristic of basin and range deformation appears to have controlled the deposition of the Cenozoic rocks.

Lithium concentrations greater than 1,000 ppm occur in rocks in at least three geographic areas: West End Wash, White Basin, and Overton Ridge. High concentrations of lithium are associated with clays, borate mineralization, and magnesite deposition. In West End Wash and White Basin, lithologies and sedimentary structures suggest that the Horse Spring Formation and the borate minerals within it accumulated in a saline lake or hot spring environment. At Overton Ridge the magnesite member of the Horse Spring Formation probably formed in a similar environment, and associated coarse conglomerate within the Horse Spring indicates a nearby source of clastic material.

There is evidence that the Horse Spring Formation was deposited in a single, closed basin that may have covered much of the Muddy Mountains and the southern part of the Virgin Mountains. The deposition of the Muddy Creek Formation appears to have been confined to valleys presently in existence in southern Nevada.

INTRODUCTION

A varied section of upper Tertiary and Quaternary sedimentary rocks rims the west and south sides of the Muddy Mountains in southern Nevada (fig. 52); it is rich in lithium, magnesium, sodium, boron and manganese. This section, which contains abundant clay-rich clastic material, magnesite, dolomite, limestone, gypsum, halite and volcanogenic sedimentary rocks probably originated in a large, closed bolson because many of the deposits are characteristic of alluvial fans, playa lakes and river flood plains. Longwell (1928, 1949) and Longwell, Pampeyan, Bowyer, and Roberts (1965) subdivided the Tertiary rocks in some places, into the Miocene Horse Spring and Miocene(?) and Pliocene Muddy Creek Formations, but they included equivalents of these units and some older rocks in the Cretaceous(?) and Tertiary

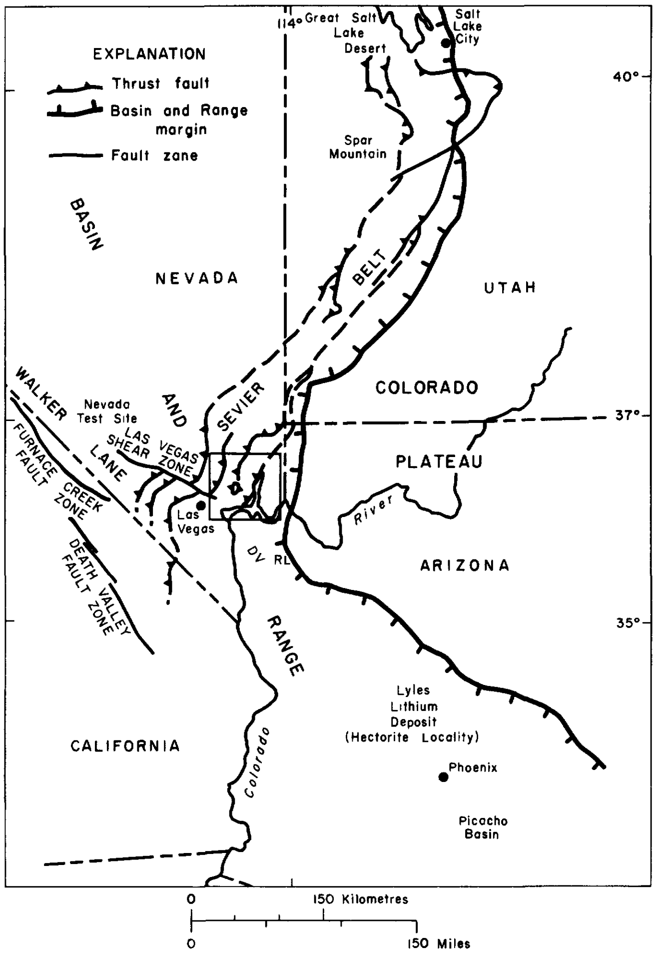


FIGURE 52.—Index map of the major structural features in the vicinity of the Muddy Mountains, Nev. Square in left center of the diagram outlines the Muddy and Virgin Mountains and Frenchman Mountain. DV, Detrital Valley; RL, Red Lake.

Gale Hills and Thumb Formations in other places. Although geologic mapping is incomplete, much of the enrichment in light metals and boron and most of the exotic lithologies appear to be part of the Horse Spring Formation; the more uniform, clastic Muddy Creek Formation contains local pockets of manganese (McKelvey and others, 1949).

Because of the enrichment in lithium and other light elements within the Tertiary sedimentary section in the vicinity of the Muddy Mountains, a detailed study of these rocks is underway. These rocks are well suited for a study of lithium and its behavior in a nonmarine sedimentary environment because they are well exposed. Hence a good three-dimensional view of the rocks is possible, but complex geologic structures must be understood first. Once the details of the structural geology are ironed out, geochemical sampling of all the different sedimentary facies and environments can yield information relating to the localization of lithium, the chemical and mineralogical associations of lithium, the most likely sedimentary environments for lithium accumulation, the possible sources of lithium, and any necessary tectonic or volcanologic controls on lithium accumulation. This paper marks the beginning of such a long-range study; and, although the work is just in the stage of geologic mapping, the major structures and Tertiary sedimentary environments of the area can be described and preliminary geochemical data discussed.

ACKNOWLEDGMENTS

This paper has benefited from many discussions with geologists associated with the U.S. Geological Survey's lithium program, and most of the chemical data referred to in the report were supplied by Allen Meier. Chemical analyses for lithium were performed in the field using an atomic-absorption apparatus. Powdered solid samples were dissolved in hydrofluoric acid and nitric acid and the solution taken to dryness. Hydrochloric acid was used to redissolve the remaining residue; distilled water was employed to dilute that solution.

TECTONIC SETTING

The Muddy Mountains occur where several major tectonic elements of differing ages come together (fig. 52). A late Mesozoic zone of thrust faults and folds, the Sevier Orogenic belt (Armstrong, 1968), extends from northern Utah to southern California and includes most of the Muddy Mountains. The Glendale thrust and the Muddy Mountain thrust (Longwell, 1949) are the two principal low-angle faults resulting from this deformation. Also, the Walker Lane (Locke and others, 1940), which trends northwest through most of western and southern Nevada, terminates in the vicinity of the Muddy Mountains. Albers (1967) proposed that the right-slip Las Vegas Shear Zone (Longwell, 1960) is part of the Walker Lane—which he claimed is as old as Jurassic but was active through the Miocene—and that the Muddy Mountains are a giant right-lateral "oroflex." Anderson (1973) however, has documented several left strike-slip faults north of Lake Mead within the right-lateral "oroflex", as proposed by Albers (1967), and these left-slip faults appear to be of about the same magnitude as the Las Vegas Shear Zone (Stewart and others, 1968). Also, Fleck (1970) concluded that the Las Vegas Shear Zone is no older than 10.7 million years, or about the same age as Anderson's (1973) left-slip faults. More research is needed in order to resolve some of these conflicting details of the structural setting of the Muddy Mountains.

Several other major tectonic features also occur in the vicinity of the Muddy Mountains, and these may have a direct bearing on lithium accumulation in the area. The Wasatch Line, a term commonly applied to the zone that divides the thick "geosynclinal" Paleozoic sedimentary sections in the western Cordillera from the thinner cratonal sections in the eastern Cordillera and on the Colorado Plateau, passes through the Muddy and Virgin Mountains. In the Muddy Mountains, this transition takes the form of a major thrust fault—the Muddy Mountain thrust, which juxtaposes the thick Paleozoic carbonate rocks characteristic of south-central Nevada on top of the thinner carbonate and red bed sections characteristic of the Colorado Plateau. In central Utah, the Wasatch Line roughly corresponds to the tectonic transition from the Basin and Range Province into the Colorado Plateau, but in southern Nevada and northwestern Arizona, this transition is about 70 km east of the faulted sedimentary facies change in the Muddy Mountains. The Muddy Mountains, then, occur within the Basin and Range Province but are near the margin of the Colorado Plateau. Other areas of anomalous lithium accumulations and thick evaporite deposits, mentioned below, share the above characteristics.

LITHIUM AND THE TERTIARY ROCKS

Geologic mapping is incomplete in the Tertiary rocks of the Muddy Mountains; thus, subdivisions within these rocks are poorly defined and understood. Several rock units have been named (Longwell, 1949; Longwell and others, 1965; Anderson, 1973); these include the Horse Spring (Miocene) and Muddy Creek (Miocene? and Pliocene) Formations, Gale Hills and Thumb Formations (Cretaceous? and Tertiary) and the Overton Fanglomerate (Tertiary). The Baseline Sandstone and Willow Tank Formation have been referred to as Cretaceous (Longwell, 1949), but may be, in part, Tertiary as well. Lithium occurs in abundance throughout all the above-named rocks, with the possible exceptions of the Willow Tank and Baseline; but it is most concentrated in three areas: the magnesite near Overton, the White Basin borate area, and the West End Wash borate area (fig. 53). All three areas are thought to be part of the Horse Spring Formation.

The two borate areas appear to be similar in their overall lithology. In addition to the presence of borate minerals, both areas contain sections of well-bedded, predominantly clastic rocks that have abundant sedimentary structures such as ripple marks and small-scale crossbedding. In both areas, carbonate beds, gypsum veins, and claystone are common as well. Although no detailed geologic mapping or sedimentological study has been conducted in either area, the lithologies, bedding, mineralogy, and sedimentary structures that occur in both areas suggest a saline lake and (or) spring environment for their deposition.

Reconnaissance surface sampling was conducted at both the West End Wash and White Basin localities, and some drill cuttings were sampled from the White Basin area. The results of lithium determinations on the surface samples are summarized in tables 49 and 50; the average lithium concentration from 194 samples taken from five drill holes in the White Basin is 474 ppm. The highest lithium value from the drill cuttings is 1,600 ppm and the lowest is 22 ppm. Most of these values,

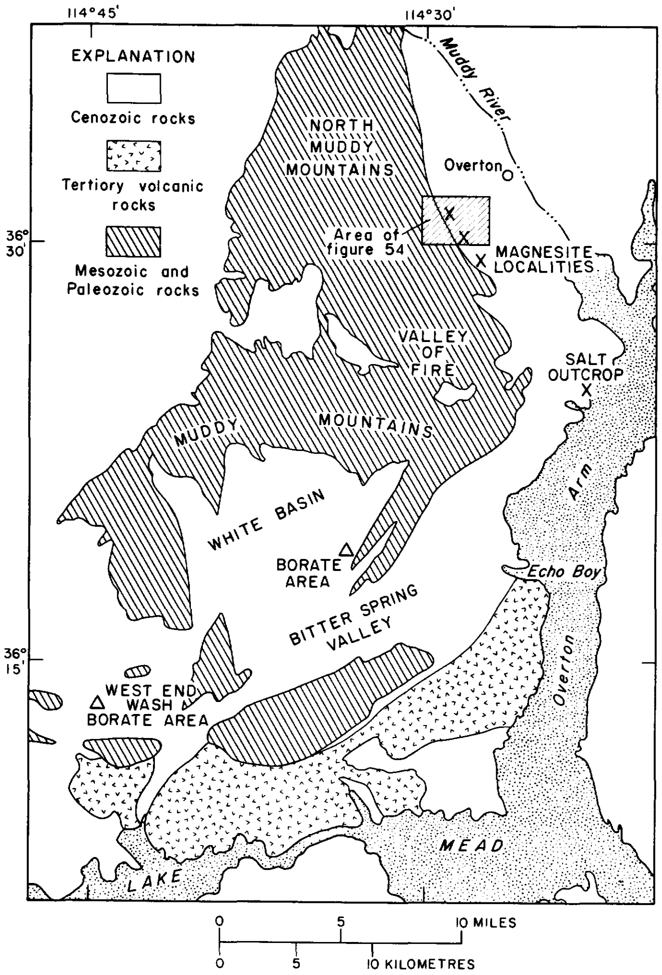


FIGURE 53.—Map showing the distribution of three lithium-rich areas in the Muddy Mountains area. Geology modified from Longwell Pampeyan, Bowyer, and Roberts (1965).

TABLE 49.—*Lithium analyses of the West End Wash surface samples in the Muddy Mountains*

Sample No.	Description	Li(ppm)
MAI 161	Carbonate rock	230
162	Clay	590
163	Borate ore	600
164	do	560
165	Channel near ore zone	660
166	Channel 1.8 m above ore	730
167	Magnesite(?)	360
168	do	420
169	Colemanite(?)	110
170	Clay debris	470
171	Clay and magnesite	670
172	Chert	67
173	Shaley zone	700
174	Clay	540
175	unknown	410
176	Volcanic ash	130
177	do	72
178	do	130
179	Clay with borates	750
180	Clay	470
181	Chert(?) from biotite ash	45
182	Clay	830
183	do	770
184	Carbonate	11
185	do	33

TABLE 50.—*Lithium analyses of the White Basin surface samples in the Muddy Mountains*

Sample No.	Description	Li(ppm)
MAG 617	Clay	300
618	do	800
619	Gypsiferous clay	220
620	Clay	110
621	Sandstone	130
622	Clay	760
623	do	670
624	do	680
625	Siltstone	100
626	Clay	330
627	Clay and borate	420
628	Claystone	330
629	do	1,250
630	Siltstone	1,000
631	Claystone	400
632	do	750
633	Siltstone	540
634	Clay gouge in sandstone	250
635	Concretion	130
636	Borate concretion	120
637	Tailings	540
638	Volcanic ash	550
639	Fault-zone clay in borates	1,000
640	Tailings	920
641	Gypsum and clay	540
642	Calcareous sandstone	160
643	Tailings	450

which are anomalously high with respect to crustal averages, are based on the value of 20 ppm reported for the upper crust by Heier and Billings (1970), and many values seem to be much higher than average for most nonmarine basins (J. D. Vine, oral commun., 1975). Values above 1,000 ppm are among the highest reported in sedimentary rocks (pure hectorite runs about 3,000 ppm Li). On the average, fine-grained clastic rocks such as claystone and siltstone contain the highest concentrations of lithium, but the borate zones themselves are also rich in lithium. There does not seem to be a noticeable trend of lithium values with depth in the drill holes.

Recent geologic mapping in the vicinity of the Overton magnesite deposits shows several changes from the original map of Longwell (1949) (fig. 54). The older conglomerate stratigraphically below and west of the conglomerate on Overton Ridge is not a laterally continuous unit; but rather the conglomerate interfingers to the south with the quartz arenite of the Baseline Sandstone (fig. 54) and is the same age as the Baseline Sandstone. In this report, the above-mentioned unit is retermed conglomerate and is assigned to the Baseline Sandstone as the Overton Conglomerate Member. Also, the Horse Spring Formation has been divided into four informal members: the conglomerate member, the dolomite member, the magnesite member, and the sandstone and claystone member. The younger conglomerate that makes up Overton Ridge is conformable with and is mapped as the basal member of the Horse Spring Formation (fig. 54). This same unit was formerly included with the conglomerate and quartz arenite below it as part of the Overton Fanglomerate (Longwell, 1949), but it rests above these older rocks with a slight angular discordance, and there is evidence of channeling at its base. The Muddy Creek Formation has been divided into two members: The conglomerate member, which only occurs near Overton Ridge; and the sandstone member, which occurs east of the conglomerate member. The general stratigraphic relationships found in Magnesite Wash are depicted in figure 55. Data on the age of the rocks has been supplied by Anderson, Longwell, Armstrong, and Marvin (1972) and Longwell, Pampeyan, Bowyer and Roberts (1965).

Figure 55 also shows the averages of analyses for lithium in several of the units in Magnesite Wash. Lithium values in the dolomite member of the Horse Spring Formation are averaged from 62 samples with a high value of 580 ppm and a low value of 24 ppm. In the magnesite member of the Horse Spring, they are averaged from 118 samples with a high of 1,400 ppm and a low of 90 ppm, and in the sandstone and claystone member of the Horse Spring, the average is from 26 samples with a high of 850 ppm and a low of 90 ppm. The average lithium value in the Muddy Creek Formation is from seven samples that range in value from 75 to 190 ppm.

The highest concentrations of lithium occur in the magnesite member of the Horse Spring Formation, where maximum values above 1,000 ppm occur in several beds. This member appears to have accumulated in place as a sedimentary deposit. The lines of evidence supporting this conclusion are the well-preserved bedding and other sedimentary structures such as ripple marks; the fact that the member occurs as a discrete sedimentary body; the fact that the relative proportion of magnesite to other minerals is controlled by bedding; and the fact that beds of tuff occur interbedded in the member and are unaltered. Lithium also appears to have accumulated with the sediments, because lithium concentrations show strong bedding control. The dolomite member of the Horse Spring Formation has slightly lower lithium values and appears to be, in part, a clastic carbonate rock. X-ray analysis shows that both dolomite and calcite occur in this member and thin-section analysis indicates the presence of angular, sand-sized grains of carbonate in a micritic carbonate matrix. It is likely that the clastic grains are calcite; the matrix is dolomite. Lithium concentrations are probably low owing to "diluting" of the material that formed in place by lithium-poor clastic grains. This idea, however, is not documented. Clay occurs in all the members of the Horse Spring and Muddy Creek Formations. In the magnesite member of the Horse Spring Formation the clay is a trioctahedral smectite (Harry Starkey, written commun., 1976) that contains as much as 3,300 ppm lithium.

The coarse conglomerate interbedded with the fine-grained rocks of the Horse Spring Formation suggests that a nearby source of clastic material existed for the Horse Spring Formation in this area and that the magnesite may have formed near the edge of the Horse Spring basin. Although no detailed sedimentologic work has been attempted on this conglomerate, derivation from a terrane of carbonate rocks can be assumed on the basis of the abundance of carbonate clasts; the most logical nearby source is a carbonate terrane to the west in the north Muddy Mountains. That the Horse Spring basin east of this probable source was a closed basin is suggested by the widespread occurrence of gypsum in the Horse Spring Formation and by rock salt, which probably also originated in the Horse Spring Formation (Mannion, 1963).

CONCLUSIONS

Rocks called the Horse Spring Formation have been mapped in many areas in southern Nevada. These rocks are also described in the Virgin Mountains, east of the Muddy Mountains (Morgan, 1964) and in the Nevada

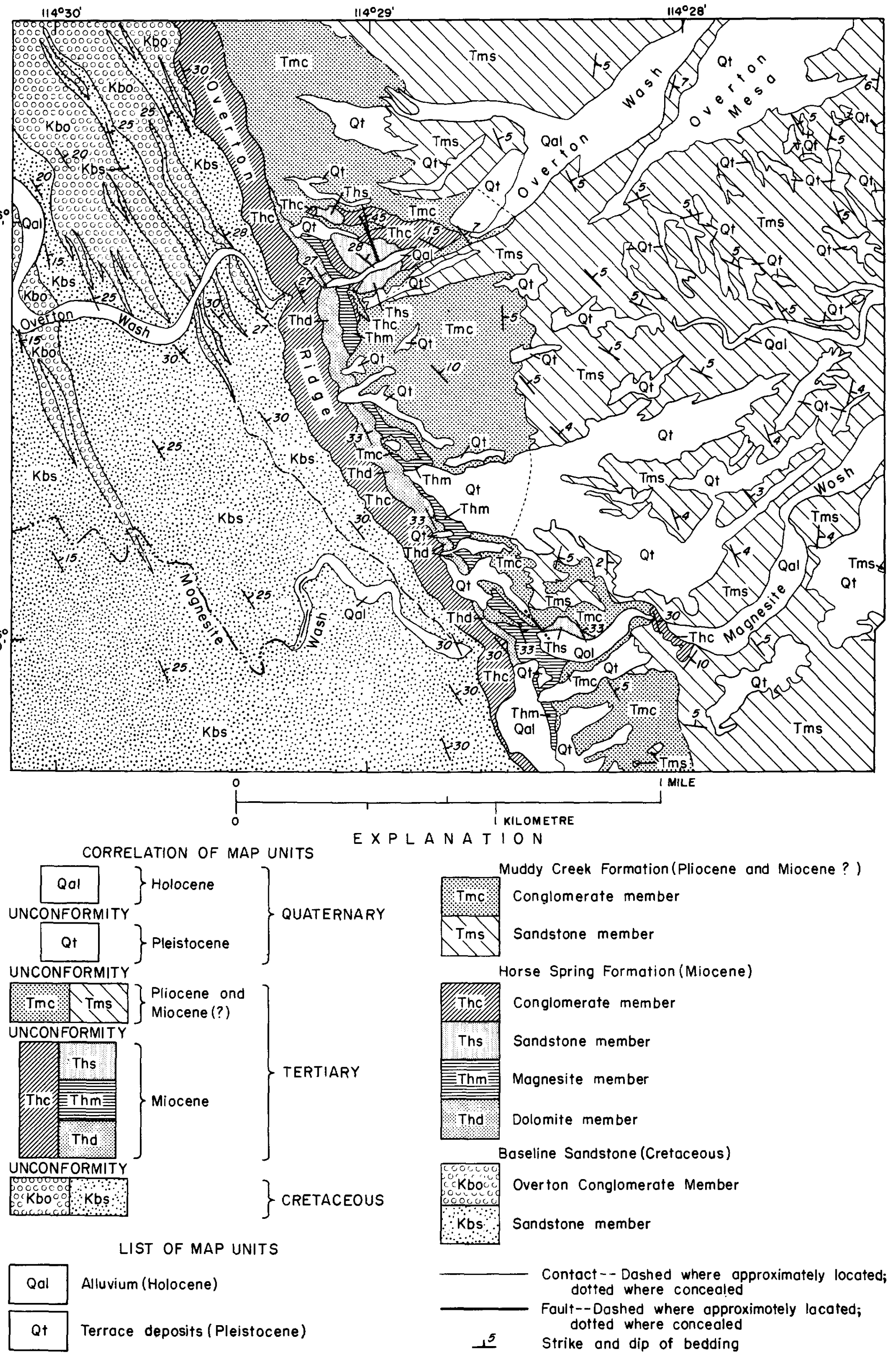
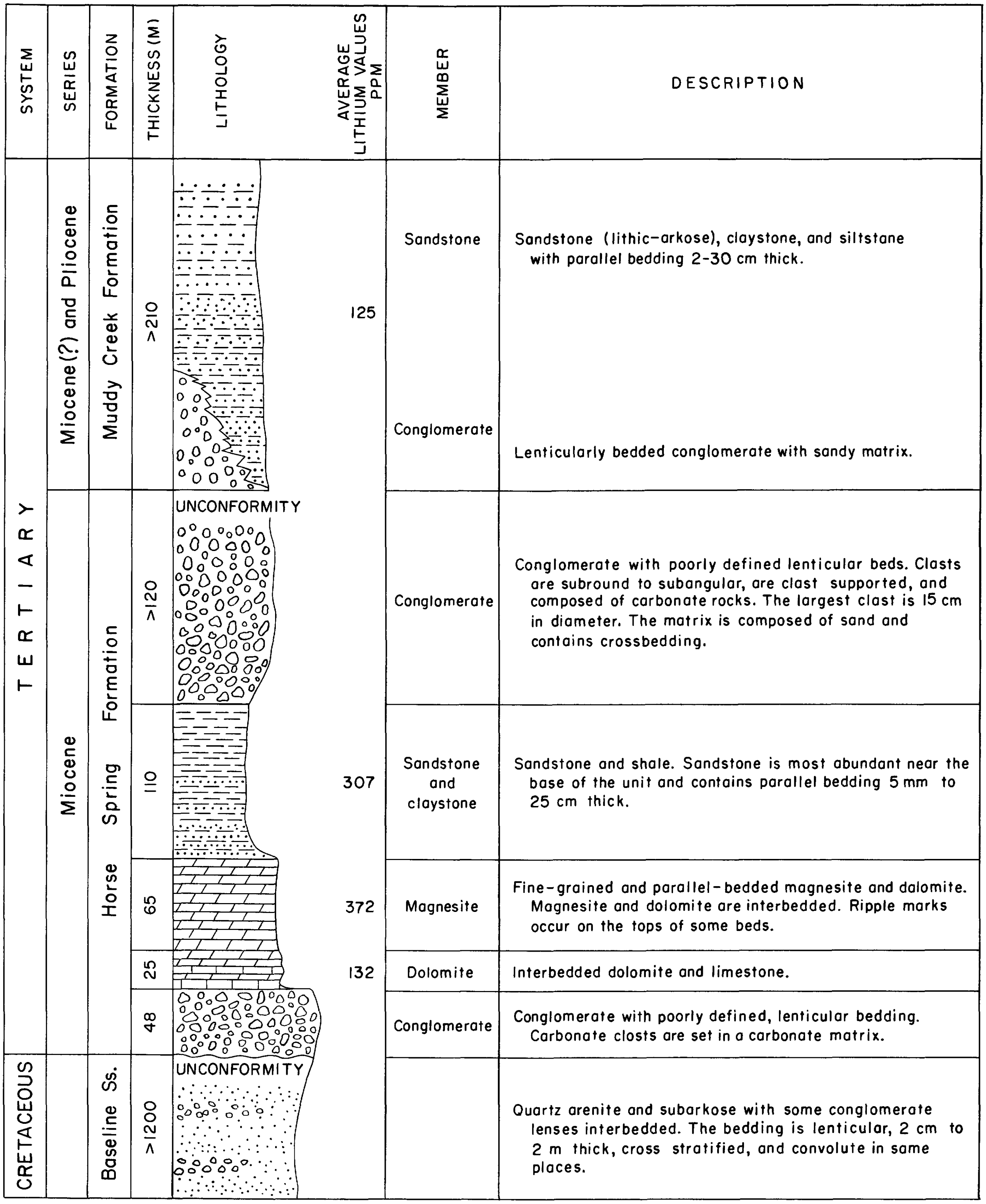


FIGURE 54.—Geologic map of the area west of Overton, Nev. Geology from this report.

Test Site, 100 km northwest of the Muddy Mountains (Sargent and others, 1970; Sargent and Stewart, 1971). In the Nevada Test Site, however, Sargent, McKay, and Burchfiel (1970) reported that the Horse Spring Formation is about 29 m.y. old which is older than the date of 21 m.y. reported for it in the Muddy Mountains (Anderson and others, 1972). Also, Will Carr (oral commun., 1974) suspects that the Horse Spring Formation in the



SYSTEM	SERIES	FORMATION	THICKNESS (M)	LITHOLOGY	AVERAGE LITHIUM VALUES PPM	MEMBER	DESCRIPTION
TERTIARY	Miocene(?) and Pliocene	Muddy Creek Formation	>210		125	Sandstone	Sandstone (lithic-arkose), claystone, and siltstone with parallel bedding 2-30 cm thick.
						Conglomerate	Lenticularly bedded conglomerate with sandy matrix.
	Miocene	Horse Spring Formation	>120	UNCONFORMITY		Conglomerate	Conglomerate with poorly defined lenticular beds. Clasts are subround to subangular, are clast supported, and composed of carbonate rocks. The largest clast is 15 cm in diameter. The matrix is composed of sand and contains crossbedding.
			110		307	Sandstone and claystone	Sandstone and shale. Sandstone is most abundant near the base of the unit and contains parallel bedding 5 mm to 25 cm thick.
			65		372	Magnesite	Fine-grained and parallel-bedded magnesite and dolomite. Magnesite and dolomite are interbedded. Ripple marks occur on the tops of some beds.
			25		132	Dolomite	Interbedded dolomite and limestone.
			48			Conglomerate	Conglomerate with poorly defined, lenticular bedding. Carbonate clasts are set in a carbonate matrix.
CRETACEOUS		Baseline Ss.	>1200	UNCONFORMITY			Quartz arenite and subarkose with some conglomerate lenses interbedded. The bedding is lenticular, 2 cm to 2 m thick, cross stratified, and convolute in some places.

FIGURE 55.—Stratigraphic section of Tertiary rocks in Magnesite Wash, near Overton, Nev. Average lithium values are shown.

test-site area was deposited in flood plains or possibly in a single large flood plain, which might have included some small lakes. He does not think, however, that evidence that these rocks formed in a closed basin is conclusive. In the Nevada Test Site, rocks that are equivalent to the Horse Spring Formation near its type section in the southern part of the Virgin Mountains are probably mostly volcanic types. In the southern part of the Virgin Mountains, the Horse Spring Formation is probably similar in age to the same formation in the Muddy Mountains; it has high concentrations of lithium, to about 800 ppm in some beds (Dick Glanzman, oral commun., 1975); and it is similar in lithology to the same formation near Overton.

Prior to the Oligocene, no evidence of any Tertiary basins is present in the Muddy Mountains, in the Virgin Mountains, or at the Nevada Test Site. Southern Nevada appears to have been an area of erosion (assuming that the Willow Tank Formation and Baseline Sandstone are Cretaceous). About 29 million years ago, a broad downwarp must have formed in the test-site area and the rocks of the Horse Spring Formation and slightly younger rocks were deposited in flood plains within it. During this time the Muddy Mountains appear to have been undergoing erosion. The 21 m.y. old evaporite deposits of the Horse Spring Formation in the Muddy and southern part of the Virgin Mountains represent the first evidence of a closed basin—similar to modern basin and range basins—to form in southern Nevada. Other nearby basin and range valleys contain rocks similar to the Horse Spring and may be as old as it is, but these valleys are not now at the same level of erosion. Peirce (1972, 1973) described thick salt and anhydrite deposits that occur in Arizona in Detrital Wash, in Red Lake Valley, near Phoenix (Luke salt body), and in Pinal County (Picacho Basin). All of these deposits, and the Lyles lithium deposit in Arizona (Norton, 1965), lie on a trend with the Horse Spring Formation in the Muddy Mountains and may be some of the initial basins to form in the eastern part of the Basin and Range Province. The above-mentioned trend occurs near the eastern margin of the Basin and Range Province, near its border with the Colorado Plateau. Other lithium-rich areas occur in this area as well. These include the Spor Mountain area, the Great Salt Lake Desert, and the Great Salt Lake itself.

In summary, the lithium-rich rocks in the vicinity of the Muddy Mountains that appear to be concentrated in the Horse Spring Formation occur in at least three succinct localities rather than throughout the formation. The Horse Spring Formation appears to have accumulated in a closed basin about 21 m.y. ago at the earliest, and it represents the earliest known basin and range basin in this part of southern Nevada. Other basins and volcanic centers that lie near the eastern margin of the Basin and Range Province are also high in lithium or contain abundant evaporite deposits; they must share some common source or other characteristic with the Horse Spring Formation that allows such lithium-rich chemical deposits to form. However, this common factor is not well understood at the present.

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LITHIUM ABUNDANCES IN OILFIELD WATERS

By A. Gene Collins,
U.S. Energy Research and Development Administration,
Bartlesville, OK

ABSTRACT

The abundance of lithium in oilfield waters was surveyed because of its potential use in energy production. Waters from several locations were found to contain about 500mg/l of lithium and one approached 700mg/l. It is postulated that the high lithium concentrations in some waters in the Jurassic Smackover Formation originated from lithium-enriched continental waters.

INTRODUCTION

The demand for lithium in the United States may increase because of its use in the manufacture of lithium batteries and in the generation of electrical power by controlled thermonuclear power. Electric batteries used to power vehicles require about 45 kg of lithium in the electrolyte and electrodes. Batteries in only 130,000 vehicles would have consumed the entire 1974 production of lithium in the United States (about 6,000 tonnes). Thermonuclear power plants now being designed will require lithium to produce tritium, the prime fuel. The required amount of lithium is dependent upon the design, but it could be on the order of 3–900 kg of lithium per megawatt of electrical power yielded. Lithium is used in several other industries, such as ceramics, glass, greases, air conditioning, brazing, welding, and metallic alloys (Cummings, 1970). Subsurface brine in Clayton Valley, near Silver Peak, Nevada, in which lithium concentration is about 300 mg/l, has been a major source of lithium since about 1967; however, the economic life of this deposit is limited to only a few more decades at the present rate of production.

Most oilfield waters contain lithium, and some studies indicate that lithium concentrations can be used to explore for petroleum (Miodrag, 1975). Several oilfield waters contain more than 50 mg/l of lithium, and this study was conducted to determine the availability of information concerning waters in this category.

LOCATIONS OF OILFIELD WATERS CONTAINING LITHIUM IN EXCESS OF 50 MG/L

Table 51 lists the state, county, location, depth, geologic unit, specific gravity of the water, and concentrations in milligrams per litre of lithium, sodium, potassium, rubidium, cesium, and fluoride for several oilfield waters in the United States. These analyses were derived from an oilfield-water data bank at the ERDA (Energy Research and Development Administration) Energy Research Center in Bartlesville, Okla. Lithium concentrations as much as 692 mg/l were found in the Jurassic Smackover Formation in Texas, 400 mg/l in an unnamed Devonian formation in North Dakota, 345 mg/l in the Mississippian Madison Group in North Dakota, 118 mg/l in the Devonian Saskatchewan Group of Baillie (1953) in North Dakota, 90 mg/l in the Pennsylvanian Minnelusa Formation in Wyoming, 93 mg/l in the Cretaceous Rock Springs Formation in Wyoming, 70 mg/l in the Tertiary Wilcox Formation in Oklahoma, and 51 mg/l in the Cambrian and Ordovician Arbuckle Group of Oklahoma. Although several oilfield water systems have been analyzed for lithium, many others have not. It is therefore possible that an oilfield water exists that contains lithium in excess of 700 mg/l.

GENERAL GEOLOGY OF THE SMACKOVER FORMATION

Because of the relative abundance of data concerning lithium concentrations in Smackover Formation oilfield waters (table 51), it was decided to try to determine the origin of the lithium in the Smackover. According to Imlay (1940), the Smackover Formation was named after the Smackover oilfield in Arkansas, where the unit

TABLE 51.—*Sampling locations, depths, geologic unit, specific gravity, concentrations (mg/l) of lithium, sodium, potassium, rubidium, cesium, and fluoride of some oilfield waters of the United States*

State	County	Location, section-township-range	Depth, metres	Unit	Specific gravity	Li	Na	K	Rb	Cs	F
Alabama	Choctaw	35-11N-4W	3,560	Smackover Fm.	1.222	61	75,370	8,000	----	----	----
Arkansas	Columbia	23-19S-23W	3,326-3,364	do	1.197	86	66,100	163	3.75	4.0	3.6
Do	do	8-18S-20W	2,603-2,667	do	1.231	462	70,200	4,670	13.8	7.0	3.1
Do	do	31-17S-20W	2,572-2,662	do	1.231	481	77,900	6,950	14.5	9.0	6.9
Do	do	2-18S-20W	2,544-2,635	do	1.229	423	78,400	5,640	12.0	6.0	3.4
Do	do	11-18S-20W	2,533-2,621	do	1.229	404	75,700	5,330	12.5	6.0	7.6
Do	do	7-18S-20W	2,638-2,721	do	1.230	481	73,800	5,260	14.0	6.0	7.5
Do	do	1-18S-21W	2,624-2,713	do	1.231	519	73,000	7,460	16.0	8.0	3.2
Do	do	5-18S-20W	2,588-2,682	do	1.128	481	71,400	5,550	15.5	10.0	6.4
Do	do	5-18S-20W	2,583-2,675	do	1.230	442	74,000	4,410	15.0	9.0	7.1
Do	do	32-17S-20W	2,559-2,654	do	1.231	462	64,900	6,230	14.5	8.0	4.7
Do	do	6-18S-20W	2,610-2,697	do	1.230	462	64,200	11,100	14.5	10.0	7.1
Do	do	23-18S-20W	2,591-2,614	do	1.221	308	84,400	5,790	9.5	3.0	4.8
Do	Lafayette	12-15S-25W	1,997-1,998	do	1.183	75	59,400	720	3.5	2.0	5.1
Do	Union	13-17S-13W	1,897	do	1.157	50	55,470	614	----	----	----
Florida	Santa Rosa	21-5N-29W	4,783	do	1.226	102	73,100	7,650	----	----	----
Do	do	40-5N-30W	4,740	do	1.209	81	79,200	5,360	----	----	----
Louisiana	Webster	10-23N-9W	3,363-3,369	do	1.227	66	113,000	616	----	----	----
Do	Claiborne	10-23N-6W	3,048	do	1.186	101	87,400	1,090	----	----	----
Do	do	19-23N-6W	3,048	do	1.191	80	82,800	1,380	----	----	----
Mississippi	Jones	22-9N-10W	3,959	do	1.209	75	70,947	800	----	----	----
Do	Smith	9-1N-9E	4,834	do	1.188	67	55,200	4,260	----	----	----
Do	Wayne	26-10N-6W	3,867	do	1.210	80	74,500	650	----	----	----
North Dakota	Divide	3-152N-96W	3,317-3,323	Saskatchewan Gp. [1]	1.223	118	51,300	13,400	----	----	----
Do	Williams	6-155N-95W	3,106-3,210	Unnamed Devonian	1.238	400	58,200	9,500	----	----	----
Do	Burke	10-162N-92W	1,935-1,942	Madison Gp.	1.210	345	106,000	633	----	----	----
Do	do	15-162N-92W	1,890	do	1.231	164	115,000	3,850	----	----	----
Oklahoma	Noble	22-20N-2W	1,564	Wilcox Fm.	1.161	70	74,400	860	----	----	----
Do	Carter	4-4S-3W	942	Arbuckle Gp.	1.140	51	56,700	1,340	----	----	----
Texas	Cass	G. J. Aerrod Sur.	3,063	Smackover Fm.	1.105	473	26,800	280	----	----	----
Do	do	Bryan Mills Unit	3,198	do	1.211	404	69,300	6,390	----	----	----
Do	Franklin	B. J. Putoff	3,712	do	1.129	293	49,000	4,660	----	----	----
Do	Hopkins	W. L. Houghton Sur.	2,888	do	1.160	99	53,600	2,400	----	----	----
Do	Van Zandt	M. Dewberry	3,897	do	1.081	100	25,300	2,860	----	----	----
Do	Robertson	----------	4,351	do	1.237	624	90,000	15,820	----	----	----
Do	Rains	B. Deosinia Survey	4,188-4,206	do	1.233	224	75,500	6,645	----	----	----
Do	Wood	Oscar Engledow Sur.	3,891-3,901	do	1.210	692	75,400	7,430	25.0	25.0	----
Utah	Daggett	22-3N-24E	----------	Madison Gp.	1.044	85	15,000	1,700	----	----	----
Do	San Juan	16-30S-24E	2,553	Unnamed Mississippian	1.049	56	21,400	1,400	.5	.2	----
Do	do	19-43S-22E	1,478	Ismay zone[2]	1.052	58	19,700	1,010	----	----	----
Do	Grand	16-23S-17E	2,623	Leadville Ls. equivalent	1.148	53	59,600	2,400	5.0	1.0	----
Do	Duchesne	2-15N-2W	1,799	Green River Fm.	1.064	68	28,900	408	----	----	----
Wyoming	Campbell	16-47N-70W	2,939	Minnelusa Fm.	1.103	90	52,400	2,100	----	----	----
Do	do	16-47N-70W	3,031	do	1.082	75	41,800	950	----	----	----
Do	do	16-47N-70W	2,939	do	1.103	70	52,800	2,100	----	----	----
Do	do	16-47N-70W	3,031	do	1.082	75	41,820	950	----	----	----
Do	Sweetwater	1-12N-107W	2,676	Rock Springs Fm.	1.106	93	54,830	700	----	----	----

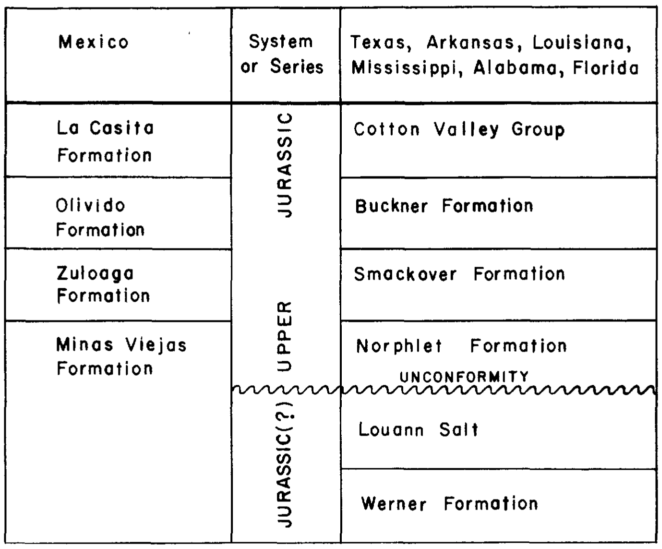
[1] Of Baillie, 1953

[2] Of Paradox Formation.

comprises 213 m of oolitic limestone. Smackover equivalents have been identified in Mexico, Texas, Arkansas, Louisiana, Mississippi, and Alabama (fig. 56) and on the basis of good paleontological evidence correlated with the Upper Jurassic Argovian Substage of the Oxfordian Stage in England (Imlay, 1945).

The Smackover Formation is the equivalent of the Zuloaga Formation in Mexico (fig. 56). The Zuloaga carbonate crops out west of the Tamaulipas Peninsula in northeast Mexico. The Smackover in the United States overlies a salt basin in the western part of the Rio Grande embayment in southwest Texas. From there it extends across the crest of the San Marcos arch, the northwest part of the east Texas salt basin, the northern part of the north Louisiana-Arkansas salt basin, and then southeastward across the north area of the central Mississippi salt basin to the Florida panhandle and offshore areas, as illustrated in figure 57. The Smackover Formation does not crop out.

The northward boundary of the Smackover Formation follows the approximate updip edge of the subcrop of the Jurassic rocks. Regional and local subsidence in the Gulf Coast geosyncline have caused thousands of fault trends associated with slumpage and folding.



Mexico	System or Series	Texas, Arkansas, Louisiana, Mississippi, Alabama, Florida
La Casita Formation	UPPER JURASSIC	Cotton Valley Group
Olivido Formation		Buckner Formation
Zuloaga Formation		Smackover Formation
Minas Viejas Formation		Norphlet Formation UNCONFORMITY
	JURASSIC(?)	Louann Salt
		Werner Formation

FIGURE 56.—Correlation chart of Jurassic and Jurassic(?) formations in Mexico and in Gulf Coast areas of the United States.

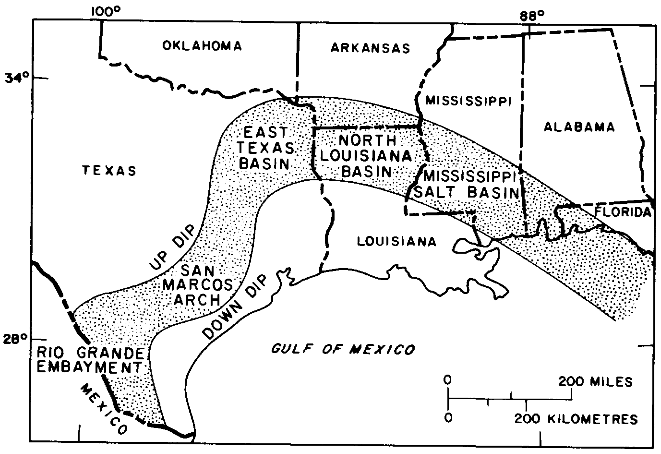


FIGURE 57.—Approximate geographic extent of the Smackover Formation.

Structural deformation of the Smackover also has been caused by tectonics related to the flow of the underlying Louann Salt, a nearly pure coarsely crystalline salt.

The Zuloaga Formation in northeast Mexico lies below La Casita and Olivido Formations (fig. 56). The western limit of the Zuloaga lies west of and parallel to the Tamaulipas Peninsula. Surface exposures of the Minas Viejas Formation are found in the Galeana area south of Monterrey and northwest of the Carcia Caves anticline of Sierra del Fraile (R. W. Eaton, written commun., 1970). More than 915 m of anhydrite, salt, and gypsum constitute the Minas Viejas Formation and underlie the 425-m-thick Zuloaga carbonates. The Zuloaga thins northeastward toward the northern updip limit of Jurassic sedimentation. The top of the Zuloaga is about 3,000 m deep, and the formation is about 180 m thick near the Mexico-United States border.

Bishop (1969) divided the Smackover into members based on an interpretation of environments of deposition: (1) an upper member deposited in shallow water with various types of agitation and composed of different types of nonskeletal carbonate and mud; and (2) a lower member deposited in a quiet, toxic environment, composed primarily of carbonate mud with pyrite and abundant carbonaceous material. Dickinson (1968) divided the Smackover into lower, middle, and upper members based on lithologic differences. In this scheme, the upper member is predominantly oolitic limestone, the middle is mostly a dense limestone, and the lower member is predominantly a dark-brown, silty to argillaceous, commonly laminated limestone. Locally, various units of the Smackover and Zuloaga Formations are absent. The updip areas are truncated by erosion as a result of uplift west of the Tamaulipas Peninsula and uplift to the north of the Gulf Coast area prior to the close of the Jurassic Period.

Figure 58 illustrates types of rocks found in strata in the Werner, Louann, Norphlet, Smackover, and Buckner Formations and Cotton Valley Group in northeast Texas (Dickinson, 1968).

ORIGIN OF SMACKOVER FORMATION WATERS

Oilfield waters originate through many complex natural processes. Some of the mechanisms that cause oilfield waters to differ in composition from the water

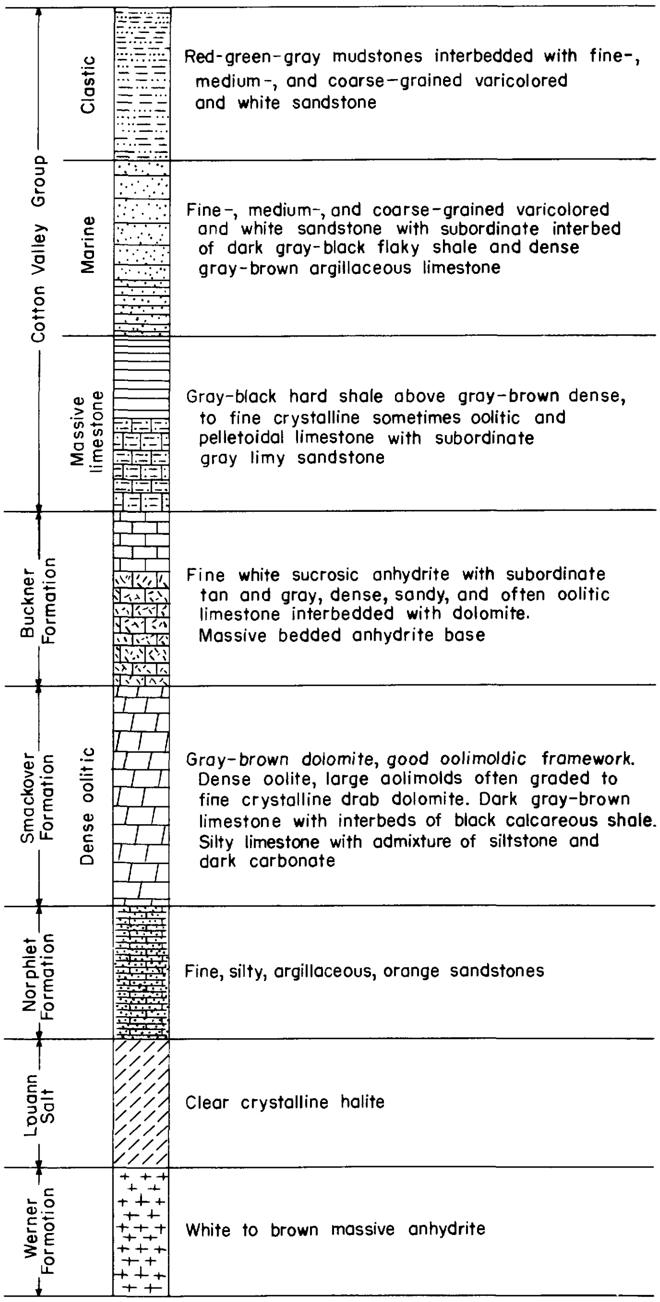


FIGURE 58.—Generalized section of Jurassic and Jurassic(?) rocks in northeast Texas showing types of lithologies in each unit. The units are not to scale.

originally deposited with the sediments include ion exchange, infiltrating waters, sediment leaching, mineral formation, sulfate reduction, and ultrafiltration through clay-shale membranes (Collins, 1974).

Most of the Smackover brines are defiicient in magnesium relative to an evaporite-formed brine. Table 52 illustrates the approximate amounts of calcium, magnesium, bromide, and sulfate that could exist in a water before and after precipitation of gypsum.

Assuming that the residual sulfate 1,644 mg/l was removed by the dolomitization reaction,

$$\cancel{MgCl_2}+2CaCO_3\rightarrow\cancel{CaCl_2}+CaMg\,(CO_3)_2 \qquad (1)$$

$$\cancel{CaCl_2}+MgSO_4\rightarrow CaSO_4+\cancel{MgCl_2} \qquad (2)$$

$$\overline{MgSO_4+2CaCO_3\rightarrow CaSO_4+CaMg\,(CO_3)_2} \qquad (3)$$

then the Mg/Br ratio would be about 883/65=13.6, as illustrated by the data in table 52.

However, if the residual sulfate was removed by bacterial reduction,

$$C_nH_m+Na_2SO_4 \rightarrow Na_2CO_3+H_2S+CO_2+H_2O, \qquad (4)$$

the Mg/Br ratio would be about 1,300/65=20.

Magnesium will react with $CaCO_3$ (calcite) to form dolomite; thus, the concentration of calcium is increased in the brine, and the Smackover brines are enriched in calcium. However, the total calcium plus magnesium in the brine should remain constant; this can be calculated as $\frac{24.31}{40.08}$ ×mg/l calcium+mg/l magnesium=total equivalent magnesium or Mg′. The ratio Mg′/Mg will vary, depending upon the availability of calcite, and the ratio should be indicative of the degree of dolomitization.

For example, brines in equilibrium with sandstones should have a relatively low Mg′/Mg ratio; those in equilibrium with dolomite should have higher ratios; and those in equilibrium with limestone should have the highest ratios. The average Mg′/Mg ratio for the Smackover brines studied is 7; this ratio indicates that the brines were in equilibrium with limestone and dolomite. Previous studies have shown that the average ratio in sandstones is about 2.5 and in limestones about 9.5 (Collins, 1975).

The formation of chlorite from montmorillonite requires about 9.2 moles of MgO per mole of chlorite, as follows:

$$1.7Al_2O_3,\ 0.9\ MgO,\ 8SiO_2,\ 2H_2O+9.2\ MgO+6H_2O \rightarrow 10.1\ MgO,\ 1.7\ Al_2O_3,\ 6.4\ SiO_2,\ 8H_2O+1.6\ SiO_2 \qquad (5)$$

Such a reaction can remove large amounts of magnesium from waters.

TABLE 52.—*Approximate composition of seawater changed by mineral formation and bacterial reduction*

Ion	Gypsum precipitation		Dolomitization	Bacterial reduction
	Before (in mg/l)	After (in mg/l)	After (mg/l)	After (mg/l)
Calcium	390	0	0	0
Magnesium	1,300	1,300	883	1,300
Bromide	65	65	65	65
Sulfate	2,580	1,644	0	0

TABLE 53.—*Concentration ratios and excess factor ratios for some constituents in Smackover brines*

Constituent	Average composition, mg/l		Concentration ratio[1]	Excess factor[2]	Number of Smackover samples
	Seawater	Smackover brines			
Lithium	0.2	174	870	18.1	71
Sodium	10,600	66,973	6	.1	283
Potassium	380	2,841	8	.2	82
Calcium	400	34,534	86	1.8	284
Magnesium	1,300	3,465	3	.1	280
Strontium	8	1,924	241	5	85
Barium	.03	23	767	16	73
Boron	4.8	134	28	.6	71
Copper	.003	1.1	359	7.5	64
Iron	.01	41	4,069	84.2	90
Manganese	.002	30	14,957	311	69
Chloride	19,000	171,686	9	.2	284
Bromide	65	3,126	48	1	74
Iodide	.05	25	501	10.4	73
Sulfate	2,690	446	.2	.003	271
Mg′[3]	1,543	24,362	16	.3	284

[1] Amount in brine/amount in seawater.
[2] Concentration ratio of a given constituent/concentration of bromide.
[3] Mg′=(24.31/40.08)×mg/l calcium+mg/l magnesium.

Table 53 presents data obtained by comparing the average composition of the analyzed Smackover brines to seawater. The concentration ratio was calculated by dividing the mean average for a given constituent in the Smackover brines by the amount of the constituent found in normal seawater. The excess factor was determined by dividing the concentration ratio of a constituent by the concentration ratio of bromide. The calculation for Mg′ or total equivalent magnesium is related to dolomitization (Collins, 1975). The number of Smackover samples indicate how many samples were used in the calculation; thus, 71 Smackover brines were analyzed for lithium, whereas 283 were analyzed for sodium.

The concentration ratios indicate that with the exception of sulfate, all the determined constituents in the Smackover brines were enriched with respect to seawater. The excess factor ratios, however, indicate that sodium, potassium, magnesium, boron, chloride, sulfate, and total equivalent magnesium generally were depleted in the Smackover brines, whereas lithium, calcium, strontium, barium, copper, iron, manganese, and iodide were enriched. Furthermore, these ratios indicate that the Smackover brines have been altered considerably if it is assumed that they originally were seawater.

The concentration ratio 48 for bromide is one of the highest we have seen. In contrast, bromide concentration ratios of 1.2, 4.4, 8.8, and 7.2 were found for brines from Tertiary, Cretaceous, Pennsylvanian, and Mississippian rocks in previous studies (Collins, 1969, 1970).

Bromide does not form its own minerals when seawater evaporates. Some of it is lost from solution because it forms an isomorphous admixture with chloride in the halite precipitate. However, more bromide is left in solution than is entrained in the precipitate. Therefore, relative to chloride, the bromide concentration in the brine increases exponentially. Because of this, the bromide concentration in the brine is a good indicator of the degree of seawater concentration, assuming that appreciable quantities of biogenic bromide have not been introduced.

When a brine containing lithium is subjected to an evaporation sequence, lithium is one of the elements whose concentration does not decrease in the liquid phase as various minerals precipitate (Collins, 1975). Therefore lithium, like bromide, increases in concentration in the bitterns.

Figure 59 shows how the concentrations of calcium and sodium in the Smackover brines compare with the concentrations of calcium and sodium in some altered relict bitterns. The sodium and calcium concentrations in the bitterns are dependent upon the solubilities of their respective compounds, and the plot in figure 59 is indicative of this. In contrast, the calcium concentration increases as the sodium concentration increases in the Smackover brines (fig. 59), which indicates that the increased calcium probably results from cation exchange or perhaps mineral formation.

Figure 60 is a plot of Na′ versus Br for the Smackover brines, an altered relict bittern, evaporating seawater, and evaporite salt dissolved in water. The Na′ = mg/l Na + $\frac{46}{40}$ mg/l Ca because in an exchange reaction, 2 moles of sodium are exchanged for 1 mole of calcium. The assumption is that the sodium in the brine exchanges for calcium in the clay thus increasing the calcium concentration in the brine. Na′ was plotted versus Br because the bromide concentration should be proportional to the amount of salt redissolved. The Smackover brines contain some iodide, which indicates bioconcentration; therefore, some biogenic bromide is present, and this accounts for some of the point scatter.

The plots in figure 60 indicate that the Smackover brine is altered relative to evaporated seawater; however, the alteration apparently differs from the pattern of the altered relict bittern. The high bromide content in the Smackover brines indicates either that the Smackover brines reached the bittern state at some time, or that biogenic bromide was added to the brine. Some of the Smackover samples obviously were diluted by fresh water; that is, those samples that fall to the left of the evaporating seawater line.

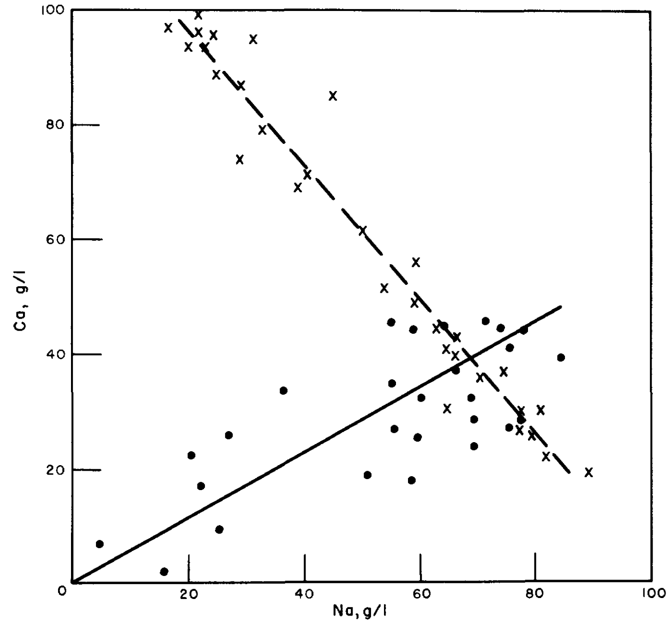


FIGURE 59.—Comparison of calcium and sodium concentrations of some Smackover brines (solid dot) to those of some altered relict bitterns(×).

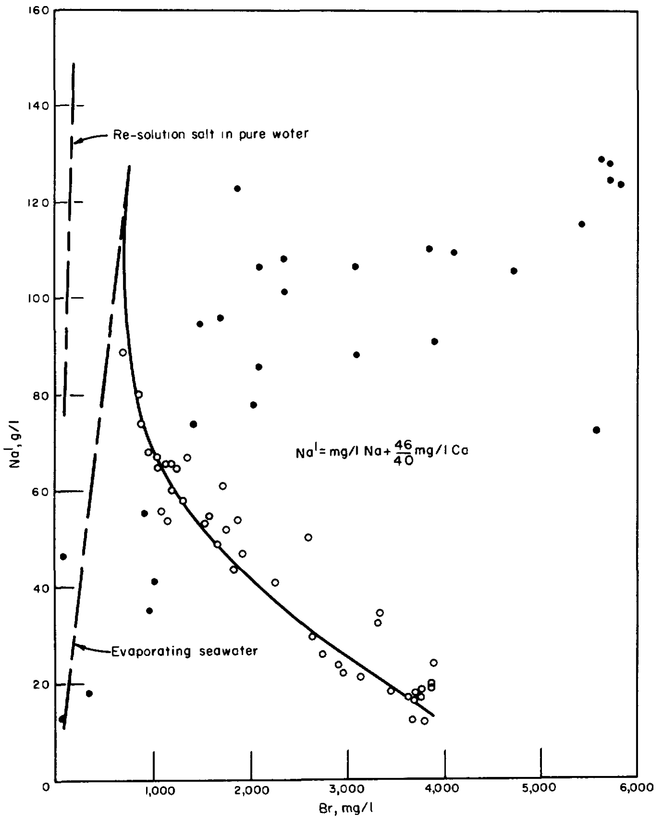


FIGURE 60.—Comparison of Na′ and Br concentrations of some Smackover brines (solid dot) to those of an altered relict bittern (open dot), evaporating seawater (long-dashed line), and redissolved salt (short-dashed line).

The concentration of Na′ decreases as the Br increases in the altered relict bittern, whereas the reverse is characteristic of the Smackover brines. It is therefore postulated that the Smackover brine is an altered seawater that has at one or more times approached or reached the bittern stage. Bitterns from the Louann Salt probably mixed with the Smackover brines; however, this study provided no proof of this.

ORIGIN OF LITHIUM IN THE SMACKOVER WATERS

Correlation coefficients of the Smackover brine data show a high degree of intercorrelation among K, Rb, Li, and B. Iodide does not correlate. Combining data from the Smackover with data from an altered relict bittern produced a high correlation between K and B, and between Li and Rb. This correlation suggests that a mechanism in addition to seawater evaporation is involved in producing the high concentration of Li and Rb in the brines.

Data shown in table 53 indicate the relative concentrations of various constituents in the Smackover brines. The excess factors were obtained by assuming that bromide, which does not form minerals, is the best single indicator of the degree to which seawater has concentrated. From table 53 it can be seen that about 80 percent of the original K is missing and that 40 percent of the original B is missing, whereas there is about 18.1 times as much lithium and about 10.4 times as much iodide.

The anomalous iodide can be reasonably explained as a result of bioconcentration (Collins, 1969). However, a similar mechanism to explain all the anomalous lithium is not available. It has been postulated that lithium enrichment results at least in part from exchange reactions with clays because lithium has a small radius, a low atomic number, a larger hydrated number than sodium, and a larger polarization than sodium. Therefore, its replacing power in the lattices of clay minerals is low. Other ions such as Ba, Sr, Ca, Mg, Cs, Rb, K, and Na will preferentially replace Li in clay minerals thus releasing Li to solutions. Also the solubility products of most lithium compounds are higher than those of other alkalies or alkaline earths, so lithium tends to stay in solution (Collins, 1975).

A plausible source of some of the anomalous lithium is continental drainage of lithium-enriched solutions into an evaporating sea, a process which is similar to that now occurring at Great Salt Lake, Utah. The effect of this mechanism can be determined if, for example, continental water with a known composition is mixed with a brine similar to that of Great Salt Lake and subjected to evaporation. Table 54 shows the result of repeatedly mixing a volume of spring water similar to that at Clayton Valley, Nevada (4 mg/l Br, and 55 mg/l Li), with an equal volume of concentrated seawater brine and evaporating to the original brine volume. (The seawater is assumed to be concentrated 48 times in order to attain the average bromide concentration of the Smackover brines, as shown in table 53.) It can be seen that a lithium concentration in excess of 500 mg/l is obtained after 9 successive cycles of mixing and evaporation. (If the fresh water source were river water containing 0.02 mg/l of lithium rather than the spring water containing 55 mg/l lithium, 9 evaporations would yield a lithium concentration of only 9.76 mg/l.)

TABLE 54.—*Compositions obtained by successively mixing one volume of Clayton Valley, Nev., spring water with one of brine and then evaporating to the original brine volume*

Item	Bromide mg/l	Lithium mg/l
Seawater	65	0.2
48× seawater	3,120	9.6
Spring water	4	55
One volume each of 2 and 3	1,562	32.3
Evaporate 4 to one-half volume	3,124	64.6
Add second volume of 3 and evaporate to one-half	3,128	119.6
Add third volume of 3 and evaporate to one-half	3,132	174.6
Add fourth volume of 3 and evaporate to one-half	3,136	229.6
Add fifth volume of 3 and evaporate to one-half	3,140	284.6
Add sixth volume of 3 and evaporate to one-half	3,144	339.6
Add seventh volume of 3 and evaporate to one-half	3,148	394.6
Add eighth volume of 3 and evaporate to one-half	3,152	449.6
Add ninth volume of 3 and evaporate to one-half	3,156	504.6

To determine how long such evaporation sequences might take under optimum conditions, again consider the Great Salt Lake. With a volume of about 12 km^3 and an annual inflow and evaporation of about 3 km^3, each equal volume dilution and evaporation would require only 4 years, or a total of only 36 years for 9 cycles.

This evaporation sequence assumption is too simplistic for total direct application, but it can be used to postulate a plausible theory for anomalously high concentrations of lithium in the Smackover brine.

The probable origin of the lithium-rich Smackover brine was an influx into the Smackover Sea of lithium-enriched continental water from springs or other sources in the vicinity of the Mexia-Talco fault system, as shown in figure 61. Volcanic rocks of Triassic age in the Gulf Coast area may be the source of lithium in the spring water that was concentrated by evaporation in the Smackover Sea.

APPROXIMATE ESTIMATE OF AMOUNTS OF LITHIUM IN SMACKOVER BRINE

The precise amount of lithium in brine from the Smackover Formation is unknown, but an estimate can be made for a unit area if assumptions are made for the thickness and porosity of the reservoir, as well as the grade of the lithium and density of the brine. If an area of 25,000 km^2 has a reservoir thickness of 60 m and an

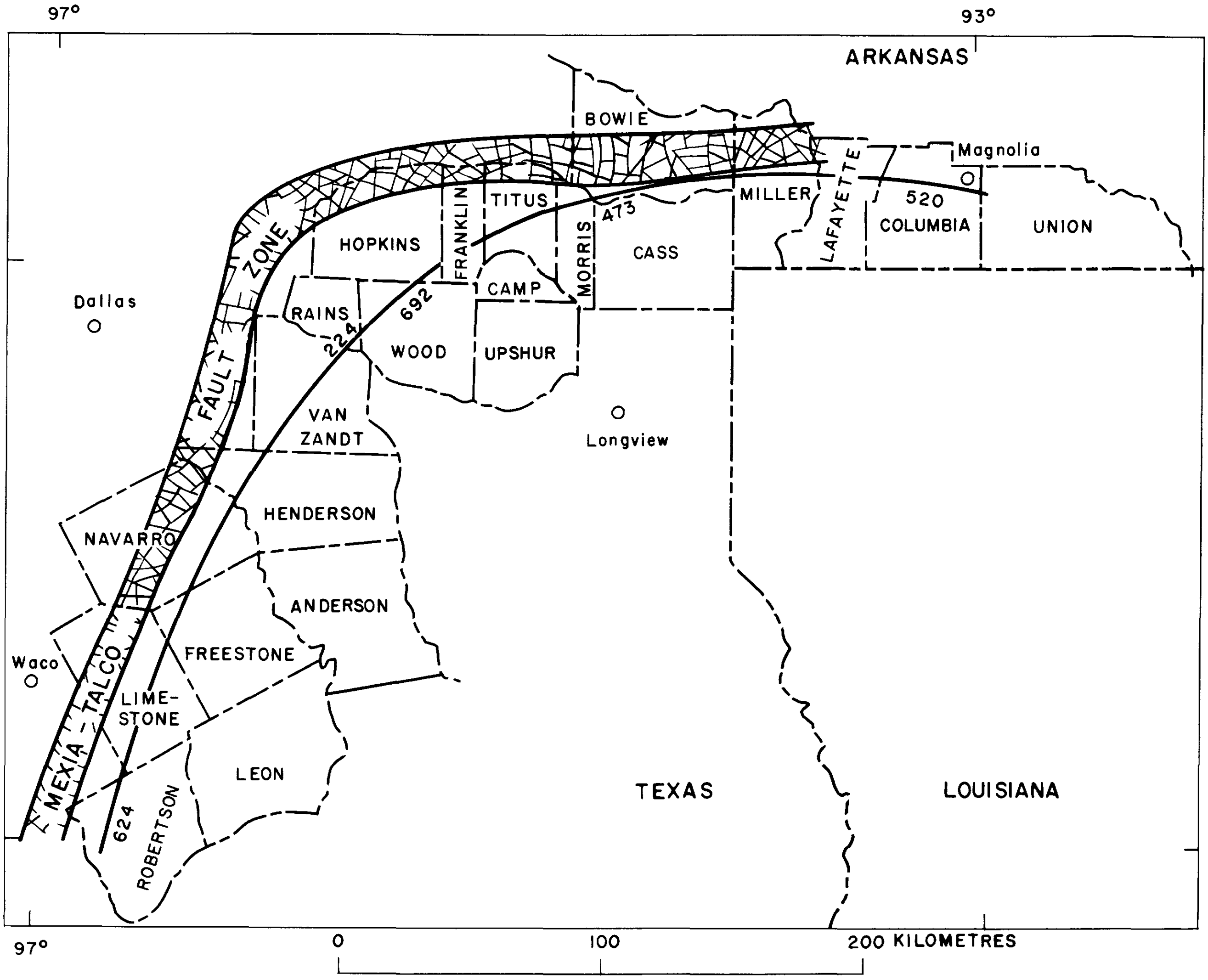


FIGURE 61.—Map showing the relation of high lithium concentrations (in mg/l) in Smackover Formation waters in Arkansas and Texas to the Mexia-Talco fault zone and to an arcuate contour line parallel to the truncated subcrop of the formation.

effective porosity of 5 percent, and if the enclosed brine has a specific gravity of 1.2 and contains an average of 100 mg/l of lithium, then about 0.75×10^6 tonnes of lithium would be contained in 7.5 km^3 of brine. While the total area underlain by the Smackover Formation may be as much as 10 times the area assumed in the above calculations, the other assumptions may be overestimated. The amount of brine that would have to be pumped from depths ranging from about 1,800 to 4,800 m and evaporated nearly to dryness makes primary product recovery of this lithium economically unsatisfactory with the technology available today. If an extraction technique could be developed to recover lithium as a byproduct of the recovery of petroleum, bromine, potassium, or other chemical products, the economic feasibility would be improved significantly.

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LITHIUM IN THE GILA CONGLOMERATE, SOUTHWESTERN NEW MEXICO

By ELIZABETH B. TOURTELOT and ALLEN L. MEIER,
U.S. GEOLOGICAL SURVEY, DENVER, CO

ABSTRACT

Reconnaissance sampling of the Gila Conglomerate of Pliocene and Pleistocene age in southwestern New Mexico revealed anomalously high lithium values in lake beds within the Gila Conglomerate. The lithium is probably derived from the volcanic rocks of the Mogollon-Datil volcanic province by postvolcanic hydrothermal activity associated with hot springs. The alkaline lake environment in which the lake beds were deposited was a sink for the elements added to surface waters by hot-spring activity. Although no deposits of economic potential were found, the geochemistry of the area suggests that beds of hectorite could occur within the lake bed sediments of the Gila Conglomerate.

INTRODUCTION

This is a preliminary report based on reconnaissance sampling and field determinations of lithium content during a reconnaissance survey of the Rocky Mountain region for lithium in 1974 and 1975. Anomalous lithium values were found in some lake-bed deposits within the Gila Conglomerate of southwestern New Mexico. Lithium was determined by atomic absorption analysis using field-exploration methods (see Meier, this volume, for discussion of analytical techniques). Fluorine and chlorine analyses were made using specific ion electrodes. Semiquantitative spectrographic analysis was used to determine the other elements discussed in this report.

In general, we have regarded any rock or sediment sample containing more than 100 ppm (parts per million) lithium as having an anomalous concentration. This value corresponds well with other studies such as that by J. R. Davis (this report), which show an average value of less than 100 ppm lithium for most common rocks and sediments.

ACKNOWLEDGMENTS

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GILA CONGLOMERATE

The Gila Conglomerate, named by Gilbert (1875), is a stratigraphic term that includes most of the basin fill in southwestern New Mexico (fig. 62). The Mimbres River or the Continental Divide generally is considered to be the eastern extent of the Gila Conglomerate; similar sediments east of this area are called Santa Fe Group. The Gila Conglomerate is not precisely dated—its age generally is given as ranging from Pliocene to Pleistocene (Heindl, 1952) and its age probably varies between basins. Fossils of late Pliocene age were described by Knechtel (1936) from southeastern Arizona. Basaltic andesite at or near the base of the Gila Conglomerate along Sapillo Creek (fig. 62) has been radiometrically dated at 20.6±0.5 m.y. (early Miocene) and basalt near the top in the Mimbres River valley was dated at 6.3 m.y. (late Miocene) (Elston and others, 1973). Heindl (1952, 1954, 1963) has discussed the problems of the name, "Gila Conglomerate" in detail. The Gila Conglomerate generally correlates with the Santa Fe Group to the east and with the Muddy Creek Formation in Nevada and Utah—all these being general names for continental rocks of late Tertiary to Quaternary age.

Most of the Gila Conglomerate is made up of

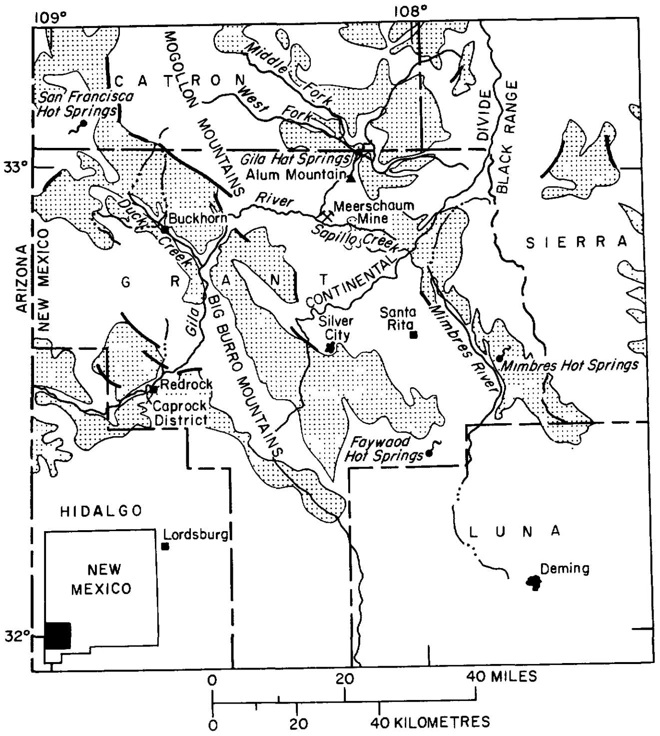

FIGURE 62.—Distribution of the Gila Conglomerate (patterned areas) in southwestern New Mexico, generalized from the New Mexico geologic map (Dane and Bachman, 1965). Heavy lines indicate faults.

TABLE 55.—*Mean content of minor elements in 14 samples of lake beds in the Gila Conglomerate, southwestern New Mexico*

[From six-step semiquantitative spectrographic analyses by J. C. Hamilton. Lithium analyses by atomic absorption by A. L. Meier. Values are in parts per million except for Fe, Mg, Ca, and Ti, which are in percent]

Element	Mean	Standard deviation	Average in shale[1]
Li (ppm)	75	43	66
Fe (percent)	2	.76	4.7
Mg (percent)	1	.41	1.5
Ca (percent)	3	2.4	2.2
Ti (percent)	.17	.05	.46
Mn (ppm)	200	70	850
B (ppm)	50	20	100
Ba (ppm)	500	180	580
Be (ppm)	1.6	.63	3
Co (ppm)	8	3.7	19
Cr (ppm)	70	27	90
Cu (ppm)	20	4.8	45
La (ppm)	30	8.9	92
Nb (ppm)	7.8	4.6	11
Ni (ppm)	17	7	68
Pb (ppm)	16	2.1	20
Sc (ppm)	8	2.6	13
Sr (ppm)	380	183	300
V (ppm)	280	130	130
Y (ppm)	16	5	26
Zr (ppm)	86	18	160

[1] Turekian and Wedepohl (1961).

salmon-colored conglomerate and sandstone which are coarser grained at the margins of basins. Towards the centers of basins, the rocks are finer grained, grading into siltstone and claystone. Locally, near the centers of the basins, gypsum deposits, tuffaceous beds, diatomaceous beds, and thin units of freshwater limestone (Heindl, 1952; Gillerman, 1964) occur. Evidence of tectonic and volcanic activity during deposition can be found in many places—lava flows and ash beds are not uncommon in the Gila. The Gila Conglomerate is locally folded and faulted (Ballmann, 1960). In some areas, such as south of Redrock, N. Mex., tufa beds, probably from old hot springs, occur in the Gila Conglomerate (Elston, 1960).

BUCKHORN AREA

Lacustrine clay, silt, and diatomite in the Gila Conglomerate crop out along U.S. Highway 180 in the valley of Duck Creek near Buckhorn, N. Mex. Although never studied in detail, these lake beds have been described by Elston (1960), Gillerman (1964), and Ratté and others (1972). The diatomite has been prospected (Gillerman, 1964) and on the southeastern margin of the old lakebed a zeolite deposit is being prospected (R. A. Sheppard, 1975, oral commun.).

Two miles (3.2 km) northwest of Buckhorn a roadcut in the lake beds exposes about 25 feet (8 m) of the diatomaceous section. The lithium values in 14 samples from this section ranged from 14 to 170 ppm—the mean value was 75 ppm, the standard deviation 43. X-ray diffraction analyses showed that besides diatoms the rock contains a montmorillonitic clay, quartz, potassium feldspar, plagioclase, biotite, clinoptilolite, calcite in some samples, and minor amphibole. Looking at hand samples through a binocular microscope revealed a rock made of diatom fragments, very small detrital grains and flakes (silt size) of quartz, feldspars, biotite, and amphiboles. In some samples pieces of reed replaced by potassium feldspar are abundant.

Spectrographic analyses of these samples show that they have a fairly uniform composition. The lithology and geochemistry of the sediments suggests that in this part of the section the lake never evaporated to dryness, but the presence of authigenic potassium feldspar and clinoptilolite suggests that it was highly alkaline. Of the elements analyzed for, only lithium and vanadium occur in anomalous amounts (table 55). However, lithium and vanadium show no correlation with each other whereas lithium does show a weak correlation with magnesium and iron.

Owing to the high (170 ppm) lithium value found in the lake beds, we decided to collect some more samples. The first sample site was a zeolite prospect pit 1.4 miles (2.25 km) southeast of the Post Office at Buckhorn, N. Mex., in NW¼ sec. 10, T. 15 S., R. 18 W. The beds in this sequence range from about 6 inches (15 cm) to 2 feet (60 cm) thick and consist of brown to gray to white zeolitic tuff, claystone, siltstone, freshwater limestone, and red, green, and gray chert. Above the excavated part of this section, limestone and chert increase. X-ray diffraction analyses showed that the claystone and siltstone consist chiefly of feldspar, quartz, clinoptilolite and clay. The lithium content of samples from this section ranged from 44 ppm in green chert to 200 ppm in the claystone. The lithium contents of the samples above the excavated part were lower (maximum 150 ppm), but this may be because the samples are more weathered.

About 1¼ miles (2 km) west of the zeolite pit another prominent section of more than 200 feet (60 m) of the lake beds is exposed in a draw. The top of this section is about 400 feet (120 m) topographically above the top of the section exposed in and near the prospect pit. A west-northwest-trending fault occurs on the north side of the draw and basalt is juxtaposed to the lake beds. According to J. C. Ratté (oral commun., 1975) the basalt is older than the lake beds. The lake beds appear to be flat lying in both areas, but detailed mapping would be necessary to determine the exact stratigraphic relationships between the two sections.

The section exposed in the cliff on the southwest side of the draw is similar to that exposed at the zeolite pit except that some prominent white beds of zeolitic tuff also occur. At the base of this section, red-gray to red-brown rocks become more prominent. Although weathered, the sediments in this section still show some anomalous lithium contents. The lithium contents range from 17 ppm in green chert to 240 ppm in a white ash bed near the base of the outcrop.

As mentioned, chert is abundant in these sections, and some of it closely resembles Magadi-type chert as described by Eugster (1967, 1969), Hay (1968, 1970), Surdam, Eugster, and Mariner (1972), and Sheppard and Gude (1974). Magadi-type chert was first reported from the Buckhorn area by D. M. Dennis (oral commun. in Sheppard and Gude, 1974). According to Surdam, Eugster, and Mariner (1972), the presence of Magadi-type chert indicates a depositional environment having a pH of at least 9.5. The lithium content of the chert sampled ranged from 17 to 84 ppm; the mean lithium content in six samples was 41 ppm and the standard deviation 23. The mean fluorine content was 1,125 ppm and the standard deviation 724. In the chert, lithium and fluorine have a correlation coefficient (r) of 0.83, indicating a strong relationship (fig. 63).

We analyzed the samples from the Buckhorn area for fluorine as well as lithium. As mentioned, the strongest correlation between lithium and fluorine was found in the chert samples. In 28 claystone and siltstone samples containing less than 1 percent fluorine the correlation coefficient between lithium and fluorine (r=0.7) indicates a fairly strong relation. However, in the samples containing more than 1 percent fluorine, there is almost no correlation between lithium and fluorine (r=0.26 for five samples). In the samples containing less than 1 percent fluorine, lithium increases as fluorine content increases; in the samples containing more than 1 percent fluorine, lithium content tends to decrease as fluorine content increases (fig. 63).

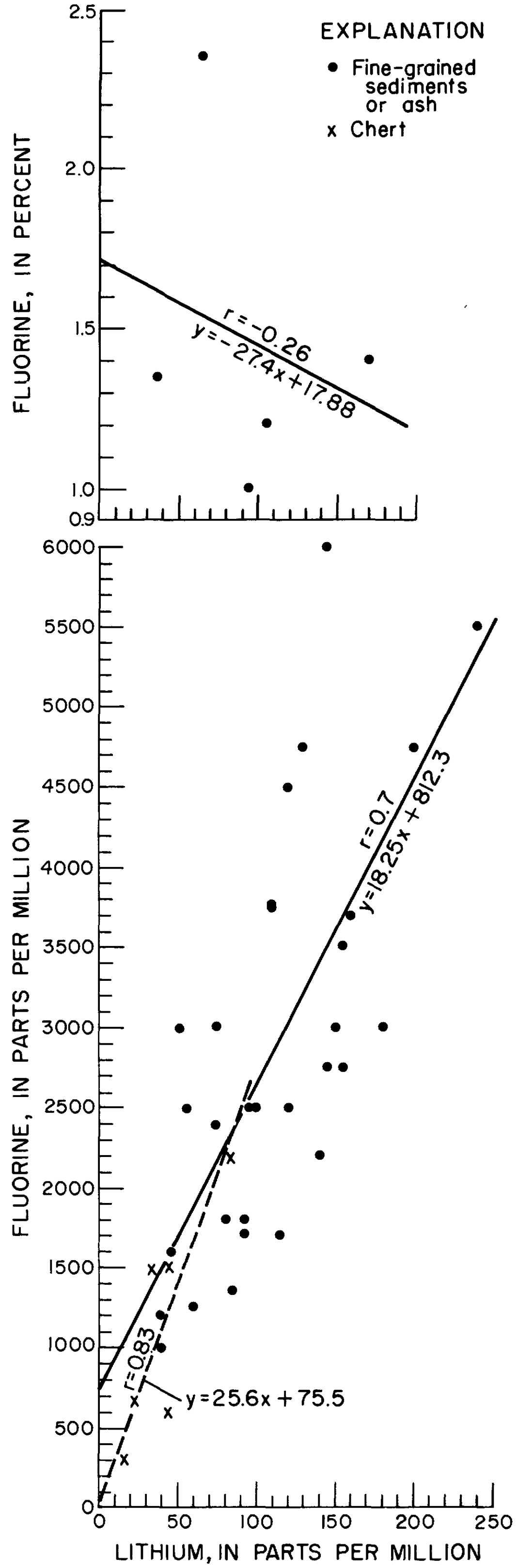

FIGURE 63.—Lithium-fluorine correlations in samples of lake-bed sediments in the Gila Conglomerate near Buckhorn, N. Mex. Correlations based on least squares linear regression equation, $y=mx+b$. x, lithium value; y, fluorine value, r, computed correlation coefficient.

HYDROTHERMAL ALTERATION OF THE GILA CONGLOMERATE

Mineralizing episodes have occurred repeatedly throughout the geologic history of southwestern New Mexico, and in several places the Gila Conglomerate is mineralized. Chrysocolla coats boulders and forms veinlets in the Gila Conglomerate in the northern Big Burro Mountains (Hewitt, 1959, p. 92; Gillerman, 1964, p. 59–60). Fluorite veins occur in the Gila (Elston, 1960, 1970), and south of Redrock, N. Mex., manganese was mined from veins in the Gila Conglomerate (Elston, 1965, p. 212). North of Silver City, N. Mex., veins of meerschaum (Sterrett, 1908; Ratté and others, 1972) occur in the Gila. Areas of hot-spring alteration are evident between Silver City and the Gila Cliff Dwellings National Monument, and hot springs are common in the area.

In the Caprock district, south of Redrock, N. Mex. (fig. 62), manganese oxide veins in the lower part of the Gila Conglomerate are associated with travertine deposits and have other features suggesting that the viens were deposited from hot springs. The lower part of the Gila in this area consists of very coarse bedded conglomerate and sandstone; cobbles as large as 15 cm in diameter occur near the manganese veins. The veins are steeply dipping to vertical and fill faults which are alined parallel to major regional structures (Gillerman, 1964, p. 168). Along with psilomelane and pyrolusite, calcite, white fluorite, and quartz occur in the veins, The quartz ranges from opaline to coarsely crystalline and generally occurs near the center of the veins. The manganese oxides replace the matrix of the conglomerate near the veins, and calcite locally cements the conglomerate. Elston and others (1973) reported that the manganese mineralization is younger than the basaltic andesites in the area dated at 20.6± 1.6 m.y.

To check the possibility of lithium occurring in the mineralizing solutions, we took some grab samples of the manganese ore, vein materials, and country rock. Lithium contents of the eight samples taken ranged from 10 to 40 ppm, so we have to conclude that either the mineralizing solutions did not contain much lithium or that the lithium was not precipitated with the manganese and fluorine. The evidence we have now, which is mostly negative, suggests that the lithium in the system was carried in the hot springs to surface drainage.

Another area of mineralized Gila Conglomerate occurs approximately 1 mile (1.6 km) north of New Mexico Highway 25 where meerschaum was mined (fig. 62). Meerschaum is a lightweight, tough clay that can be carved and is used for pipes (for smoking tobacco), as insulation for pipes, and for radio insulators. The occurrence was described by Sterrett (1908) and Ratté and others (1972). The meerschaum is in steeply dipping veins and veinlets in Gila Conglomerate and the underlying basaltic andesite (Ratté and others, 1972). Meerschaum is usually defined as sepiolite (American Geological Institute, 1957), but X-ray diffraction analysis shows the vein material from the meerschaum deposit to be palygorskite, $(Mg,Al)_2Si_4O_{10}(OH)\cdot 4H_2O$. The material also contains calcite crystals, clinoptilolite, a small amount of quartz, and and undetermined clay mineral having a sharp peak at 15 A. The altered conglomerate near the veins consists of quartz grains in a matrix of clay, clinoptilolite, palygorskite, and calcite. The lithium contents of samples from the area were low: 10 ppm in the vein material and 25 ppm in the altered conglomerate. In contrast, a sample of coarse sandstone from several miles north of the meerschaum deposit contained 105 ppm lithium. A sample of altered andesite underlying the Gila Conglomerate about 3 miles (5 km) northwest of the meerschaum deposit contained 6 ppm lithium which is half the average content (12 ppm) reported for andesites by Heier and Adams (1964). These few preliminary data suggest that lithium may have been leached from the country rock and carried out by the same solutions that deposited the palygorskite, and that similar hot-spring systems have leached the andesite underlying the Gila Conglomerate. Systematic sampling in altered and unaltered areas of Gila Conglomerate is needed to confirm or refute the leaching hypothesis.

HOT SPRINGS

Many hot springs occur in and near the Mogollon Mountains. The average lithium content of hot springs in this region, from our data and from published data (table 56), is approximately 0.25 mg/l. Chlorine averages 35 mg/l and conductivity averages 713 micromhos for eight springs. The lithium/chlorine ratios plot along a curve which has a slope normal for hot springs (Smith, this report). However, even though dilute, these springs do supply lithium.

SUMMARY

Reconnaissance sampling in southwestern New Mexico suggests an opportunity for detailed study of a geochemical cycle of lithium. We have preliminary evidence of leached rocks (a source), of mineralizing fluids (transport), and lake beds (deposition). Lakes, similar to those represented by the rocks in the valley of Duck Creek, can be a sink for the elements leached by hot springs. Although reconnaissance did not disclose anything more than anomalous lithium contents in the lake beds in the Gila Conglomerate in the Valley of Duck Creek, higher concentrations of lithium may occur within the lake bed sequence, possibly in beds of hectorite.

TABLE 56.—*Chemistry of hot springs in southwestern New Mexico*
[Leaders(----) indicate no data]

Location	Name	Temperature (°F)	Temperature (°C)	Li (mg/l)	Cl (ppm)	Conductivity (micromhos)	Specific gravity
NE¼ sec. 5, T. 13 S., R. 13 W.	Gila	148	64	0.21	110	600	1.0006
SE¼ sec. 24, T. 12 S., R. 14 W.	Unnamed	152	66	.34	115	700	1.0005
NE¼ sec. 10, T. 13 S., R. 13 W.	---- do ---------	[1]106.5	41	[1].20–0.23	[1] 98–103	[1]568–581	---
NE¼ sec. 31, T. 12 S., R. 13 W.	---- do ---------	[1]149.6	65	[1].37–0.40	[1]105–110	[1]720–771	---
NW¼ sec. 20, T. 13 S., R. 13 W.	---- do ---------	---	---	[1].25	---	---	---
NW¼ sec. 20, T. 20 S., R. 11 W.	Faywood	[2]129.2	54	.18	[2] 17	[2]610	[2]1.000
NE¼ sec. 12, T. 18 S., R. 10 W.	Mimbres	[2]129.2	54	.12	[2] 19	[2]440	[2]1.000
NE¼ sec. 14, T. 12 S., R. 20 W.	San Francisco	[2]117	47	.44	[2]473	[2]1,300	[2]1.001
Average --		133	56	.25	135	713	---

[1] Summers (1972).
[2] Summers (1965).

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LITHIUM IN CLAYEY ROCKS OF PENNSYLVANIA AGE, WESTERN PENNSYLVANIA

By HARRY A. TOURTELOT and ALLEN L. MEIER, U.S. GEOLOGICAL SURVEY, DENVER, CO

ABSTRACT

Clayey rocks of Pennsylvanian age in western Pennsylvania have a wide range of lithium concentrations. The first of three data sets consists of analyses of 162 samples of clay and shale from the Greater Pittsburgh region which were selected for testing because of possible ceramic usefulness. Lithium concentrations for shale range from less than 33 ppm to 165 ppm and for underclay from less than 33 ppm to 270 ppm; 25 samples contain 100 ppm lithium or more. Formation name, geometric mean, geometric deviation, and number of samples are as follows: Pittsburgh Formation, 15 ppm, 3.25, 27; Casselman Formation, 12 ppm, 4.13, 34; Glenshaw Formation, 47 ppm, 2.39, 22; Freeport Formation, 93 ppm, 1.97, 8; Kittanning Formation, 23 ppm, 4.19, 29, and Clarion Formation, 56 ppm, 2.83, 16. The relatively large geometric deviations indicate that the stratigraphic variation among the formation means should be viewed judiciously.

The second data set consists of analyses of 38 samples of shale, underclay, and siderite from Beaver County, Pa. The range of lithium concentrations is similar to that in the first data set, but one shale sample contains 280 ppm lithium and an underclay sample contains 330 ppm. Siderite contains 15–40 ppm lithium. Within two stratigraphic sections, lithium concentrations greater than 100 ppm may represent marine shale and concentrations less than 100 ppm may represent nonmarine shale.

The third data set consists of a subset of analyses of 13 samples of shale and underclay from Armstrong and Butler Counties and another subset of analyses of about 20 samples of flint clay from Clearfield, Jefferson, and Somerset Counties. The shale and underclay have smaller lithium concentrations than similar rocks in Beaver County, the highest value being 160 ppm in a shale. Perhaps these rocks were deposited in an area in which marine influences were very slight.

Flint clay tends to contain more lithium than any other clayey rocks analyzed: 17 of 20 flint clay samples contain 300 ppm or more and 10 of these 17 contain more than 500 ppm. In addition 6 of the 20 values cluster at about 300 ppm and another 6 cluster at about 900 ppm. Although a diaspore clay contains only 40 ppm, no differences in mineral composition that might be related to lithium content can be detected by whole-sample X-ray diffraction analyses. Flint clay is made up almost entirely of well-crystallized kaolinite. Quartz was detected in only two samples. Illite and boehmite each are present in a few samples but there is no evident relation between mineral composition and lithium content. In one set of samples through a clay bed, lithium concentrations are largest in the upper part of the bed.

Structural substitution of magnesium and lithium for aluminum may account for the occurrence of lithium in polymineralic shale and underclay that contain considerable illite as well as kaolinite if lithium concentrations are less than perhaps 300 ppm. Some lithium may be held in cation-exchange positions, but the amounts should be small because other cations should replace lithium in clay minerals in near-surface rocks in a humid climate. The small magnesium content of flint clays makes unlikely magnesium-lithium substitution in the kaolinite in flint clay, and cation exchange seems even more improbable because of the small cation-exchange capacity of well-crystallized kaolinite. The lithium content of flint clays may be due to the presence of small amounts of a lithium mineral that has not been recognized. If a mineral contains 1.5 percent lithium, 1 percent of the mineral in a sample would give the sample a lithium concentration of 150 ppm.

Underclays are thought to be the result of relatively pure accumulation of clay in low-energy coal-swamp environments or the result of severe leaching following coal-bed deposition. Flint clay and more aluminous minerals are generally interpreted as the result of extreme leaching. Another view is that flint clay, and perhaps other occurrences of kaolinite as well, are the result of silication of preexisting aluminum-hydroxide minerals. Under the conditions of either extreme leaching or silication, it is possible that lithium-bearing minerals could be formed. Although lithium aluminosilicates are known so far only from igneous rocks, the wide range of authigenic silicate minerals in the Eocene Green River Formation makes it clear that the mineral-forming potential of unusual sedimentary environments is not completely understood.

INTRODUCTION

Clay minerals are widely believed to be the primary residence sites for trace constituents, including lithium, in sedimentary rocks. Clayey rocks contain more lithium than other kinds of sedimentary rocks, the lithium contents of which are grossly proportional to their clay contents. Horstman (1957, p. 3) estimated the average lithium content of worldwide shales to be 66 ppm, an estimate accepted by Turekian and Wedepohl (1961, table 2) and Heier and Billings (1972, p. 3–k–1); other recent estimates range from 60 ppm (Ohrdorf, 1968, p. 207) to 80 ppm (Ronov and others, 1970, p. 86).

Keith and Degens (1959, p. 42) reported that marine shales of Pennsylvanian age in western Pennsylvania contain an average of 159 ppm lithium, whereas associated nonmarine shales contain 92 ppm. The geochemical interest in lithium in shales of Pennsylvanian age was reemphasized by publication of plate-reader spectrographic analyses of shale and clay in the six-county Greater Pittsburgh region as part of the U.S. Geological Survey's program of environmental studies there (O'Neill, 1973). Of the 162 samples of shale and clay selected for their possible ceramic uses, 25 have a lithium content of 100 ppm or more, and the maximum value was about 270 ppm. Brief reconnaissance sampling therefore was undertaken in 1974 and 1975 in conjunction with other work in the Greater Pittsburgh region.

This paper deals with three sets of data: (1) the plate-reader semiquantitative spectrographic analyses for lithium of 162 samples of shale and clay from the Greater Pittsburgh region; (2) atomic absorption analyses for lithium in 38 samples from Beaver County, Pa. (table 57); and (3) two data subsets, first, atomic absorption analyses for lithium of 13 samples of shale and clay from

Armstrong and Butler Counties, Pa. (table 57), and second, 21 samples of flint clay and related materials from Clearfield, Jefferson, and Somerset Counties, generously supplied for lithium analysis (table 57) by the General Refractories Company, Pittsburgh, Pa.

SHALE AND CLAY FROM DIFFERENT AREAS

GREATER PITTSBURGH REGION SHALE AND CLAY

Shale and clay resources in the Greater Pittsburgh region (Allegheny, Armstrong, Beaver, Butler, Washington, and Westmoreland Counties, figure 64) are being investigated by the Pennsylvania Bureau of Topographic and Geologic Survey in cooperation with the U.S. Geological Survey and the U.S. Bureau of Mines (O'Neill, 1973). The lithologic, physical, chemical, mineralogic, and use data obtained will contribute to broadening the natural resource base of the region. Reginald P. Briggs of the U.S. Geological Survey supplied the stratigraphic positions of most of the samples (written commun., 1974).

The 162 samples collected by the Pennsylvania Bureau of Topographic and Geologic Survey were selected primarily for the possible ceramic usefulness of the rock units sampled. Shale and clay of possible ceramic use are not particularly more prevalent in marine than in nonmarine strata, nor do these shale and clay units have other characteristics that would exclude them from the general class of fine-grained rocks called shale. The wide range of values found for lithium, from less than 33 ppm to 270 ppm, is thought probably to represent a major part of the potential spectrum of lithium contents in such rocks. Lithium concentrations in 96 of the 162 samples were reported as qualified values, that is, as "less than 33 ppm;" this value suggests that current estimates of the abundance of lithium in shale may be too large.

The lithium contents of the samples from the formations of the Allegheny, Conemaugh, and Monongahela Groups of Pennsylvanian age are summarized in figure 65. The frequency distributions are positively skewed, thus the geometric mean is the best estimate of the most common value. For some formations, more than half the samples were reported as containing less then 33 ppm lithium. Logarithmic transformations and the Cohen method of dealing with qualified values in

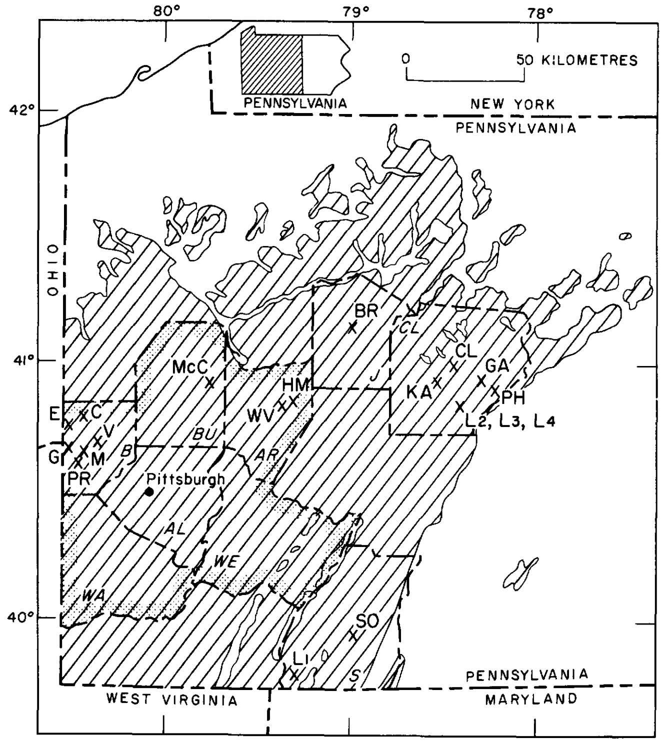

FIGURE 64.—Distribution of sample localities and rocks of Pennsylvanian and Permian ages in western Pennsylvania Pennsylvanian and Permian rocks patterned. Stipple-outlined six counties constitute the Greater Pittsburgh region. Italic capital letters indicate counties: *AL*, Allegheny; *AR*, Armstrong, *B*, Beaver; *BU*, Butler, *CL*, Clearfield; *J*, Jefferson; *S*, Somerset; *WA*, Washington; *WE*, Westmoreland. Roman capital letters, sample localities in table 57.

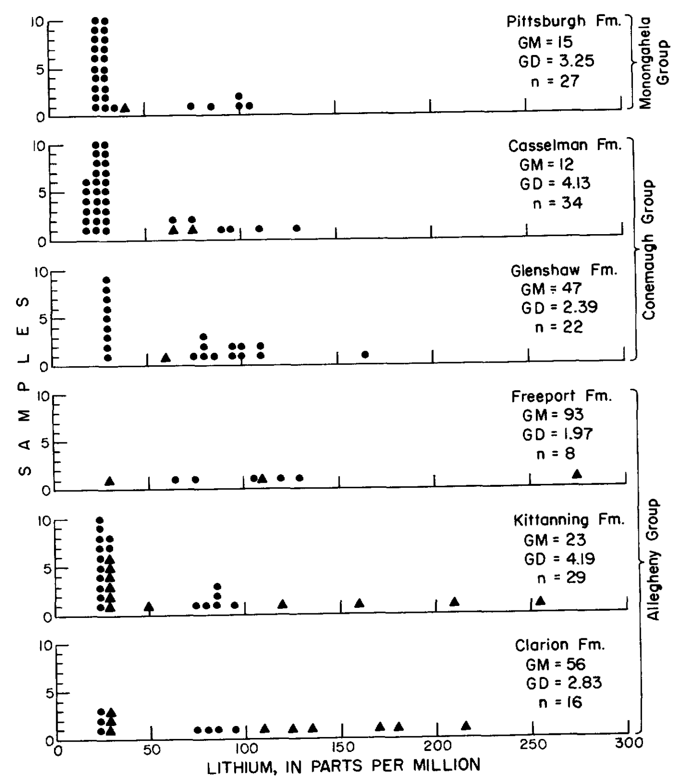

FIGURE 65.—Frequency distribution of lithium concentrations by geologic formation in Greater Pittsburgh region. Solid triangle, underclay; solid circle, shale and clay; GM, geometric mean; GD, geometric deviation; n, number of samples.

geochemistry as discussed by Miesch (1967) were used in analysis of the data.

The Freeport and Clarion Formations of the Allegheny Group and the Glenshaw Formation of the Conemaugh Group have geometric means for lithium of 93, 56, and 47 ppm, respectively. These figures are markedly different from those of the Pittsburgh Formation (15 ppm), the Casselman Formation (12 ppm), and the Kittanning Formation (23 ppm). To the extent that sample selection has not introduced large biases, these figures clearly point to the Freeport, Clarion, and Glenshaw Formations as the most interesting for future studies on lithium in shale in the Greater Pittsburgh region.

Among the samples from all formations that contain 100 ppm lithium or more, shales and underclays[1] are about equally divided with 13 and 12, respectively. It is obvious, however, that all the samples containing more than 100 ppm lithium in the Kittanning and Clarion Formations are underclays, and also these formations are the only formations in which underclays make up a significant proportion of the samples that contain less than 33 ppm lithium. This data may partly be a result of sampling, inasmuch as underclays seem to be thicker and more suitable for ceramic use in these formations than in the others and would receive more attention in sampling for ceramic testing. With respect to lithium, however, the data imply that the lithium contents of underclays are independent of the special composition and position in the sedimentational sequence of the underclays compared to the shales that make up the bulk of the coal-bearing sequences. The reason for the variability in lithium is not evident to us.

BEAVER COUNTY, PENNSYLVANIA

The sampling in Beaver County, Pa., mostly within the Kittanning Formation, was intended primarily to investigate localities reported by O'Neill (1973) that had yielded samples containing more than 100 ppm lithium, although the exact beds yielding those samples could not be identified in the field. The correspondence between the localities shown in figure 64 and those in O'Neill (1973) is shown below (capital letters are localities from figure 64 and numbers are from O'Neill):

C (Cain mine)	58 (approximately)
E (Ellsman mine)	58–60
G (Glasgow)	62
M (Midland)	63
PR (Peggs Run)	64
V (Vanport)	76–79 (approximately)

Shale, underclay, and siderite nodules were sampled to get information on the relations between lithium content and rock type and to estimate variation within stratigraphic sections. Siderite nodules were sampled because S. Landergren reported 100 ppm lithium in marine siderite iron ores (Rankama and Sahama, 1950, p. 428). The method of atomic absorption analysis is described by Meier (this report). The analyses in table 57 confirm the general magnitude of the plate-reader spectrographic analyses reported by O'Neill (1973).

The frequency distribution of lithium in shale, underclay, and siderite nodules in shale is shown in figure 66. The distribution is very similar to those derived from the spectrographic data in figure 65. The lithium contents of both shale and underclay vary widely. Most of the concentrations in shale less than 100 ppm come from the Glasgow and Vanport localities (table 57). The siderite nodules contain less than 50 ppm lithium.

The shales range in clay content from 50 to 70 percent (table 57) with quartz making up the remainder except for minor amounts of plagioclase feldspar and siderite. The clay fraction is made up chiefly of illite, but kaolinite predominates in some of the underclays and almost equals the amount of illite in many samples. Chlorite occurs in the shale in amounts of 5–10 percent, but it is generally absent from the underclays. No relation is evident between lithium content and the mineral composition of the samples.

The stratigraphic and lithologic distributions of lithium are shown in figure 67. Stratigraphic assignments are based on the geologic map of Patterson (1963), but uncertainty remains in our interpretation of the stratigraphic position of the Glasgow section. If an underclay exists beneath the Middle Kittanning coal, it is very thin compared to the underclay of the Middle Kittanning at the Ellsman mine. In addition, we did not find the Middle Kittanning coal at the Midland section, although it may be present above the sandstone at the top of the section in figure 67, at a much greater interval than separates the Middle and Lower Kittanning coals at the Ellsman mine.

Few regularities in distribution of lithium content by lithology and stratigraphic position are evident in figure 67. The largest lithium concentration is 330 ppm in a sample of the underclay of the Middle Kittanning coal at the Ellsman mine but the next largest (280 ppm) is a siderite-rich sample of black shale at the Midland locality. Samples from the Lower Kittanning underclay contain about 150 ppm lithium at both the Ellsman mine and the Midland locality.

The stratigraphic distribution of lithium in the Ellsman mine and at the Midland sections seems to be partly interpretable in terms of the difference in lithium content of marine and nonmarine shales reported by

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[1] "Underclay. A layer of fine-grained detrital material, usually clay, lying immediately beneath a coal bed or forming the floor of a coal seam" (Gary and others, 1972, p. 766). Mineralogically, most underclays consist chiefly of mixtures of kaolinite and illite in contrast to associated shales that consist of illite, kaolinite, and chlorite with admixed quartz and commonly carbonate minerals. For example, see table 57.

TABLE 57.—*Lithium contents and X-ray mineralogical analyses of clayey rocks of Pennsylvanian age, western Pennsylvania*

[Lithium analyses by A. L. Meier; X-ray diffraction analyses by H. A. Tourtelot using the method of Schultz (1964). Mineral percents in parentheses are result of different kind of X-ray analysis that yields order-of-magnitude figures only; x, mineral detected; n, mineral not detected; leaders indicate no data]

Clayey rocks	Sample locality	Li (ppm)	Clay minerals			Mineral composition		
			(Percent of total clay)			(Percent)[2]		
			Kaolinite[1]	Chlorite	Illite and expanding clay	Total clay	Quartz	Other minerals
Armstrong County								
Heilman mine								
Varicolored clay	HM1	77	21	(n)	[2]79	70	13	---
Gray clay	HM2	80	22	(n)	[2]78	40	21	Calcite 5, Dolomite 2.
West Valley mine								
Lower Freeport coal								
Dark-gray shale	WV1	160	17(2)	23	60	45	15	Siderite 5
Gray shale	WV2	72	15	(n)	[2]85	40	30	---
Coal	WV3	64	---	---	---	---	---	---
Beaver County								
Cain mine								
Underclay (Middle Kittanning coal)	C1	85	(60)(2)	(n)	[2](40)	(60)	(40)	---
Shale	C2	81	(50)	(10)	[2](40)	(55)	(45)	---
Ellsman mine								
Underclay (Lower Kittanning coal)	E1	150	(80)(2)	(n)	[2](20)	(70)	(30)	---
Dark-gray shale	E2	100	(45)(2)	(10)	[2](45)	(50)	(50)	---
Gray shale	E3	110	(40)	(10)	[2](50)	(60)	(40)	---
Siderite from above	E3s	21	(x)	(n)	(x)	(x)	(x)	Siderite(90)
Gray shale	E4	75	(40)(2)	(10)	(50)	(60)	(40)	---
Siderite from above	E4s	40	(x)	(n)	(x)	(x)	(x)	Siderite(95)
Underclay (Middle Kittanning coal)	E5	330	(60)(2)	(n)	[2](40)	(75)	(25)	---
Gray shale	E6	110	(40)	(10)	[2](50)	(50)	(50)	---
Black shaly siderite	E7	110	(x)	(x)	(x)	(30)	(20)	Siderite(50)
Gray shale	E8	100	(40)(2)	(10)	[2](50)	(50)	(50)	Plagioclase(x)
Gray shale	E9	100	(35)(2)	(15)	(50)	(50)	(50)	---
Siderite from above	E9s	18	(x)	(n)	(x)	(x)	(x)	Siderite(90)
Gray shale	E10	90	(25)(2)	(15)	(60)	(50)	(50)	Siderite(x)
Glasgow								
Gray shale	G1	67	(40)(2)	(10)	[2](50)	(55)	(45)	Plagioclase(x)
Siderite from above	G1s	14	(x)	(n)	(x)	(x)	(x)	Siderite(90), Pyrite(x)
Underclay (Middle Kittanning coal)	G2	36	(35)(2)	(n)	[2](65)	(60)	(40)	---
Black shale	G3	76	(40)	(15)	(45)	(55)	(45)	---
Siderite from above	G3s	21	(x)	(n)	(x)	(x)	(x)	Siderite(90)
Midland								
Gray shale	M1	48	(30)	(5)	(65)	(50)	(50)	Plagioclase(x)
Silty siderite from above	M1s	25	(x)	(x)	(x)	(x)	(x)	Siderite(75)
Gray shale	M2	74	(35)(2)	(n)	[2](65)	(60)	(40)	---
Siderite from above	M2s	40	(x)	(n)	(n)	(x)	(x)	Siderite(75)
Underclay (Lower Kittanning coal)	M3	160	(40)(2)	(5)	[2](55)	(60)	(40)	---
Black shale	M5	280	(45)(2)	(15)	[2](40)	(60)	(40)	---
Gray shale	M6+2	130	(40)	(10)	(50)	(55)	(45)	Plagioclase(x)
Gray shale	M6+8	150	(35)	(10)	[2](55)	(55)	(45)	Plagioclase(x)
Sandstone	M6+9	14	(75)(2)	(x)	(25)	(35)	(65)	Plagioclase(x)
Peggs Run								
Gray shale	PR1	80	(35)	(10)	(55)	(50)	(50)	Plagioclase(x)
Vanport								
Gray shale	V1	88	(35)(2)	(5)	(60)	(60)	(40)	Plagioclase(x)
Siderite from above	V1s	24	(x)	(n)	(x)	(x)	(x)	Siderite(90), Calcite(x)
Gray shale	V2	100	(40)(2)	(x)	[2](60)	(60)	(40)	---
Gray shale	V3	64	(40)(2)	(10)	(50)	(55)	(45)	---
Calcite concretion from above	V3s	16	(x)	(n)	(x)	(x)	(x)	Calcite(70), Siderite(20).
Gray shale	V4	140	(40)(2)	(10)	(50)	(55)	(45)	Plagioclase(x)
Underclay (Lower Freeport? coal)	V5	160	(35)	(10)	[2](55)	(55)	(45)	---
Gray shale	V6	130	(40)	(10)	[2](50)	(50)	(50)	Siderite(x)
Butler County								
McCall mine								
Black shale	McCl	120	12(1)	24	64	40	15	---
Underclay	McC2	13	50(2)	n	[2]50	60	15	Siderite15
Underclay	McC3	78	27(2)	2	[2]71	75	22	---
Hard clay	McC4	110	31(2)	n	69	45	18	Goethite?
Gray shale	McC5	28	26(2)	n	[2]75	40	21	---
Gray shale	McC6	80	---	---	---	---	---	---
Coal	McC7	57	---	---	---	---	---	---
Clearfield County								
Altoona flint clay	L2	950	100(1)	(n)	(n)	100	(n)	---
Freeport flint clay	CL1	320	100(1)	---	---	85	15	---
Galbraith Property, Mercer clay								
Flint clay	GA1	880	100(1)	n	n	95	n	---
Do	GA2	900	100(1)	n	x	95	---	---
Do	GA4	900	---	---	---	---	---	---
Do	GA5	840	100(1)	n	n	95	n	---
Do	GA6	550	100(1)	n	x	95	n	---
Do	GA7	590	---	---	---	---	---	---
Do	GA8	330	100(1)	n	n	95	n	
Do	GA9	320	---	---	---	---	---	---
Do	GA10	340	100(1)	n	n	95	n	---
Do	GA11	330	---	---	---	---	---	---
Do	GA12	450	100(1)	n	x	95	n	---
Curwensville-Anderson Creek area, Prospect Hole 1, Mercer clay								
Dark-gray flint clay	KA1	1400	100(1)	n	n	95	n	Boehmite x
Light-gray flint clay	KA2	850	100(1)	n	x	95	n	Boehmite x
Jeffries mines, Decatur Twsp., Mercer clay								
Dark-gray flint clay	L3	290	100(1)	n	x	95	n	---
Jeffries mines, Woodward Twsp., Mercer clay								
Diaspore flint clay	L4	41	10(1)	n	n	10	n	Diaspore 90
Philipsburg								
Gray silty shale	PH1	63	22(2)	15	63	45	26	---
Jefferson County								
Brookville flint clay	BR1	700	100(1)	n	n	95	n	Boehmite x

TABLE 57.—*Lithium contents and X-ray mineralogical analyses of clayey rocks of Pennsylvanian age, western Pennsylvania*—Continued

Clayey rocks	Sample locality	Li (ppm)	Clay minerals (Percent of total clay) Kaolinite[1]	Chlorite	Illite and expanding clay	Mineral composition (Percent)[2] Total clay	Quartz	Other minerals
Somerset county								
Mercer flint clay	L1	210	100(1)	n	n	95	n	----------------
Star Mining Co. plastic clay	SO1	150	78(1)	n	22	70	23	----------------

[1] Crystallinity shown by figures in parentheses if determinable: (1) well crystallized; (2) poorly crystallized.
[2] Illite contains much expandable material.

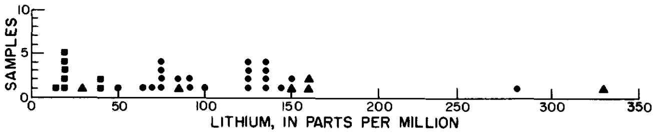

FIGURE 66.—Frequency distribution of lithium concentrations in underclay (solid triangles), shale and clay (solid circles), and siderite (solid squares) from Beaver County, Pa.

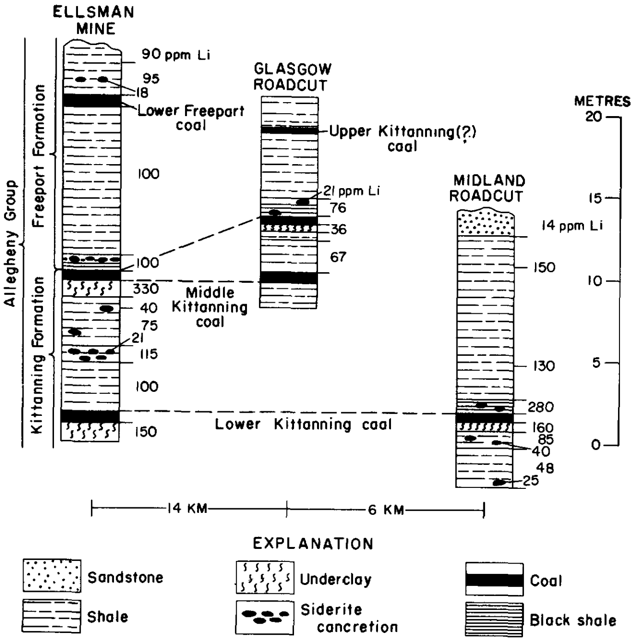

FIGURE 67.—Ellsman mine, Glasgow, and Midland stratigraphic sections, Beaver County, Pa., showing lithium concentrations by rock types.

Keith and Degans (1959) and the cyclic sequences of environments of coal deposition conceived by Edmunds (1968, p. 25–37). Although such an interpretation is highly speculative, it seems worthwhile in order to point out a potential relation between sedimentation and geochemistry of an unusual type that needs further study.

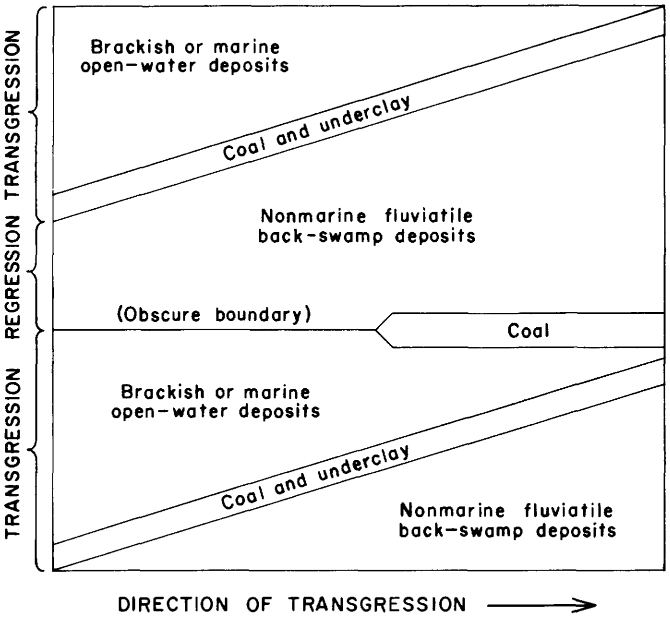

FIGURE 68.—Idealized cyclic sequence of depositional environments for coal-bearing rocks in west-central Pennsylvania. Modified from Edmunds (1968).

Edmunds' ideal sequence (fig. 68) begins with sediments deposited landwards of a coal swamp, which are transgressed by the swamp itself. The resulting underclay and coal may be regarded as generally a single unit. As transgression continues, the coal is overlaid by sediments deposited in brackish or marine open water, that transgresses the swamp. The beginning of a regression may be marked by a coal, usually without much of an underclay, but the relation between a regressive unit and the underlying transgressive unit may be obscure (Edmunds, 1968, p. 34–35). The nonmarine fluviatile deposits making up the regressive unit are complex in lithology and arrangement and are characterized by concurrent erosion-and-deposition features. Such cycles of deposition theoretically would result in nonmarine fluviatile shale containing a relatively small amount of lithium overlain by coal and then brackish or marine shale containing relatively large amounts of lithium.

If the above models hold, the beds containing less than 100 ppm lithium beneath the Lower Kittanning coal at Midland would be nonmarine, whereas the beds containing more than 100 ppm lithium above the coals at Midland would be marine. The sandstone at the top of the local section probably is a fluviatile sandstone of the regressive unit and the base of the sandstone a disconformity. Similarly, at the Ellsman mine the section between the Lower and Middle Kittanning coals could consist of transgressive marine shale containing 100 or more ppm of lithium; it is separated obscurely from an overlying regressive nonmarine shale containing less than 100 ppm lithium. The situation for the section between the Middle Kittanning and Lower Freeport coals is not clear because the sample for lithium analysis was a composite of the entire unit and the possible variation in lithium concentration from botttom to top is not determined.

The Glasgow and Vanport sections are not interpretable in these simplistic terms, perhaps partly because neither field observations nor samples were closely enough spaced to reveal a complex depositional sequence.

Keith and Degens (1959, p. 43–44) did not explain the mineralogical basis for the difference in lithium contents between marine and nonmarine shales other than to suggest that lithium and some other trace elements would be more abundant in the marine environment and might be incorporated in clay mineral structures. It was also suggested that lithium can proxy for magnesium in illite and chlorite. Nicholls and Loring (1962, p. 207–208) deduced that a substantial amount of the lithium in their rocks was an original constituent of detrital illite. At concentrations of 150 ppm or so, it seems unlikely that the mode of occurrence of lithium in polymineralic shales can be determined.

ARMSTRONG AND BUTLER COUNTIES, PENNSYLVANIA

A few samples were collected at the Heilman and West Valley coal strip mines in Armstrong County (HM and WV in figure 64) and the McCall mine in Butler County (McC in fig. 64). Very wet ground made it impossible to observe the rocks well or to collect samples systematically. The stratigraphic position of the coals is uncertain, but they are within the Allegheny Group.

The lithium concentrations are much lower than in Beaver County, the highest value being 160 ppm in a dark-gray shale at the West Valley mine. Only two other samples contain 100 ppm or more. One underclay (McCall mine, table 57) contains only 13 and 78 ppm lithium in two samples.

These rocks in Armstrong and Butler Counties may have been deposited in an area of little marine influence even though transgressive and regressive cycles are present (Edmunds, 1968, p. 30). On the other hand, if only a limited amount of lithium were available in the environments of deposition, then only small amounts of lithium could be incorporated in the rocks regardless of their marine or nonmarine origin.

FLINT CLAY

Clearfield, Jefferson, and Somerset Counties

Samples from these counties were provided by the General Refractories Company from a collection of bulk samples maintained at the Company's field office at West Decatur, Pa. The collection had accumulated over a period of years, and most if not all the samples represent mined-out deposits. Most of the samples are flint clay[2] that commonly occurs as an underclay. The flint clay in National Bureau of Standards standard sample 97 was known to be a Mercer flint clay from Clearfield County and to contain 0.23 percent Li_2O (1,070 ppm Li) (Bureau of Standards, 1931, 1955). Consequently, the opportunity to investigate the lithium content of material of this kind was a welcome one even though field observations could not be made.

Most samples of flint clay contain more lithium than do any other clayey rocks analyzed, 17 of 20 samples containing 300 ppm or more and 10 of these 17 containing more than 500 ppm (fig. 69). The range of concentration is 41 to 1,400 ppm. The lowest lithium concentration is found in a diaspore clay, which is included here with flint clay for convenience. The next lowest values, 150 and 200 ppm, come from Somerset County and may indicate regional variation in lithium content of flint clays in this part of Pennsylvania. Although most of the samples come from Clearfield County, the single sample from Jefferson County to the northwest contains 700 ppm lithium (table 57), which is in the upper range of values for all flint clay samples.

According to X-ray diffraction analysis (table 57), the flint clays are made up almost entirely of well-crystallized kaolinite. Illite is a significant component of the clay fraction only in sample SO1, which probably should be classified as a semi-flint clay (Hosterman, 1972, p. 4). However, illite is also present in detectable amounts in several other samples. Quartz was detected in only two samples. Boehmite is present in three samples in detectable amounts that might be as large as 5–10 percent. Only diaspore was detected in the diaspore sample.

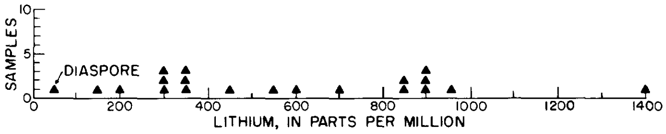

FIGURE 69.—Frequency distribution of lithium concentrations in flint clays and one diaspore clay, from Clearfield, Jefferson, and Somerset Counties, Pa.

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[2] "Flint clay is defined as a sedimentary, microcrystalline clay (rock) composed dominantly of kaolin, which breaks with a pronounced conchoidal fracture and resists slacking in water" (Keller, 1968, p. 113).

None of these mineralogic variations, except diaspore, have any evident relation to the lithium contents of the samples.

A section through the Mercer flint clay bed is shown in figure 70. Each sample represents about 15 cm (6 in.) of the bed (G. P. Jones, General Refractories Co., written commun., 1975); the bed is thus about 180 cm (6 ft) thick. The upper 75 cm of the bed contains from 840 to 900 ppm lithium in contrast to the lower 105 cm of the bed which contains from 320 to 600 ppm lithium. The bottom sample contains 450 ppm compared to the sample just above which contains 330 ppm. This marked pattern of variation within the bed does not correlate with any megascopic features of the samples and contrasts with the uniform mineral composition of the samples based on X-ray diffraction. The pattern of variation is similar, however, to that for germanium and several trace elements in coal, which is interpreted as indicating post-burial addition of elements to the coal from diagenetic, or later, circulating solutions (Nicholls, 1968, p. 289–290). Data are needed on the behavior of other elements besides lithium in sections such as this before any explanation can be offered.

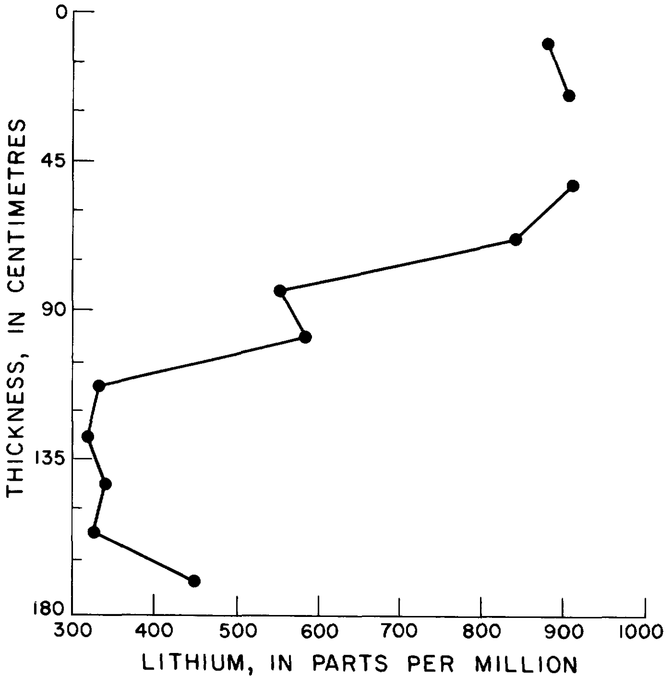

FIGURE 70.—Variations in lithium concentrations within the Mercer clay bed, Galbraith Property, Clearfield County, Pa.

OCCURRENCE OF LITHIUM IN CLAY MINERALS

The mode of occurrence of lithium in most clay minerals is not definitely known. In hectorite and stevensite, however, lithium seems to occur with magnesium in the octahedral layer (Deer and others, 1962, p. 230; Weaver and Pollard, 1973, p. 79). This mode of occurrence of lithium has led to the interpretation that lithium and magnesium are similarly paired in other clay minerals such as illite (Nicholls and Loring, 1962, p. 217–218; Tardy and others, 1972, p. 407). The lithium contents of perhaps 300 ppm or so in some of the shales and illite-rich underclays may be explainable in this way. Some lithium also may be held in ion-exchange positions, but the amounts should be very small in clay minerals in near-surface rocks, in moist climates such as in Pennsylvania, because any Li^+ likely would be displaced by more abundant cations. Lithium is the most easily replaced of the common cations in ion-exchange processes (Grim, 1968, p. 212).

Neither magnesium-lithium pairing nor cation exchange seems to explain the relatively large amounts of lithium found in these flint clays. Nearly pure kaolinites contain very little magnesium. The 14 readily recognizable sedimentary kaolinites for which Weaver and Pollard (1973, p. 132, 134) give chemical analyses contain only 0.05 to 0.46 percent magnesium oxide (0.03–0.28 percent magnesium). Most of the alkali and alkaline earth elements in kaolinite are attributable to impurities; Deer, Howie, and Zussman (1962, p. 200) give 0.15 percent magnesium oxide (0.09 percent magnesium) as the average magnesium content of a number of analyses of kaolinite with few impurities. This amount of magnesium would be equivalent to about 250 ppm lithium if Horstman's theoretical "most effective magnesium-lithium ratio" of 3.5 is applicable, which is unlikely. The magnesium-lithium ratio ranges from 6 to 490 and the median value is 30 (Horstman, 1957, p. 7, 25). Foose (1944, p. 568) gives an analysis of a typical flint clay from Clearfield County that contains 0.28 percent magnesium oxide (0.17 percent magnesium), which would correspond to about 500 ppm lithium according to Horstman's most effective ratio if all the magnesium is assigned to kaolinite, but only about 100 ppm lithium according to the median ratio of 30. Although magnesium analyses are not available for the flint clays discussed here, the published data suggest that magnesium-lithium pairing may have little to do with the lithium content of flint clays.

The cation-exchange capacity of kaolinite is the smallest of all the clay minerals and is chiefly an effect of broken crystal edges (Grim, 1968, p. 189, 193). The cation-exchange capacity of sample Kal (table 57) is about 9.5 milliequivalents per 100 grams ((H. C. Starkey, U.S. Geological Survey, written commun., 1976).

The leachate contained lithium equivalent to removing 22 ppm of the 1,400 ppm that the sample contains. Lithium in this sample thus is very tightly held. If kaolinite is the mineral in these samples in which lithium is strongly bound in structural positions, substitution to the extent of 1,000 ppm or so has not been documented.

Alternatively, the lithium in these flint clay samples may not be associated at all with kaolinite but may be occurring in a specific lithium-bearing mineral. The amounts of such a mineral could be so small as to go undetected in whole-sample X-ray analysis. Only 1 percent of a mineral containing 1.5 percent lithium (3.2 percent lithium oxide) would need to be present in the sample for the sample to contain 150 ppm lithium. If the lithium content of a sample is based on such a mineral, a sample containing 1,000 ppm lithium would contain only about 7 percent of the mineral.

Such a mineral could be derived from the same source minerals or rocks from which the kaolinite was derived. This seems a logical origin for the few to several hundred ppm lithium found in the kaolinites of Great Britain and other kaolinites derived by alteration or weathering of igneous rocks (Horstman, 1957, p. 25). The Pennsylvania kaolinites, however, and the detrital rocks with which they are associated were derived predominantly from sedimentary rocks of pre-Pennsylvanian age (Glass, 1972, p. 88) in which lithium-bearing minerals are not likely to occur. In addition, lithium-bearing flint clays in Missouri (National Bureau of Standards, 1969) seem to have been derived ultimately by weathering of a terrane made up chiefly of carbonate rocks of pre-Pennsylvanian age, in which it also seems improbable that lithium-bearing minerals would occur.

This line of thought suggests that the lithium-bearing mineral in flint clays, if such a mineral exists, is formed by the same processes by which the flint clays themselves are formed.

ORIGIN OF UNDERCLAYS AND FLINT CLAYS

The origin of underclays, of which flint clays are a special type, still is much debated despite persuasive arguments for each of two principal viewpoints. The first view is that underclays, in which kaolinite is more abundant than in the underlying shales, formed by the sedimentational concentration of clay in the quiet waters that preceded the development of most coal swamps. The beginning of the coal swamp, which may be represented only by roots and disseminated plant fragments in the underclay, may have had a preferential effect by trapping the very fine sediment. This was roughly the view of Schultz (1958) which he based on underclays in the Eastern Interior Coal Region, and of Wilson (1965) which he based on underclays in Great Britain. They observed that highly kaolinitic underclays are usually associated with highly kaolinitic shales, from which they concluded that most of the kaolinite must have developed before the sediment entered the coal swamp. They believed that only minerals highly susceptible to leaching, such as chlorite, were systematically leached in most coal swamps; and more resistant minerals, such as illite or quartz, were not generally much altered except locally under extreme leaching conditions under which flint clays developed. The second view is that underclays formed by diagenetic alteration of normal polymineralic shales beneath the coal bed. Organic-rich solutions are considered to be powerful leaching agents. This was the view of Huddle and Patterson (1961) which they based on the published record and much experience with underclays, and of Patterson and Hosterman (1962), which they based on studies in Kentucky. They observed all gradations between highly kaolinitic plastic underlays and flint clays, from which they concluded that both types of rock resulted from the same process—authigenic leaching. Implicit in the concept is that flint clay and aluminum hydroxides are the result of intensification or long continuance of the process that formed kaolinite from other clay minerals.

These two views have been combined to some extent by Keller, Westcott, and Bledsoe (1954), Keller (1968), and Williams, Bergenback, Falla, and Udagawa (1968), all of whom were concerned specifically with flint clays and more aluminous materials. Great emphasis is placed on the accumulation of colloidal material in back swamps and other special environments, the colloidal material then being leached and undergoing dialysis to remove cations. The fabric of flint clays consists of tightly interlocking crystals of kaolinite, which probably accounts for the flint-like character of typical flint clay (Keller, 1968). The fabric is similar to that of igneous rocks that have crystallized from a melt, but it seemingly results from reorganization and crystallization of colloids.

Curtis and Spears (1971) suggested that flint clays, and probably other kinds of kaolinite accumulations as well, form by silication of aluminum hydroxides such as gibbsite, and aluminum oxyhydroxides such as boehmite and diaspore. Silication of gibbsite has been demonstrated in the Arkansas bauxite deposits (Goldman and Tracey, 1946; Goldman, 1955) and was a widespread process there. Other occurrences of mixed gibbsite and kaolinite, such as the Eufaula bauxite deposits in Alabama (Warren and Clark, 1965), may have had a similar origin.

A flint clay in Australia (Loughnan, 1970) is unusual in that it occurs in a red-bed sequence instead of a coal-bearing sequence, and it contains odd minerals such as gorceixite (a complex phosphate) and gyrolite (a calcium silicate cement mineral). The minerals seem to be authigenic. This flint clay may represent an original sedimentary deposit of aluminum hydroxide and oxyhydroxide minerals that were silicated to kaolinite after deposition. The hypothesis that silication of aluminum-hydroxide and oxyhydroxide minerals is a principal process in the development of flint clay has not, however, been tested by an integrated field and laboratory investigation.

The contrasting ideas on the genesis of flint clay also identify two possible chemical regimens under which small amounts of lithium-bearing minerals could perhaps form: (1) an extreme leaching regimen that forms kaolinite or aluminum-hydroxide minerals from cation-rich aluminum-silicate minerals, whether this leaching takes place in the source area prior to the deposition of an underclay or whether it takes place afterwards; (2) a silication regimen, whether it takes place in a residual bauxite deposit or an underclay, or whether it takes place during or after the erosion and sedimentation of aluminum-hydroxide minerals.

The leaching hypothesis implies a relatively closed and short-lived chemical system, in that the process is confined to the environments of coal-forming sedimentation. The silication hypothesis implies a relatively open and long-lived chemical system in that silica would be introduced into the system from sources extraneous to the coal-forming environment and after, perhaps long after, the underclay is formed. Intuitively, the regimen of the silication hypothesis seems the more likely regimen for the formation of small amounts of lithium-bearing minerals simply because an open, long-lived system allows for a wider range of geochemical conditions, even though it may be very difficult to learn about them.

A possible lithium-bearing mineral in flint clays might be a lithium aluminosilicate, with or without other cations, of a type ordinarily thought of as occurring only in igneous rocks; or such a mineral might be a lithium aluminate. Considering the startling range of authigenic silicate minerals found in the oil shale of the Green River Formation (Milton and Eugster, 1959; Milton and others, 1960) and the unusual minerals in the Australian flint clay (Loughnan, 1970), the possibility of lithium-bearing minerals in flint clay should not be dismissed peremptorily.

CONCLUSIONS

Further investigation of lithium in flint clay and related materials is needed to determine the applicability of the three alternative modes of occurrence of the lithium that now seem possible: (1) in the well-crystallized kaolinite of the flint clays by structural substitution in the kaolinite, perhaps in association with magnesium; (2) in detrital minerals derived from the source areas of the kaolinite; (3) in a previously unrecognized authigenic mineral that formed under the same conditions and by much the same processes as the kaolinite was formed.

Such an investigation has significance not only for clarification of the origin of flint clays and related aluminous materials, but also for the possible discovery of sedimentary rocks that contain enough lithium to be ultimately of economic interest.

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LITHIUM MINERALIZATION IN ARKANSAS

By Charles G. Stone and Charles Milton, Arkansas Geological Commission, Little Rock, AR; The George Washington University, Washington, DC; U.S. Geological Survey, Reston, VA

ABSTRACT

Three lithium minerals are found in Arkansas, all in the Ouachita Mountains. Cookeite, a lithium chlorite, is associated with many small hydrothermal milky-quartz veins in the Jackfork Sandstone of Mississippian and Pennsylvanian age, in an area extending some 77 km (48 mi) from Little Rock, in Pulaski County, westward into Perry County. Cookeite has been tentatively identified in association with antimony, lead, and zinc in quartz veins in Sevier County, some 240 km (150 mi) southwest of Little Rock. Taeniolite, a rare lithia mica, occurs in smoky-quartz veins and in recrystallized novaculite adjacent to alkalic syenites at Magnet Cove, Hot Spring County, and in a milky-quartz-fluorite vein in the "V" alkalic intrusive, Garland County, some 16 km (10 mi) west of Magnet Cove. Lithiophorite, a lithium-cobalt-aluminum manganese oxide, has been reported in the manganese ore deposits in Polk and Montgomery Counties; and it also occurs with quartz veins in many other Arkansas localities.

The bromine-rich brines in the Upper Jurassic Smackover Formation in Columbia County, southwestern Arkansas, contain as much as 445 parts per million Li; smaller quantities are reported from various water wells and springs, hot and cold, in the State.

The widespread distribution of lithium minerals, for the most part unrecognized until recently, warrants further search for economic concentrations of lithium in Arkansas. Furthermore, because the three known lithium minerals appear very similar to common non-lithium species, their discovery may require somewhat sophisticated methods of identification, such as emission spectroscopy, and X-ray diffraction.

LOCATION OF LITHIUM MINERALIZATION IN ARKANSAS

The lithium minerals cookeite, taeniolite, and lithiophorite occur in Arkansas only in the Ouachita Mountains, in the west-central part of the State (table 58; fig. 71). In this region, cookeite and taeniolite each

Table 58.—*Arkansas lithium minerals*

Mineral	Formula	Li_2O (in percent)	Reference
Taeniolite	$KLiMg_2Si_4O_{10}F_2$	4	Miser and Stevens, 1938
Lithiophorite	$LiAl_2Mn_3O_93H_2O$	0–8	Fine and Frommer, 1956
Cookeite	$LiAl_5Si_3O_{10}(OH)_8$	3	Miser and Milton, 1964

occur in a limited area, but lithiophorite is widespread. Figure 72 shows the distributions of the lithium minerals in more detail. The bromine-rich brines of the Smackover Formation, which contain lithium, are in the southwest corner of the State, beneath the Coastal Plain sediments.

LITHIUM CONTENT OF ARKANSAS MINERALS

Figure 73 is a histogram showing spectrographic determinations of lithium content of many Arkansas minerals. It is evident that only the three minerals discussed in this paper have significant lithium content—the "sericite" and "fault gouge" are probably altered cookeite. Table 59 also lists these minerals, with the serial number of the X-ray powder pattern by which the mineral was identified.

TAENIOLITE

The first lithium mineral reported in Arkansas was taeniolite ($KLiMg_2Si_4O_{10}F_2$) at Magnet Cove in Hot Spring County (Miser and Stevens, 1938). It contains 4

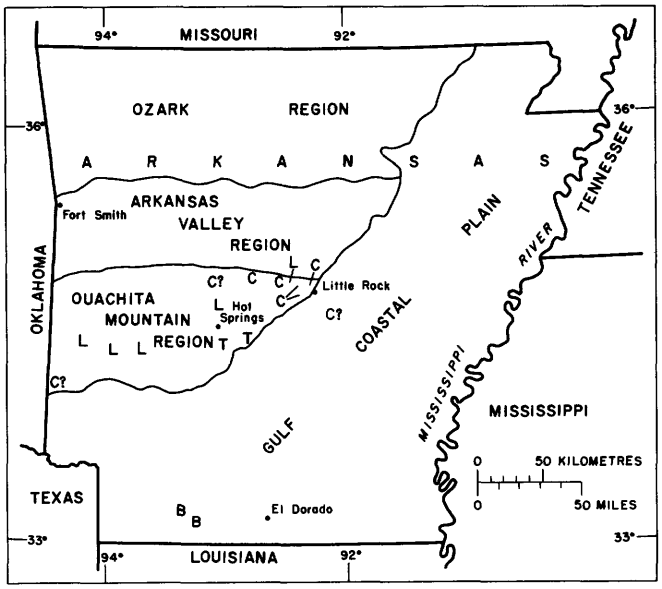

FIGURE 71.—Major areas of lithium mineralization in Arkansas. C, cookeite; T, taeniolite; L, lithiophorite; B, bromine-rich brines of Smackover Formation.

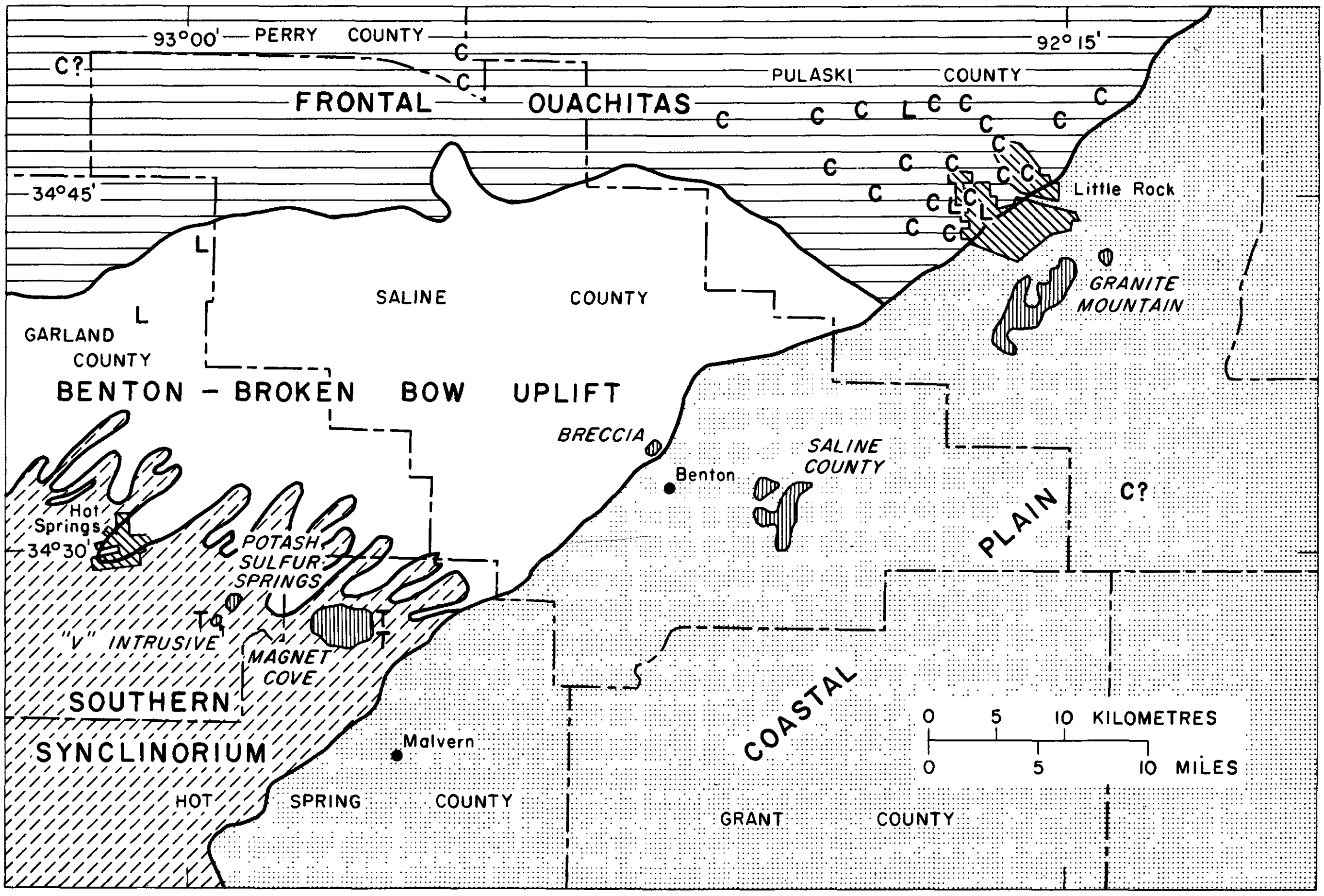

FIGURE 72.—Spatial distribution of lithium minerals in central Arkansas, showing occurrences of cookeite (C), lithiophorite (L), and taeniolite (T). Dark shading represents Cretaceous alkalic intrusives as shown by Hollingsworth (1967). Geology is from Haley (1976).

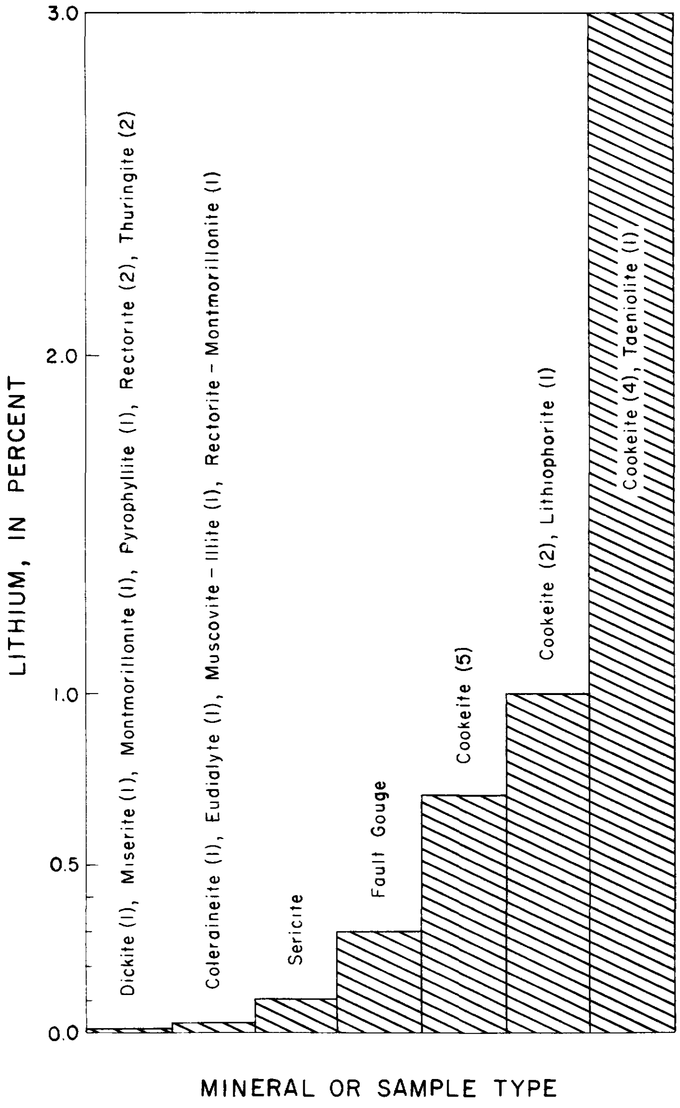

FIGURE 73.—Precentage of lithium in Arkansas minerals and fault gouge. Numbers in parentheses indicate the number of determinations on each mineral that yielded the values shown. Determinations showing less than 0.01 percent lithium were made on the following minerals: adularia (1); albite with quartz (2); K-Na feldspar (1); K feldspar with quartz (1); anthraxolite (1); chlorite (2); dickite (5); halloysite-kaolinite (6); hornblende (1); lithiophorite (3); K-Fe mica (1); miserite (1); muscovite (1); montmorillonite (2); narsarsukite (1); natrolite (1); pyrophyllite (2); narsarsukite (1); rutile (1); sphalerite (1); tetrahedrite (1); thuringite (1); wollastonite (1).

TABLE 59.—*Arkansas minerals on which lithium determinations have been made*

[Numbers are X-ray films identifying the minerals. A spectrographic analysis was made of each. Only those italicized contain significant lithium]

Adularia	348
Albite+quartz	126, 639
Na-K feldspar	645
K-Na feldspar+quartz	125, 16976, 16980
Anthraxolite	
Chlorite	16662, 16669
Cookeite	124, 1275, 1280
Cryptomelane	1261, 1267, 1213
Dickite	589, 17028, 16873, 16875, 17016
Halloysite-Kaolinite	16874, 16875, 16983 (5?), 16877, 16902, 16868
Hornblende	7/1/65 Union Carbide
Lithiophorite	573, 590, 597, 598, 1268
K-Fe mica	588
Miserite	
Muscovite	16989, 1281, 1257
Sericite	1253, 1257
Montmorillonite	16664, (0.001%), 16666
Narsarsukite	16671
Natrolite	16675
Pyrophyllite	17017, 17018
Quartz+muscovite+cookeite(?)	1247, 1248
Rectorite	16666, 16674, 16677, 16992
Rutile	341
Sphalerite	
Stevensite	1285
Taeniolite	17037
Tetrahedrite	130
Thuringite	16899, 16977, 1282
Wollastonite	

percent Li_2O. Previously, taeniolite had been discovered in Narsarsuk, Greenland, and again found in the Kola Peninsula, U.S.S.R. (Later it was found elsewhere in the Soviet Union.) In Arkansas, Milton has now found a second occurrence of Taeniolite at the "V" intrusive in Garland County, some 16 km (10 mi) west of the first. The two Arkansas localities are shown in figures 71 and 72.

In Arkansas, as elsewhere, taeniolite is associated with alkalic syenitic intrusives. The Arkansas taeniolite is related to early Late Cretaceous volcanism (Zartman and others, 1967).

At Magnet Cove, taeniolite occurs in small smoky-quartz-brookite veins and in recrystallized Arkansas Novaculite of Devonian-Mississippian age; it is associated with dickite, brookite, and rutile (Miser and Stevens, 1938; Fryklund and Holbrook, 1950). Significant concentrations of vanadium and columbium accompany the taeniolite. Herman Jackson (written commun., 1973) found that the quartz-brookite veins crystallized at a temperature under 440°C. Taeniolite generally forms less than 1 percent of the veins or of altered chert-novaculite; but locally there are concentrations as high as 20 percent (Fryklund and Holbrook, 1950).

Erickson and Blade (1963) also reported 0.03 percent lithium in some molybdenite- and rutile-bearing veins at Magnet Cove, but the lithium mineral has not been identified.

At the "V" intrusive, taeniolite occurs in a milky-quartz-fluorite vein, associated with opaline silica or chalcedony, pyrite, sulfur, gypsum, rutile, anatase, goethite, jarosite, sphalerite, dolomite, zircon, sanadine, and tourmaline; present in lesser amounts are barite, witherite, galena, brookite, and zeolite minerals; there are also small quantities of gold and silver.

In 1955, taeniolite was synthesized; it was the first synthetic mica. Miller and Johnson (1962) reported a synthetic fluor-mica intermediate between taeniolite and hectorite ($Li_xMg_{6x}Si_8O_{20}$ $(OH)_4$ <Na); it is like the

former physically and optically and like the latter in number and configuration of cations. The relationship of taeniolite, Li-Mg mica, to hectorite, a Li-Mg clay, may be compared to that of paragonite, Na-mica, to rectorite (allevardite), a Na-clay.

Table 60 gives the X-ray powder patterns of taeniolite from Magnet Cove and from the "V" intrusive, with those of the Miller and Johnson (1962) synthetic. They are all very similar.

COOKEITE

Cookeite ($LiAl_5Si_3O_{10}(OH)_8$), containing 3 percent Li_2O, was first found in Arkansas at the Jeffrey Quarry, North Little Rock, Pulaski County (Miser and Milton, 1964). It occurs in many small milky-quartz veins in the Jackfork Sandstone of Mississippian and Pennsylvanian age. Since 1964, it has been recognized in numerous other Arkansas localities, as far east as the old Kellogg Mines (about 8 km [5 mi] northeast of the Jeffrey Quarry), and possibly as far west as south-central Perry County (fig. 72)—a total east-west distance of 77 km (48 mi). Usually the cookeite forms no more than 1 or 2 percent of the quartz veins, but at the Jeffrey Quarry it may be found in much greater abundance—some kilogram-size chunks of pure cookeite are obtainable. Recently, Milton has found what may be another occurrence of cookeite associated with antimony-lead-zinc ores in quartz veins in Sevier County, about 240 km (150 mi) southwest of Little Rock.

TABLE 60.—*X-ray diffraction patterns of taeniolite*

"V" intrusive Hot Springs County		XRPD 15-256 LaLonde (1963 $KLiMg_2Si_4O_{10}F_2$ Magnet Cove, Hot Springs County		Synthetic taeniolite $K_{1.3}Mg_{4.8}Li_{1.25}Si_{7.96}O_{20.03}F_{3.97}$ Miller and Johnson (1962)	
I	*d*(*A*)	*I*	*d*(A)	*I*	*d*(a)
VS	10.02	75	10.04	86	9.949
MS	5.00	45	5.01	33	4.984
Wb	4.52	----	------	23	4.512
----	----	8	4.48	25	4.479
----	----	----	------	9	4.329
Wb	4.11	----	------	5	4.112
VWb	3.88	8	3.87	8	3.873
W	3.63	18	3.60	21	3.611
VVS	3.34	100	3.34	100	3.325
MS	2.12	25	3.12	32	3.196
MS	2.89	25	2.88	24	2.883
VVW	2.71	12	2.68	11	2.681
MS	2.60	12	2.60	22	2.602
----	----	14	2.575	24	2.575
VW	2.49	10	2.50	9	2.493
----	----	----	------	8	2.468
MS	2.38	18	2.398	33	2.396
VVW	2.26	2	2.25	5	2.257
----	----	2	2.23	5	2.236
----	----	----	------	3	2.207
VW	2.15	12	2.145	12	2.143
S	2.00	35	1.999	30	1.995
----	----	4	1.997	2	1.742
----	----	----	------	1	1.728
----	----	--	------	4	1.711
MS	1.66	18	1.655	11	1.656
----	----	----	------	5	1.619
----	----	----	------	4	1.590
----	----	8	1.521	----	----
W	1.51	6	1.507	12	1.509
----	----	4	1.491	----	----
----	----	4	1.423	----	----
VW	1.35	12	1.350	9	1.350
VW	1.30	6	1.30	7	1.304
VW	1.25	----	------	4	1.248

In a letter (Sept. 11, 1929) to Arkansas State Geologist G. C. Branner, C. S. Ross noted a possible occurrence of cookeite in granitic or pegmatitic microcline, "altered to a micaceous mineral, calcite, and a little purple fluorite." He said the micaceous mineral was in "coarse radial groups, uniaxial or nearly so." Ross gave no further details, but he probably noted the positive optical character of the mineral in support of his tentative identification. The location he gave was 1,544 ft (470 m) down in the Wilson No. 1 well of the Wonder State Development Co., in the NE¼SW¼ sec. 21, T. 2 S., R. 11 W., Pulaski County; this place is 24 km (15 mi) southeast of Little Rock.

The Arkansas cooketie is quite variable in appearance; forming coarse crystals (up to a centimetre in size), finely crystalline granular aggregates, and fibrous masses. The cookeite can be colorless, white, yellow, brown, blue, or, where impregnated with manganese oxide, black. It is often weathered to clayey masses darkened by iron-manganese oxides.

Unlike many other occurrences of cookeite, where it is found in pegmatites with other lithium minerals such as tourmaline, spodumene, and lepidolite, nearly all the Arkansas cookeite is a hydrothermal quartz vein accessory. Characteristically, it is associated with rectorite (allevardite) $NaAl(Al, Si)O(OH)\cdot 2H_2O$, a montmorillonite-type clay mineral, and thuringite, a green iron-aluminum chlorite. Ankerite, pyrite, sphalerite, and galena accompany the cookeite and rectorite in places; at the abandoned Kellogg Mines, these minerals have been mined along with chalcopyrite, freibergite (Ag-tetrahedrite), and tennantite.

Two periods of complex folding and thrust faulting which occurred mostly during the late Paleozoic are recognized in the frontal Ouachita Mountain area and the southwestern Arkansas antimony district. In each period, quartz veins were formed. In the Little Rock

TABLE 61.—*Lithium concentrations in Arkansas manganese ores (by spectroscopic analysis)*

Region	Concentration of Li (in ppm)	Number of samples	Occurrence of MnO
Batesville district (Independence County and vicinity) ----------	9.1–43.0	7	Lenticular and irregular masses in Fernvale Limestone and Cason Shale (Ordovician) and in St. Joe Limestone (Mississippian).
Ouachita Mountains:			
Martindale area (Pulaski County, west of Little Rock) ----------	2.8–51.1	3	Veins in Arkansas Novaculite (Devonian-Mississippian).
	36	1	Accumulation in Holocene bog.
Hot Springs area (Garland County) ----------------------	8.2, 47, 95	3	Veinlets and coatings on fractured Arkansas Novaculite.
Crystal Mountains (Garland and Montgomery Counties) --------	48.4	1	Manganese mine (abandoned) in Crystal Mountain Sandstone (Ordovician).
	3.1	1	Quartz crystal mine.
West central Arkansas manganese district (Montgomery County --	2590.	1	Manganese mine (abandoned) in Arkansas Novaculite.
Polk County) -------------	585–1130	2	-------- do----------------
Magnet Cove contact zone, Christy titanium-vanadium prospect, (Hot Spring County)-----------	77.7	1	Metamorphosed Arkansas Novaculite.

area, the earlier veins, probably Late Pennsylvanian to Early Permian in age, carry dickite; while the later veins, probably Early Permian to Triassic in age, contain cookeite with rectorite (Stone, 1966). The cookeite-bearing quartz veins are older than, and unrelated to, nearby nepheline syenite, kimberlite, and other intrusives of Cretaceous age.

LITHIOPHORITE

Lithiophorite, essentially $LiAl_2Mn_3O_9 \cdot 3H_2O$, with an Li_2O content ranging from 0 to 8 percent, is fairly widespread in Arkansas, although only recently noted. Fine and Frommer (1956) first reported it in a mine near Mena, in west-central Arkansas. Michael Jones, of the University of Arkansas (written commun., 1975), indicated that lithiophorite, cryptomelane, and manganite were the dominant ore minerals at many of the mines in the area. Lithiophorite also occurs with Upper Pennsylvanian-Permian-Triassic quartz veins and associated sedimentary rocks in the central and eastern Ouachita Mountains. Good specimens are found at the Coleman and Teal crystal quartz mines in Garland County. Because lithiophorite both encrusts and is intergrown with the quartz crystals, both hydrothermal and weathering processes may be involved in the crystallization of lithiophorite.

Recently, a preliminary evaluation of Arkansas manganese ores as possible sources of lithium-bearing lithiophorite has been made, with generally negative results. Manganese oxides from two regions in the State were examined spectroscopically for lithium. Results are shown in table 61. In summary, only the samples from the west-central manganese district showed significant lithium, associated with Ba (5,000 ppm), Co (1,500–5,000 ppm), Ni (2,000–5,000 ppm), Cu (2,000–3,000 ppm), and Zn (700–3,000 ppm).

Two available analyses of Arkansas lithiophorite show a Li_2O content of 0.53 percent (Michael Jones, written commun., 1975), and 0.82 percent (lithiophorite with cookeite from near Little Rock). The latter analysis, on lithiophorite from Pulaski County, Arkansas, revealed the following composition (in percent): total MnO, 59.0; CoO, 17; Al_2O_3, 20.8; Li_2O, 0.82; total H_2O, 17.3; and SiO_2, 11. (Total percentage 100.7.) The specific gravity of the sample is 3.3. (Analytical data provided by J. Marinenko, U.S. Geological Survey, Oct. 29, 1975.)

Until Fleischer and Richmond (1943) established lithiophorite as a valid species, it was termed (lithian) wad. It is now known to have a worldwide distribution, and in some places it occurs as an ore mineral. It is widespread in the Piedmont region of the eastern United States from Georgia to New England; fine specimens are abundant near Reston, Virginia.

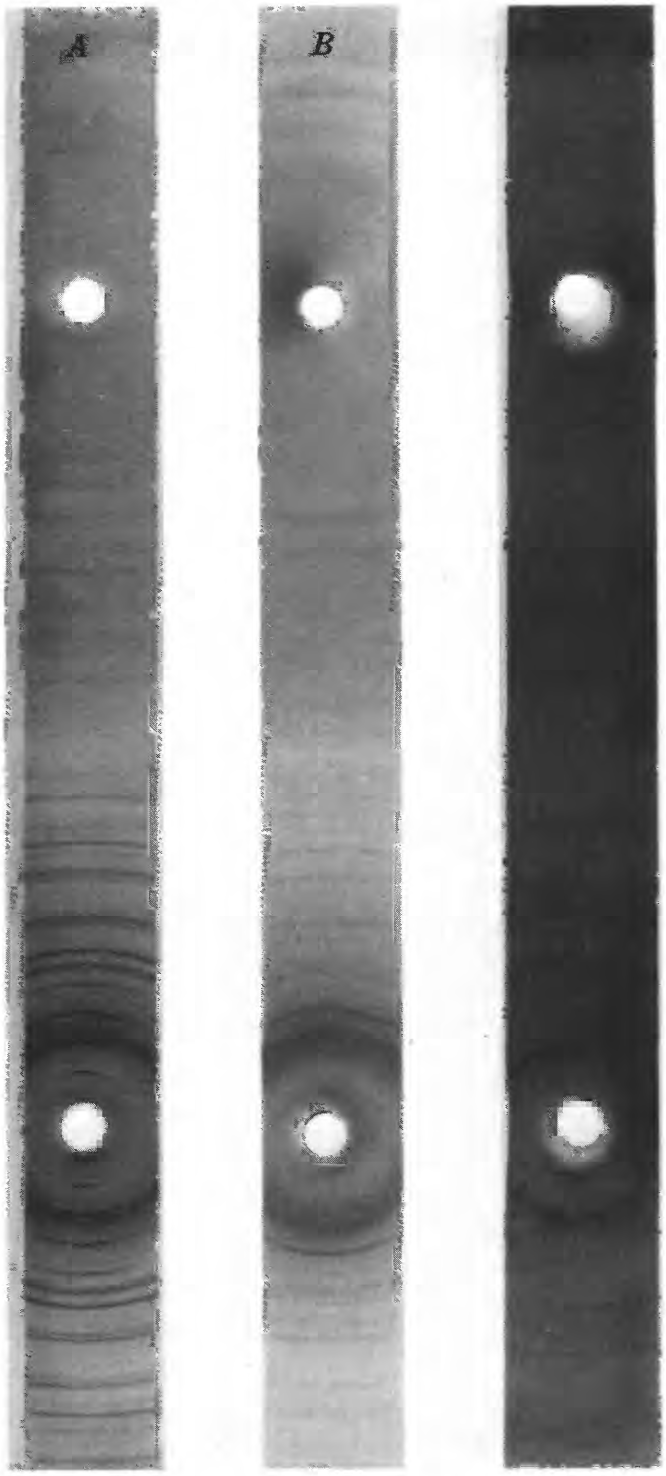

FIGURE 74.—X-ray powder patterns of cookeite *A*, taeniolite *B*, and lithiophorite *C*.

OTHER LITHIUM OCCURRENCES IN ARKANSAS

Besides the three lithium minerals discussed, and the bromine-rich brines of the Jurassic Smackover Formation, minor amounts of lithium have been noted in various hot and cold springs: Lithia Springs in Baxter County, Blaylock Springs in Polk County, and Warm Springs, in Montgomery County.

Analyses of upper Paleozoic flysch rocks in the eastern Ouachita Mountains show an average of about 100 ppm lithium, about twice that of older leptogeosynclinal rocks. Barth (1962) cites an average content of 30 ppm lithium in the earth's lithosphere.

Bauxitic clays of Arkansas are tentatively reported to carry as much as 500 ppm lithium (Harry A. Tourtelot, written commun., 1976), but presently nothing is known of the mineralogy of this lithium.

IDENTIFICATION OF LITHIUM MINERALS

All three Arkansas lithium minerals resemble common non-lithium-bearing species; taeniolite much resembles muscovite, cookeite can be confused with pyrophyllite, and lithiophorite is not markedly different in appearance from other manganese oxides. However, all three have distinctive X-ray patterns, as seen in figure 74, by which they may be conclusively recognized.

ECONOMIC POSSIBILITIES

Presently no economic concentration of lithium is known in Arkansas, but its lengthy period of geologic occurrence, its widespread distribution and local relative abundance (at Magnet Cove and North Little Rock), its presence in some manganese ores, and its presence in concentrations greater than 170 ppm in the bromine-rich brines of the Smackover Formation (191 million barrels (30.4 million m^3) of which were treated for bromine extraction in 1974) suggest the possibility of finding an economic lithium deposit in Arkansas and warrent further search.

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THE BEHAVIOR OF LITHIUM IN EXPERIMENTAL ROCK-WATER INTERACTION STUDIES

By Walter E. Dibble, Jr., and Frank W. Dickson, U.S. Geological Survey, and
Stanford University, Stanford, CA

ABSTRACT

Experiments on the interaction of granitic rock and water at temperatures as high as 275°C and pressures as high as 500 bars show that lithium can be readily removed from crystalline igneous rocks and may attain aqueous concentrations similar to those found in natural hydrothermal waters. Some of the lithium can be extracted, at high rates, from such rocks before hydrothermal alteration occurs, thus indicating that this lithium is held in cracks or on intergranular surfaces, perhaps as remnants of original pore fluids. Water-rock interaction experiments over periods of several months show that alteration of minerals in the rock will also contribute lithium to solution. Natural high-temperature water-rock interactions could be expected to contribute significant quantities of lithium to near-surface regions where it would be incorporated into stable mineral structures or would remain in subsurface solutions.

INTRODUCTION

Large resources of lithium apparently exist in the western United States in brines and sediments in topographically closed basins (Vine, 1975). Vine (1975) has suggested that these brines and sedimentary rocks have received their lithium content from hydrothermal waters. Thermal waters commonly have lithium concentrations 2 to 4 orders of magnitude higher than cold surface waters (Brondi and others, 1973). Knowledge of the source and chemical behavior of the lithium in hydrothermal solutions may increase understanding of the role of solutions in supplying lithium to the near-surface environment.

One hypothesis proposed to explain high lithium concentrations in thermal waters is that circulating hydrothermal solutions may efficiently extract lithium from the rocks through which they flow (Ellis, 1967; Brondi and others, 1973; and Vine, 1975). Another hypothesis is that the lithium is derived from primary magmatic sources. Experiments were carried out to test the former mechanism by determining the behavior of lithium in granitic rock-water interactions at elevated temperatures and pressures.

PREVIOUS WORK

Previous experiments support the contention that ordinary dilute surface waters when heated can extract lithium from a wide variety of rocks (Ellis and Mahon, 1964, 1967; Pentcheva, 1971, 1973). However, the behavior of lithium in rock-water interactions is not yet well understood. Pentcheva's studies indicate significant extraction of lithium from granite into aqueous solutions ranging in composition from pure water to dilute sodium carbonate and bicarbonate solutions. Pentcheva, who used both rock and mineral separates in her experiments, concluded that lithium was extracted from the solid phases. However, temperatures, rock-water ratios, and reaction times were unspecified.

Ellis (1967) concluded that lithium was released from crystal structures only after extensive alteration of the rock and that it could reach a concentration of 1–2 ppm (parts per million) at 500°–600°C. These conclusions were based on experiments involving the reaction of distilled water with graywacke and a variety of extrusive igneous rocks ranging from basalts to rhyolites (Ellis and Mahon, 1964, 1967). In a later report, Ellis (1970a) noted that the lithium distribution between solution and secondary minerals is not well established. Ellis (1970b) even included lithium in a group of "soluble" elements, such as chloride, bromide, boron, cesium, fluorine, and arsenic. The aqueous concentrations of these elements need not be controlled by temperature and pressure-dependent chemical equilibria involving rock minerals under some conditions.

The present work was done to determine the rates of lithium extraction from a crystalline granitic rock under controlled conditions. These experiments test whether lithium can be a "soluble" element with respect to rock leaching as Ellis (1970b) proposed.

EXPERIMENTS

METHODS

ROCK-WATER INTERACTION EXPERIMENTS

Two different types of rock-water interaction experiments were undertaken. In the first, a teflon reaction cell held in a stainless steel pressure vessel described by Dickson, Blount, and Tunell (1963) was filled with a rock-water mixture and heated to 275°C at a pressure of 500 bars. The rock used was ground to <140 mesh, and distilled water was added to form a mixture with a 1:1 rock/water weight ratio. The whole pressure vessel and furnace assembly was rocked to ensure thermal mixing of the contents. Internally filtered liquid samples were withdrawn at time intervals and analyzed for lithium.

Similar experiments were performed at lower temperatures and at 1 atmosphere pressure. Rock-water mixtures were continuously shaken at 25°C, and some of these similar mixtures were placed in containers in an oil bath at a constant temperature of 70°C. Water samples were taken after reaction times ranging from 1 day to 2 months and were analyzed for lithium.

The second type of apparatus consisted of a large-scale laboratory model of a geothermal reservoir (Hunsbedt, 1975) which can use large whole rocks for rock-water interaction experiments. This laboratory model was a large steel autoclave which can hold as much as 1 metric tonne of rock and which also has ancillary equipment, mainly for heating the water and providing circulation throughout the system. This system can produce pressures to as much as 50 bars and temperatures as high as 260°C. Individual maximum rock dimensions ranged from about 3 to 50 cm. The largest mean diameter of rocks in this apparatus was 11 cm. The total rock mass in this system was 825 kg (kilograms). Tap water was used and ranged in mass from 150 to 162 kg. No lithium was detected in the tap water. The absolute rock/water weight ratio ranged from 5:1 to 5.5:1. Liquid water samples were taken from this system at various times during experimental operation and were analyzed for lithium.

The rock used in all experiments was an unweathered medium-grained leuco-granodiorite from a quarry at Rocklin, east of Sacramento, Calif. The rock contains plagioclase, quartz, and some potassium feldspar and biotite. The lithium content is 43 ppm.

ANALYSIS

Lithium was analyzed by atomic absorption spectroscopy, with a precision of ±3 percent and a limit of detection of 25 ppb (parts per billion).

RESULTS

Data from the rock powder-distilled water interaction experiments (table 62) indicate the rate of lithium extraction under conditions of constant temperature and pressure. Experiment 1 (table 62) was done by use of the high temperature equipment designed by Dickson, Blount, and Tunell (1963). These experimental data show that lithium is removed from the rock powder at high rates at 275°C and 500 bars. After 5 days, the lithium concentration in solution was about 1.3 ppm which also represents the quantity removed from the rock at a rock/water ratio of 1:1. Subsequently, the value of the rock/water ratio increased to about 1.5 as liquid samples were withdrawn. The solution pH, measured at 25°C, indicated slightly alkaline experimental conditions and remained nearly constant after the first day. After 6 months, almost 2.5 ppm lithium had been leached from the rock, or about 6 percent of that originally present.

A plot of lithium concentration versus time for experiment 1 (fig. 75) illustrates the exponential increase of lithium concentration in solution with time and the approach to a nearly constant value. The same lithium concentration data plotted against the ½ power of time (fig. 75, circles) results in a straight line for the first 36 days. This line extrapolates to 750 ppb lithium at reaction times near zero. The first water sample was taken from this apparatus before the final experimental conditions were established. The lithium concentration in the first sample, 250 ppb, was attained in 8 hours after a temperature increase from 25°C to 256°C. The value of 750 ppb more closely represents the initial lithium concentration at the experimental conditions. This concentration was attained a few hours after the temperature of 275°C was reached (table 62). These data illustrate the very rapid initial lithium extraction rate.

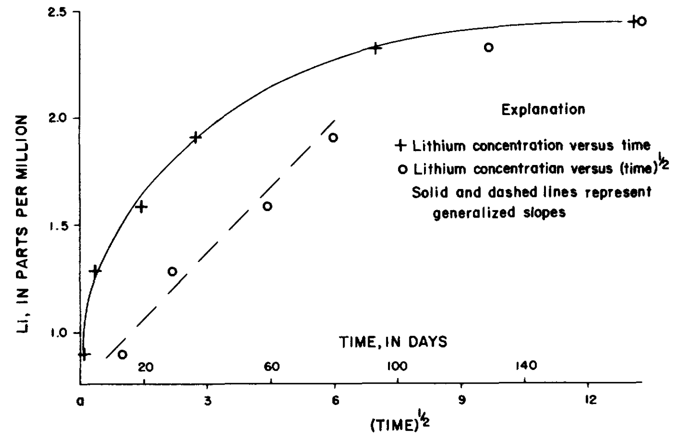

FIGURE 75.—Rock powder-water interaction at 275°C and 500 bars.

The last set of rock powder-water interaction experiments (table 62) also suggest that some lithium may be rapidly removed from the rock even when negligible alteration occurs. At 70°C, 300 ppb lithium was leached after 2 months as shown by experiment 2 (table 62). Experiments 3, 4, and 5 represent the successive leaching of the rock powder at 25°C. In these experiments, the same rock powder was leached three times. The first and second extractions removed 150 and 100 ppb lithium from the rock respectively. The third leach removed 55 ppb lithium from the same powder. These mixtures had been shaken for as long as 36 hours. The total amount of lithium extracted from the rock, 305 ppb, was about the same as was leached in experiment 2 (table 62). Alteration of the rock was undetectable during these experiments.

The data from the whole rock-water experiments obtained by use of the large autoclave (table 63) are useful in indicating the quantity of lithium that goes into solution from large mass rocks with small external surface area as compared to the quantity from the rock powder experiments. These experiments also closely resemble the successive extraction studies done at 25°C using rock powder. After each experiment, all the solution was

TABLE 62.—*Data from rock powder-distilled water interaction experiments*

Experiment No.	pH (25°C)	Rock/water ratio	Lithium concentration (ppb)	Temperature (°C)	Pressure (bars)	Time[1] (days)
1		1.00	----	25	1	0
1	6.65	1.00	250	256	500	.33
1	6.10	1.09	895	275	500	1.00
1	6.03	1.15	1280	275	500	4.8
1	6.11	1.21	1580	275	500	19.7
1	6.39	1.26	1903	275	500	36.8
1	6.30	1.38	2320	275	500	93.7
1	6.26	1.52	2430	275	500	174.7
2		1.00	300	70	1	65.0
3		1.00	150	25	1	1.5
4		1.00	100	25	1	1.0
5		1.00	55	25	1	1.0

[1] Measured from start of experiment.

TABLE 63.—*Data from whole rock-water interaction experiments*

Experiment No.	Temperature (°C)	Lithium concentration (ppb)	Time[1] (hrs)
1	25	n/d[2]	0
1	188	30	4
1	249	95	7
1	93	280	31
2	250	130	7
3	250	140	7
3	127	230	30
4	250	155	7
5	149	220	72
5	180	290	240
5	60	340	504
9	177	100	168
10	20	n/d[2]	0
10	246	126	28
10	20	168	336

[1] Measured from start of experiment.
[2] Not detected.

drained, and any lithium leached from the rock was removed from the system. However, in contrast to the rock powder leaching experiments, the rock/water ratio was higher (5:1–5.5:1), and the aqueous lithium concentrations were, therefore, greater than the actual amount leached from the rock. The data in table 63 indicate, however, that a surprising amount of lithium was extracted even for very short reaction times and after several successive leaches.

Ten experiments involving heating the water in contact with the rocks in the autoclave were performed. The temperature during each experiment varied from about 25°C to a maximum between 175° and 250°C and then decreased to 25°C. The pressures at all times are water-vapor pressures at the experimental temperature. In experiments 1 and 3 (table 63), some water was removed as steam after the temperature maximum. For these experiments, lithium concentrations measured after the temperature maximum may represent slightly concentrated values inasmuch as the steam contained no detectable lithium.

The variation in temperature that occurred during the experiments made it possible to determine if lithium extracted at high temperatures reentered the rock when the system cooled down. It is clear from the data (table 63) that no depletion of lithium occurred in solution during any experiment as the temperature decreased. Lithium concentrations continually increased for the duration of the experiments as is evident from experiment 10 during which the temperature increased from 20°C to a maximum of 246°C and then decreased to 20°C. The lithium concentration in solution increased at a regular rate and the last sample taken had the highest lithium content, 168 ppb. The preceding experiments show the same trend: longer reaction times invariably correlate with higher lithium concentrations.

Some evidence indicates that the maximum temperature attained during an experiment influenced the rate of lithium extraction. The data do not show this clearly, but the average lithium extraction rates were higher in experiments that attained a higher maximum temperature. This relationship is obscured somewhat by the fact that during the latter experiments and under the same conditions less lithium was being removed from the rock. The data suggest that more lithium can be removed from the rock by further leaching. More experiments are planned using the same rock load.

After eight leaching experiments, thin sections of the rock were examined and no evidence of alteration was observed. Most rock surfaces were unaltered as well.

DISCUSSION

The lithium extraction rate data from the high temperature and pressure interaction studies (fig. 75 and table 62) are useful in indicating the source of lithium and a removal mechanism. A possible diffusion control of rates is suggested during the first 36 days of experiment 1 (fig. 75) by the linear region on the $t^{1/2}$ plot. (See also Wollast, 1967.) A diffusion mechanism would be important if lithium is transported to the bulk solution through altered zones around unstable minerals (Helgeson, 1971; Luce and others, 1972). Another possibility is that diffusion through pores in an artificially lithified rock may be the dominant transport mechanism to the bulk solution. Even though the apparatus was rocking, the powder tended to settle to the bottom of the teflon cell. Similar lithification effects were noted by Bischoff and Dickson (1975), who used the same equipment to study basalt-seawater interactions. Whatever the diffusion mechansim, a rate-controlled process involving diffusion was probably important during the first 36 days of the experiment. It is uncertain whether an equilibrium concentration had been attained at the greatest reaction times or whether a much slower rate of lithium removal had been established.

The very rapid increase in the aqueous lithium concentration during the first few hours of experiment 1 (table 62) is difficult to attribute to rock alteration processes. The lithium concentration of 750 ppb obtained by extrapolating the linear part of the $t^{1/2}$ plot in figure 75 to reaction times near zero probably represents a quantity of lithium available in readily soluble form. Soluble salts containing lithium may have been derived from original pore fluid inclusions during grinding. After only 5 days, about 1.3 ppm lithium had been removed from the rock suggesting that even more lithium than 0.75 ppm may exist in some highly soluble form. It becomes increasingly difficult to estimate how much "soluble" lithium is responsible for the increase in lithium content of the aqueous phase after 5 days. Certainly a large fraction of the quantity extracted after 6 months (2.5 ppm) is derived from rock alteration processes.

The low-temperature interaction studies (table 62) also indicate a source of lithium that does not involve extensive rock alteration. The source of the lithium in these experiments is probably the same as in the higher temperature experiments at low reaction times. However, high temperatures seem to facilitate lithium extraction. Only about 300 ppb lithium could be removed from the rock powder at temperatures of 70°C or less, even for time periods as long as 2 months. From 0.75 to 1.0 ppm lithium was leached in only hours at 275°C and 500 bars. The larger quantity of lithium removed initially at the higher temperature may reflect higher transport rates or some other factors that are not well understood, such as rapid temperature-dependent ion-exchange processes.

The data from the whole rock-water interaction studies also suggested that a "soluble" source of lithium exists in the rock and that its removal is dependent on the time of interaction and the temperatures attained during the course of the experiments. Estimates of the amount of lithium removed from the whole rock can be compared directly with amounts leached from the rock powder. Reasonable estimates for the total lithium concentration decrease in the whole rock after 10 successive leaches range from 0.4 to 0.6 ppm. The calculation assumes the bulk rock/water ratio to be 5.0:1. This concentration range is within the 0.3–1.3 ppm estimated to be "soluble" lithium removed during the rock-powder extraction experiments. This lithium must have come from the rock interiors and cannot be attributed to significant observable rock alteration. This hypothesis is consistent with some lithium being present on intergranular surfaces or in original pore fluids.

Ellis and Mahon (1967, p. 519) suggested that "soluble" elements in the more crystalline samples of the rocks they studied were held simply on intergranular surfaces of the rock rather than in solid solutions in silicate minerals or glass. Sprunt and Brace (1974) showed that granitic rocks could have as much as 1.2 percent porosity. They also discussed several kinds of data that strongly implied high pore connectivity. In our experiments, the lithium in the whole rocks had to be sufficiently accessible during the relatively small times of reaction to account for the lithium concentrations observed in the bulk solution.

A diffusion mechanism or combined-diffusion-infiltration mechanism (Fletcher and Hofmann, 1974) seems necessary to account for the extraction of lithium from the rock interiors. Diffusion transport rates are strongly temperature dependent, increasing at higher temperatures. Diffusion at elevated temperatures through aqueous solutions in microcavities with a high connectivity is a reasonable mechanism to account for the observed lithium fluxes.

If it is assumed that the "soluble" lithium is contained within 1 percent fluid-saturated rock porosity, the lithium concentration in the pore fluid can be estimated. If between 0.3 and 1.5 ppm of the total lithium in the rock exists in pore fluids, the pore solution concentration must range from 80 to 400 ppm. The pore solutions, therefore, may be more highly concentrated in lithium than most dilute hydrothermal waters (Ellis, 1970b). Pore solutions contained within crystalline igneous rocks could represent water trapped in the rock just after crystallization of the solid phases (Sprunt and Brace, 1974). If this is true, lithium and other "soluble" elements extracted from pore solutions and introduced into meteoric hydrothermal waters could be considered to have a "magmatic water" source. This "magmatic" source is, of course, not the direct source that may be a possibility for some hydrothermal systems. This consideration, however, would further blur the distinction between a "magmatic" and high-temperature rock-water interaction origin for many of the elements contained in rock pores described as "soluble" by Ellis (1970b).

CONCLUSIONS

The described experimental work shows that lithium may be extracted from a crystalline granitic rock at high rates with little observable hydrothermal alteration. This fact indicates that as much as 1 ppm lithium is held on intergranular surfaces or in cracks, perhaps as remnants of original pore solutions. At a 1:1 rock/water ratio, aqueous lithium concentrations to as much as 2.5 ppm have been attained at 275°C and 500 bars in 6 months, suggesting that alteration of minerals in the rock also contributes lithium to solution.

These concentrations and higher values that would occur for greater rock/water ratios compare favorably with the lithium concentrations in many hydrothermal waters (Ellis, 1970b). Circulation within a hydrothermal system may carry lithium to regions where it does enter stable mineral structures perhaps in near-surface, lake sediment-brine systems.

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AN INTEGRATED GEOPHYSICAL APPROACH TO LITHIUM EXPLORATION

By Bruce D. Smith and Don R. Mabey, U.S. Geological Survey, Denver, CO

ABSTRACT

Integrated geological and geophysical methods can be successfully applied to lithium exploration problems. This conclusion is supported by geophysical surveys which have been made in Searles Lake, California; Clayton Valley, Nevada; and the Willcox Playa, Arizona. Gravity data from the Searles Lake area demonstrate that thick accumulation of sediments are not located in the geometric center of the basin. Similar data from Clayton Valley define the location of major normal faults not obvious from surface geologic mapping. The gravity data provide a regional setting for the tectonic and structural features of Clayton Valley which may be related to the occurrence of lithium brines. Direct current resistivity soundings conducted in this area define a sequence of conductive rocks containing brines from which lithium is produced. Consequently combined geophysical methods can be used to locate areas which may be favorable for the occurrence of brine which may contain lithium.

The geophysical features of Clayton Valley are compared to those of Sulphur Springs Valley, which has been defined as an area geochemically anomalous in lithium. Regional gravity and airborne magnetic surveys demonstrate many geologic features similar to Clayton Valley. Surface and airborne electrical surveys define a closed basin containing a thick sequence of conductive sediments which may contain lithium brines.

Though geophysical surveys can yield data capable of definition of areas favorable for the lithium bearing brines, the geological and geophysical characters of such brines are not well defined. Borehole logging methods and laboratory measurements of rock properties of evaporite sediments will provide useful information about physical parameters of sediments which may contain lithium. On a larger scale, remote sensing surveys may be used to relate possible geologic features of Clayton Valley to other closed basins within the Basin and Range Province. The geophysical characterization of areas favorable for lithium brine deposits is essential to the assessment and development of such deposits to meet the future industrial requirements of lithium.

INTRODUCTION

Integrated geological and geophysical methods can be applied successfully to exploration for lithium brines. Geophysical data and their interpretation which support this conclusion are presented in the following discussion. Geophysical methods have not generally been employed in exploration for bedded saline deposits in the United States, with the exception of the application of gravity and seismic methods to definition of salt domes. In particular, geophysical methods have not been used in exploration for lithium brines for two reasons. First, lithium minerals do not produce a direct geophysical anomaly because they are neither sufficiently abundant nor do they have a distinctive physical property to produce the kind of anomalies associated with sulfide or iron ore deposits. The second reason that geophysical methods have not been used in exploration is that they are found in sediments where drilling costs are much less than in hard rocks.

The definition of a physical model or models is fundamental in successful completion of any mineral exploration program. The physical parameters for a model of lithium brine deposits are not very well defined. Consequently an important aspect of the U.S. Geological Survey lithium program is to provide information on the physical properties of proven and potential lithium brine deposits.

GEOPHYSICAL APPLICATIONS

Geophysical surveys that are pertinent to lithium brine exploration have been conducted in three areas: Searles Lake, Clayton Valley, and Willcox Playa. The geophysical methods which we have used in exploration for bedded saline mineral deposits are seismic, gravity, magnetic, d.c. resistivity, and electromagnetic methods. Unfortunately the description of these methods in detail is beyond the scope of this report. An excellent overview of geophysical methods applied to groundwater exploration is given by Zohdy, Eaton, and Mabey (1974). Many geophysical methods used to define a brine-fresh water interface can be used in exploration for brines which may contain lithium. Basic textbooks describing geophysical theory and methods have been written by Parasnis (1962), Dobrin (1960) and Griffiths and King (1965).

SEARLES LAKE

Lithium is produced as a by-product of mining evaporite deposits at Searles Lake near Trona, California (fig. 76). Gravity and siesmic surveys were made in this area in the 1950's by the U.S. Geological Survey in conjunction with exploration for, and evaluation of, evaporite mineral deposits. The objective of the gravity survey was to define the geometry of sediment-basement rock contact of the basin. Seismic reflection surveys were carried out to determine structure within the sedimentary sequence. An interpretation of these data is given in figure 77. Much of the structure within the sedimentary sequence was interpreted from the seismic data since the density contrasts within the sedimentary sequence are not sufficiently large to interpret their internal structure solely from the gravity data. The sedimentary structure shown in figure 77 proved to be essentially correct by information obtained from subsequent commercial drilling. This success can be directly attributed to the combined use of geophysical methods integrated with geological work.

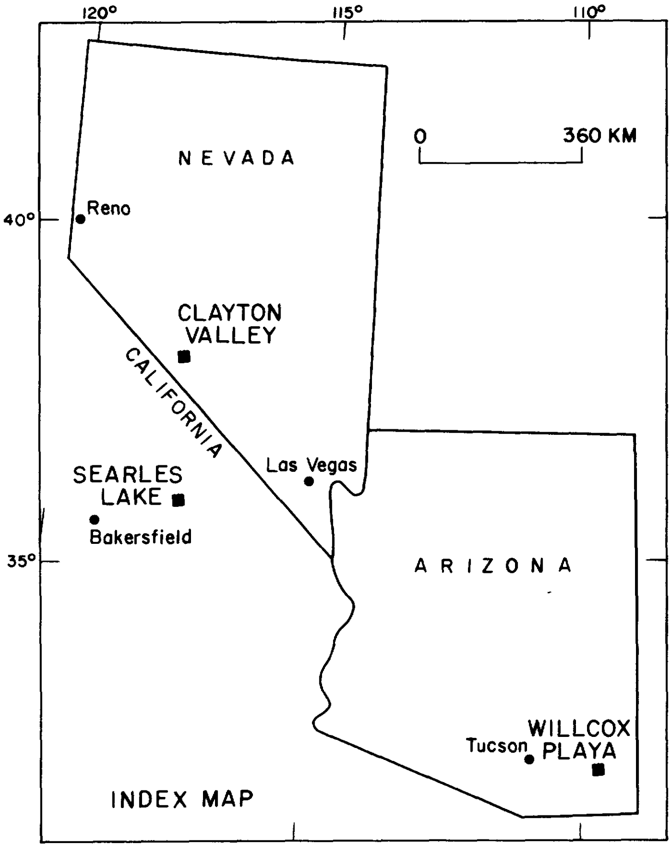

FIGURE 76.—Location of Searles Lake, Clayton Valley, and Willcox Playa.

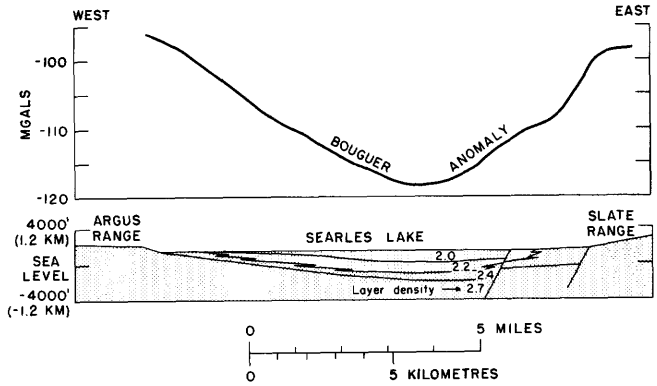

FIGURE 77.—Geological interpretation of gravity data from Searles Lake, Calif.

One feature of the structure of the Searles Lake is that the thickest accumulation of sediments is not located at the geometric center of the basin. We have observed that generally the thickest accumulation of sediments does not coincide with the geometric center of many of the basins within the Basin and Range Province. Under favorable geologic conditions, a thick sequence of sediments may constitute a favorable target area for the occurrence of lithium bearing sediments. Geological aspects of the Searles Lake Valley are described by G.I. Smith (this report) and the lithium production is described by Rykken (this report).

The geophysical data and their interpretation presented above have not directly indicated the presence or absence of lithium. However, the interpretation given in figure 77 does provide a geologocal setting for the area which could only be obtained otherwise by extensive drilling.

CLAYTON VALLEY

Clayton Valley, near Silver Peak, Nevada (fig. 76) is the only area in the free world where lithium is the major product of brine production from sediments. Consequently we will examine the area in detail.

The U.S. Geological Survey has conducted a large-scale gravity survey in Clayton Valley and Big Smoky Valley to the northeast of Clayton Valley. The complete gravity map is given in figure 78 (Wilson, 1975). The gravity map incorporated data from a small-scale survey in the area of Clayton playa made available by the Foote Mineral Company.

The first general feature of the gravity data is that there is a gravity low trending from Big Smoky Valley into Clayton Valley. This gravity low trends through the topographic high which separates the two valleys. Consequently, at some point in the geologic history of the area, the two basins may have been connected hydrologically and a connection may exist now. The major implication of this general interpretation is related to the problem of determining the source of the lithium. The possible hydrologic connection between Big Smoky and Clayton Valley suggests that rocks marginal to both basins should be considered as potential source rocks. This interpretation of the gravity data also makes Big Smoky Valley a potential target area for lithium brines.

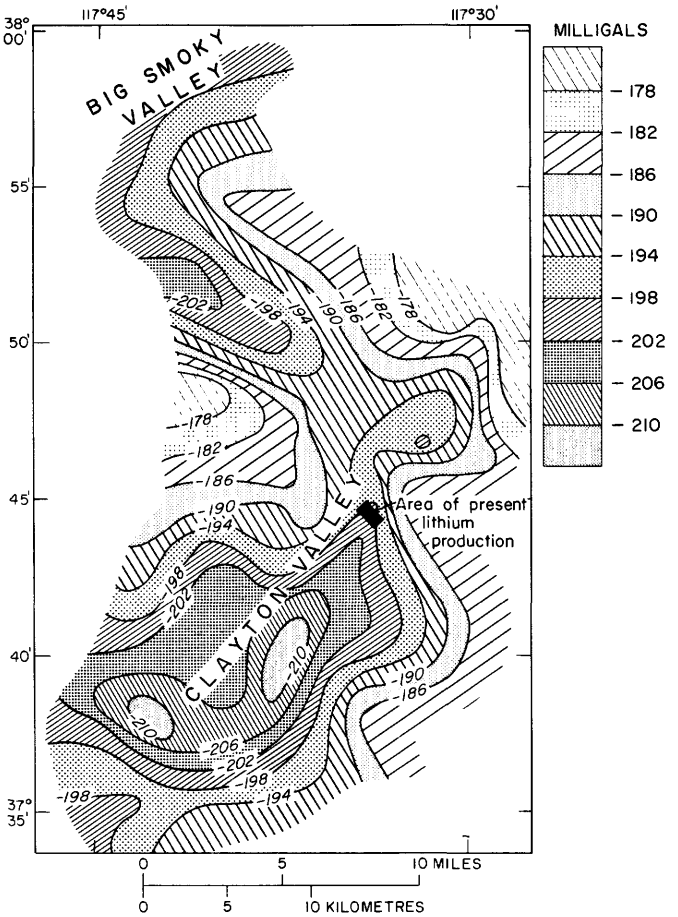

FIGURE 78.—Regional Bouguer gravity map of Clayton Valley, Nev.

A second feature of the gravity map given in figure 78 is the gravity lows at the south end of Clayton Valley. The lows indicate a thick sequence of sediments associated with the paleostructure of Clayton Valley which are not coincident with the topographic center of the basin. This sequence of sediments constitutes a potential target for evaporite deposits which may have associated lithium deposits.

The most interesting feature of the gravity map (fig. 78) is the location of current lithium production in relation to the gravity anomalies. Present lithium production is approximately located by the hachured area of figure 78. The mineralized area is terminated to the north in the same geometrical pattern as the gravity contours. The steep gravity gradient adjacent to the area of the lithium production probably reflects a major normal fault. Generally faults may be sites of introduction of hydrothermal waters which could contain lithium and (or) influence the circulation of waters containing lithium.

The Foote Mineral Company recognized that surface geophysical data could be useful in their development program and contracted for a number of different geophysical surveys. A portion of the electrical sounding data taken in the area of current lithium production has been released by the company for this report.

The electrical sounding data were collected with the Wenner d.c. resistivity array. This is one of two popular arrays used in groundwater exploration problems. The other array is termed the Schlumberger array. Figure 79 illustrates the geometry of the two arrays. Basically, a reading of the resistivity of the earth is obtained by transmitting a current through the transmitter electrodes (A,B) and measuring a voltage across the receiving electrodes (M,N). Once a measurement has been made, the distance between the transmitter electrodes is increased. For the Schlumberger array, the distance between receiving electrodes is increased only when the voltage becomes too small to measure. For the Wenner array, both the transmitting and receiving electrodes are moved to maintain the value "a" (fig. 79) as one third the distance between the transmitting electrodes. Generally as the distance between transmitting electrodes is in-

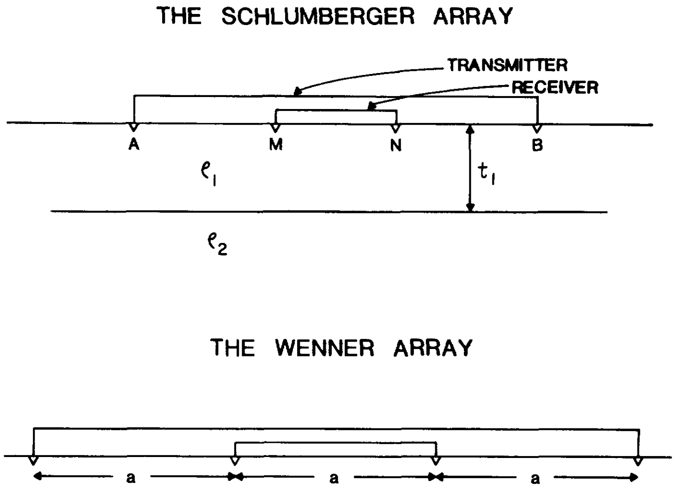

FIGURE 79.—Wenner and Schlumberger arrays used in d.c. resistivity sounding.

creased, the resistivity measurements reflect deeper parts of the earth. Since the resistivity measurements are not always the true resistivity of the earth, they are termed apparent resistivity values. Zohdy, Mabey, and Eaton (1974) give an excellent discussion of d.c. resistivity measurements.

One set of Wenner d.c. resistivity measurements taken in the Clayton Valley area is given in figure 80. The measurements are plotted as a function of increasing electrode separation or the value "a" as discussed previously. These data are then interpreted in terms of a horizontally layered earth with each layer having a certain thickness and true resistivity. The interpreted layered earth structure is also given in figure 80. The theoretical fit to the measured values of apparent resistivity is given by the solid curve.

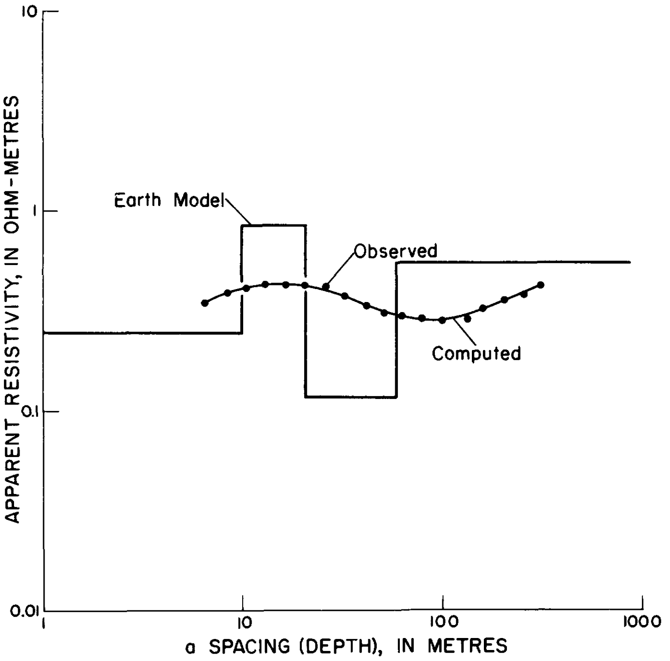

FIGURE 80.—Wenner sounding data and interpretation from Clayton Valley, Nev

A lithologic log of a drill hole near this sounding reveals that the geologic section consists of a number of layers of halite and clay. The lithologic log demonstrates that the lithology is much more complex than the interpreted resistivity variation given in figure 80, Consequently the resistivity data only reflect an average of the actual lithologic variation. However, the variations between different sets of resistivity measurements can and do imply important variations in the lithology.

An interpreted geoelectric cross section of the earth can be constructed from a number of d.c. resistivity soundings. Figure 81 illustrates a geoelectic cross section across the area of lithium production. Wenner sounding #2 is located well outside of the area of current lithium production. The interpreted sequence of conductive rocks is thinnest for this sounding. The resistive strata interpreted for all three of the soundings is not the bed rock or basement for the sedimentary sequence but is probably less permeable sediments than the conductive rocks.

In general there is a good correspondence between the thickness of very conductive sediments (low resistivity) and the reported area of lithium production. The d.c. resistivity data supplements the gravity data in that each set of data reveals particular aspects of the basin structure.

WILLCOX PLAYA

The Willcox area, near Tucson Arizona (fig. 76), has been identified by the U.S. Geological Survey lithium exploration group as an area with an above average potential for the occurrence of a lithium brine. Geophysical surveys consisting of a regional airborne magnetic

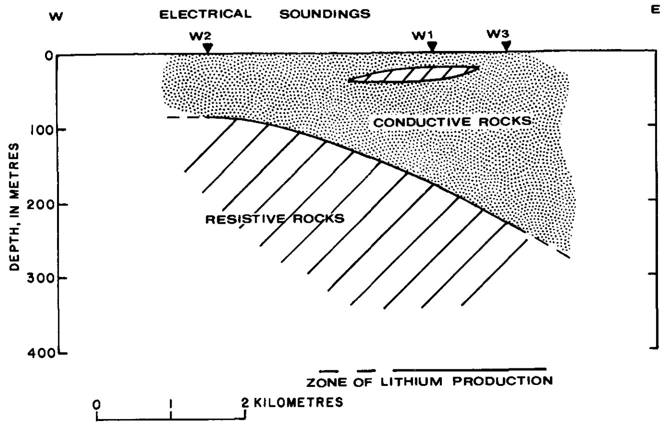

FIGURE 81.—Interpreted geoelectric section across the zone of lithium brine production in Clayton Valley, Nev.

survey (Dempsey and others, 1963), a regional gravity survey (Peterson, 1966), a limited airborne electromagnetic survey, and a reconnaissance resistivity survey using the Schlumberger array were made. The Willcox playa is located at the south central end of Sulphur Springs Valley.

The location of the Schlumberger soundings is shown in figure 82. An additional electromagnetic sounding made by Wynn (1974) has been incorporated in the interpretation of the Willcox Playa structure. The interpretation of the d.c. sounding data is limited by a lack of subsurface control. Hence we have only interpreted the soundings in terms of minimum depth to resistive rocks. The strata above the resistive rocks have a resistivity on the order of 0.25 ohmmetres. This is the same order of resistivity as the corresponding section at Clayton Valley. Here again the resistive rock is not the crystalline or basement rock for the sedimentary sequence.

The minimum depth to the resistive rocks determined from each Schlumberger sounding is shown in figure 82. The contours represent a minimum depth since the actual resistivity of the resistive sequence cannot be determined from the Schlumberger sounding. A further complication is that the conductive strata above the resistive rocks probably consist of a number of alternating very thin layers. This situation creates an electrical anisotropy which in turn tends to make the depth estimates too large. However, the degree of electrical anisotropy probably does not vary significantly from sounding to sounding. Consequently the thickening of the conductive rocks by a factor of six in the southern portion of the playa is a real geological feature.

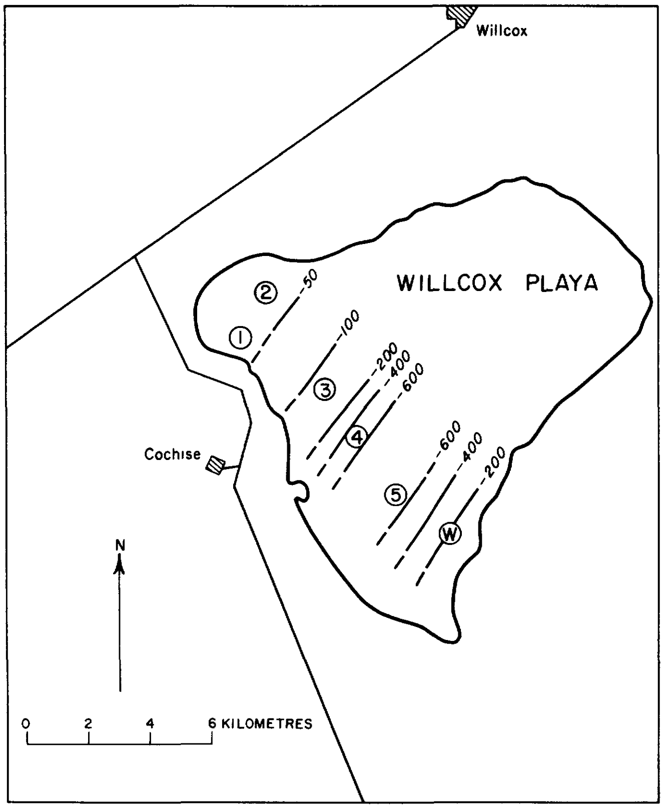

FIGURE 82.—Location of d.c. resistivity soundings and interpretation of minimum depth to resistive rocks in metres. W denotes EM sounding by Wynn (1974).

Although the resistivity data have indicated that there is a thickening of conductive sediments, there are not enough sounding stations to determine whether there is a closed basin favorable for the formation of brines. However, the airborne electromagnetic survey data can be used to answer this question. This geophysical method involves transmission of a half sine wave of current through a loop of wire transported by an airplane (Keller and Frischknecht, 1966). This signal is modified by the conductivity structure of the earth. The modified signal is measured by a receiver consisting basically of a loop of wire carried on the airplane. The distortion of the transmitted signal can be used as a measure of the ability of the earth to conduct electricity. The results of this airborne survey are shown in figure 83. Transmitted and received signals are shown in the lower right corner of figure 83. The contours depicted in figure 83 are related to the conductivity of the earth as sensed by the electromagnetic measurements. The larger numbers indicate lower resistivities or a greater thickness of conductive rocks. Comparison of figure 82 and figure 83 indicates that the airborne electromagnetic survey and the d.c. resistivity survey define the same conductive area of the playa. An important addition to the surface geophysical survey is that the airborne geophysical data indicates the conductive sediments form a closed basin.

The regional gravity survey provides the general geological setting of the Sulphur Springs Valley, within which Willcox Playa is located. Figure 84 is a generalized gravity map of the valley (Peterson, 1966). The most prominent feature of the map is the 24 milligal gravity low northwest of Willcox. This gravity low is part of a generally northwest to southeast trending gravity low which is coincident with the Sulphur Springs Valley. Lesser gravity lows occur within this low trend on the northside of Willcox Playa and to the southeast. Without additional geological evidence, we hypothesize that the gravity contours generally indicate basement topography. However, a consideration in this interpretation is the presence of volcanic flows in the exposed strata at the south end of the basin, which may occupy a significant portion of the sedimentary sequence. Consequently, the higher gravity values at the south end of the Sulphur Springs Valley may indicate a thicker volcanic sequence rather than a shallower basement.

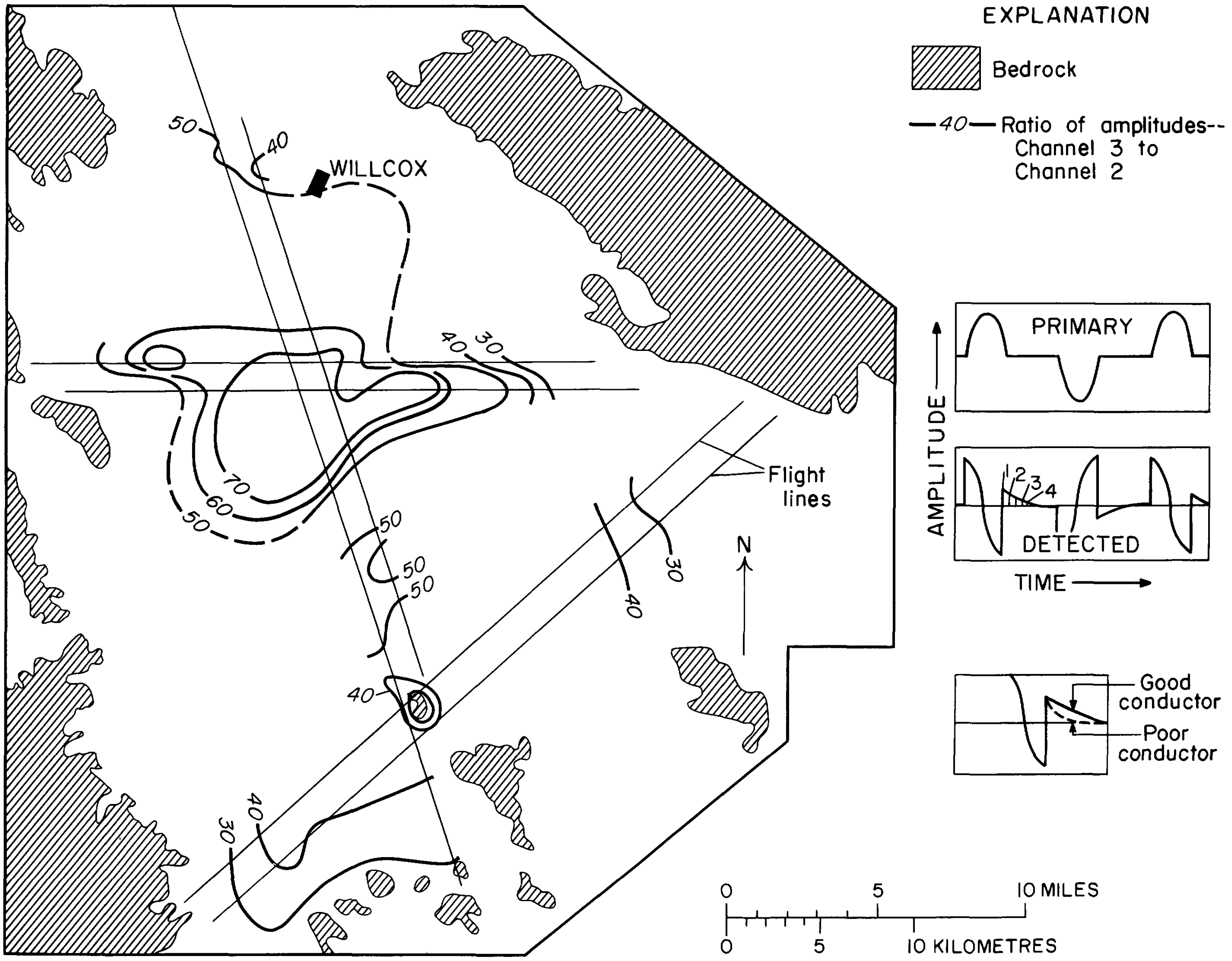

FIGURE 83.—Contoured airborne electromagnetic survey data for the Willcox Playa area, Arizona.

Figure 84 also shows the location of a prominent total magnetic field anomaly defined by the airborne magnetic survey referenced previously. This is a magnetic high of about 300 gammas whose contours define a ridge-shaped feature. The trend of the feature is oblique to the gravity and topographic trend of Sulphur Springs Valley. A general interpretation of the magnetic anomaly is that it is due to a volcanic intrusive dikelike feature related to the volcanic activity at the south end of the valley. We note that the local gravity contours transect Willcox Playa and tend to parallel the trend of the magnetic anomaly. The magnetic feature then is of significant dimensions to alter the main trend of the local gravity low.

The following statements summarize the important geological and geophysical features of the previous discussion and the implications for lithium occurrences.

1. A thick section of conductive sediments on the order of a few hundred meters is located at the south end of Willcox Playa. Though the sediments occur within a gravity low they are not associated with closed gravity lows. This corresponds roughly to the relationship between the lithium occurrence at Clayton Valley and the associated gravity. The resistivities of the conductive rocks are the same generally as those associated with the lithium producing area at Clayton Valley.
2. A thick accumulation of sediments is indicated by the gravity low northwest of Willcox. This sedimentary sequence could be the site of evaporite deposits.
3. Volcanic activity seems to have been frequent in the southern portion of Sulphur Springs Valley.
4. The airborne magnetic survey indicates the presence of a dikelike volcanic body beneath the Willcox Playa. This volcanic body could be a source of hydrothermal solutions.
5. Base metal mining has taken place most intensively

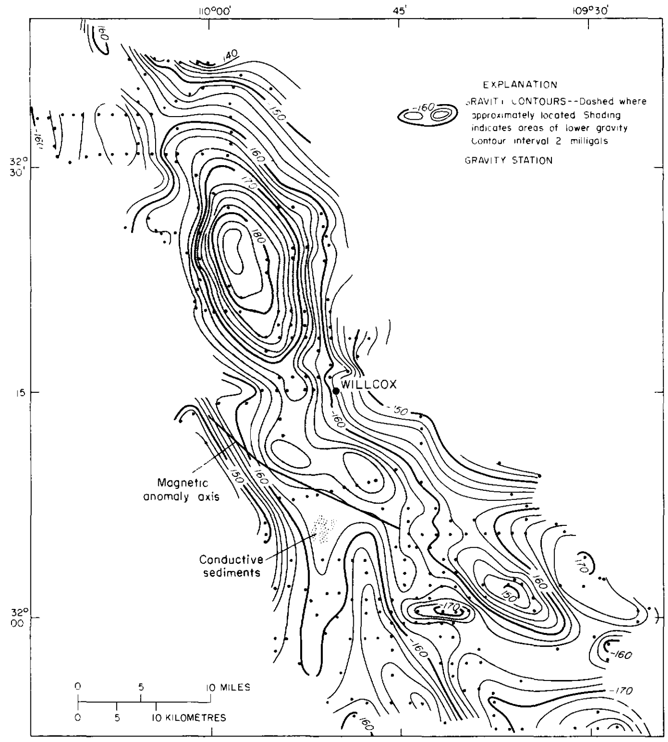

FIGURE 84.—Generalized Bouguer gravity map for the Sulphur Springs Valley, Ariz.

within the exposed rocks at the south end of the valley. Base metal mining has also been extensive in the exposed strata adjacent to Clayton Valley.

The overall picture which emerges from this analysis is that the south end of Sulphur Springs Valley seems to be the most likely area for the occurrence of lithium. The interpreted thick sequence of sediments north of Willcox should be investigated for potential evaporite deposits. An integrated electromagnetic survey and seismic survey would provide the best information about this sedimentary sequence.

DISCUSSION

The interpretation of geophysical surveys given in the previous discussion indicates areas for research in lithium exploration methods. As discussed in the introduction the most important general research objective is to define physical models for lithium deposits. We will concentrate on the geophysical aspects of this general research objective.

One aspect of a model for lithium exploration is the nature and character of basin sediments. Clearly an important question is how typical or atypical is Clayton Valley, the only valley of its kind producing lithium brine, in comparison to other sedimentary basins within the Basin and Range Province. The characteristics of the sedimentary sequence is a consideration in seeking an answer to this question. The previous examples of electrical surveys have shown that they are valuable tools in defining the nature of a sedimentary sequence. However, a very real limitation exists in their interpretation since only general conclusions can be made about the lithology itself. Fortunately the state-of-the art for electrical methods has made rapid advances in recent years. For example, using alternating electrical currents and measuring the resistivity as a function of the frequency has been advocated as a means to distinguish copper sulfides from noncopper sulfides (Zonge and Wynn, 1975). We are currently starting a research program which will employ such a method to try to deduce more about the nature of the basin sediments. An important part of this research is the measurement of resistivity as a function of frequency in the laboratory for small rock samples whose mineralogy and geochemistry are relatively well known. We are confident that this laboratory study, when used in conjunction with field measurements, will enable a geophysical estimate to be made of the nature of the sedimentary sequence.

Another class of geophysical methods which can be applied in lithium exploration are the bore-hole logging techniques. These methods have an application in support of surface electrical measurements and in supplementing lithologic logging. For example, in situ measurements of the physical properties of a given sedimentary sequence greatly aids interpretation of geophysical surveys used to map the lithologic variations. Combined use of borehole logging methods and a surface geophysical survey has proven to reduce drilling costs significantly. Neutron activation methods are one recently developed class of borehole logging methods which have a potentially interesting application to lithium exploration. The use of lithium in shielding for nuclear reactors (for example, activation potential) may also prove to lead to a method for in situ detection of lithium.

Another broad class geophysical method which will prove useful in characterizing sedimentary deposits in the Basin and Range Province is the remote sensing method. One obvious application is thermal or infrared remote sensing. If indeed lithium has a hydrothermal origin or has a correlation with hydrothermal activity, then shallow lithium deposit target areas may be associated with thermal anomalies.

CONCLUSION

Lithium deposits will not be defined by a characteristic geophysical anomaly at least with present geophysical methods and interpretation techniques. Consequently geophysical methods cannot be thought of as a black box which produces a geophysical anomaly directly indicating the location or presence of a mineral deposit. Geophysics must be thought of as analogous to a tool box with each tool being a geophysical method appropriate to the geological problem at hand. The most successful application of geophysical methods to any mineral exploration problems will involve integration of several geophysical and geological techniques.

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LITHIUM—DATA BASES AND RESOURCE ESTIMATES: PROBLEMS AND POTENTIAL

By Allen L. Clark, James A. Calkins, Donald Singer,
and Mary A. Urick,
U.S. Geological Survey, Reston, VA

ABSTRACT

Data files contain raw or disaggregated information on mineral deposits and commodities. Computerized data files offer the only means presently available by which all data items (fields) are individually addressable. One operational data file is CRIB (Computerized Resources Information Bank), which is a general purpose inventory and reference file on metallic and nonmetallic mineral deposits. Other files are being constructed for special purposes.

A computer file on lithium resources should contain detailed information related to the following main categories: record identification, name and location, description of deposit, analytical data, and production and (or) reserves.

The U.S. Geological Survey is developing improved methods for the handling of mineral resource data. These include computerized data files and predictive resource models.

A resource model is a system of postulates, data, and inferences which serves to predict the resource-related outcome when key variables affecting a mineral commodity are changed. The objective is to provide several different kinds of mineral availability estimates, including: geological availability (search and occurrence model), technological availability (exploration models), and economic availability (economics models).

Information on mineral resources should be organized more efficiently and made more easily accessible so that this information can be used to greater advantage by interested parties both in government and in the private sector. As stated by McKelvey (1972), "Better methods for estimating the magnitude of potential mineral resources are needed to provide the knowledge that should guide the design of many key public policies."

The rapid changes in the lithium picture in recent years—new sources of supply from subsurface brines and the likelihood of greatly increased demand due to new uses—emphasize the general need for rapid access to current information relating to our position toward minerals and for long range mineral resource appraisals.

The U.S. Geological Survey is engaged in collecting and organizaing computerized information on mineral resources and in developing predictive resource models which will provide improved capability for making policy decisions on this subject.

This paper describes the methods being developed and suggests that some of these methods may be applicable to lithium resource studies.

Mineral resources data files, loosely called data bases, contain the basic raw or disaggregated information on mineral deposits and mineral commodities. This information is rigorously and logically organized down to the smallest unit of information for which computer access is desired; each individual datum is stored in a computer field, which is individually addressable. It is important to decide beforehand the smallest level of information that will be required because, while it is possible to aggregate small components of data into larger groups (grouped data), it is not possible to do the reverse.

Although organizing the information into a computerized file is tedious, so is the use of a manual file. In the case of a subject as complex as mineral resources, the computerized operation offers some unique advantages not available elsewhere. For example, the computer file can be addressed down to the level of the individual field, plus those two or three fields within the record, that have been sorted in advance, whereas the manual file can only be addressed down to the level of the record (document). Therefore only the computer file can disassemble the record into its individual parts, and for most uses of data this disassembly process is an initial requirement.

One of the operational data files being used for the storage of data on mineral resources is called CRIB (Computerized Resources Information Bank) (Calkins and others, 1973). CRIB is a general-purpose inventory and reference file on metallic and nonmetallic mineral deposits. As of January, 1976, this file contained about 49,000 records of varying quality and completeness; these records were supplied to the file voluntarily from various sources. Very few records specific to lithium had been contributed to the file. An example of a typical record stored in the CRIB file is shown in table 64. This record contains certain key information on the Spor Mountain beryllium district, which contains lithium as a potential resource. A second example, the printed output resulting from a search for lithium deposits in the United States, is shown in table 65. In this type of output, selected parts of the retrieved records are rearranged into fixedlength fields, sorted, and then passed to a report processing program which provides for specialized output arrangements.

Several other data files are being constructed to serve special purposes, including (1) a file specific to the mineral economics of metallic mineral deposits, (2) a special file on the 900 largest producing mines of the world, (3) a file on coal resources, and (4) a file on geothermal resources.

In order to use the computer to store and manipulate lithium data, it will be necessary to organize the data for a computer operation. In this regard we suggest the following as a preliminary list of important categories of information that should be organized and collected:

- Record Identification
  - Record number
  - Deposit number
  - Cross index number
  - Date

- Name and Location
  - Deposit name
  - Mining district/area/subdistrict
  - Country
  - State
  - County
  - Latitude
  - Longitude

- Description of Deposit
  - Commodities present
  - Deposit type
  - Size of deposit (large, medium or small)
  - Ore minerals
  - Status of exploration/development
  - Property (active or inactive)
  - Workings (surface, underground, or both)

- Analytical Data

- Production and (or) reserves
  - Annual production
  - Cumulative production
  - Reserves
  - Reserves and potential resources

The compilation of resource data into data bases provides information which can be used in resource models to create long-term-supply curves. This ultimate purpose is directly analogous to the ultimate purpose of geologic data collection, which is the historical interpretation of the earth and its phenomena. In both cases, it is imperative that the ultimate purpose be clearly established so that data collection and data banks do not become an end unto themselves; rather, they should be regarded as necessary building blocks of analysis, and used like any other tool of geologic studies.

Numerous steps must be taken, however, before one can produce the end product—a long-term-supply curve—and the first and most critical step is a mineral resource inventory. The most important reasons for such inventories are: (1) the increasing demands on world's resources by both the developed and developing nations; (2) the need for more accurate data for short- and long-range planning; (3) the need to assess national endowment in order to effectively allocate other scarce commodities such as manpower and capital; and (4) the need to ascertain the best trade-offs in terms of world food demands, environmental degradation, rational growth programs, and multiple land use within developed and developing nations.

Once an inventory of a mineral resource has been completed and a data base developed, a large number of studies can be undertaken utilizing this inventory. Within the U.S. Geological Survey and elsewhere in government and industry, much emphasis has recently been placed on resource models of various types. This emphasis has caused a great deal of confusion, contradiction, and controversy over the use of models.

TABLE 64.—*An example of a typical record stored in the U.S. Geological Survey's CRIB file*

```
CRIB MINERAL RESOURCES FILE, REVISION 8

                                        RECORD IDENTIFICATION
                                          RECORD NO.............  W000026
                                          RECORD TYPE...........  A  U
                                          COUNTRY/ORGANIZATION.   USGS
                                          FILE LINK ID..........  RASS
                                          DEPOSIT NO............  496

                                        REPORTER
                                          NAME:  WORL, RONALD G.
                                          DATE:  71 04

 NAME AND LOCATION
   STATUS OF EXPLOR. OR DEV.  4

   DISTRICT/AREA.............  SPOR MOUNTAIN

   COUNTRY CODE..............  US

   STATE CODE................  49
   STATE NAME:
    UTAH

   COUNTY....................  JUAB

   QUAD SCALE          QUAD NO OR NAME
    1: 62500             TOPAZ MOUNTAIN

   LATITUDE            LONGITUDE           ALTITUDE
    39-43-00N            113-12-00W


 COMMODITY INFORMATION
   COMMODITIES PRESENT: F   BE   U   LI

   SIGNIFICANCE:
              MAJOR......  F
              MINOR......  U   BE
              COPRODUCT..
              BYPRODUCT..
              POTENTIAL..  LI

   ORE MATERIALS (MINERALS,ROCKS,ETC.):
     FLUORITE

   DEPOSIT TYPES:
     PIPES, VEINS


 PRODUCTION
       YES
```

However, the purpose of data, data bases, and resource models is to provide an indication of the long term supply of a commodity. In this paper, we concentrate on lithium, but the general philosophy we present can apply to almost any mineral or energy commodity.

The least that is required of any model is that it serve

TABLE 64.—*An example of a typical record stored in the U.S. Geological Survey's CRIB file*—Continued

```
ANNUAL PRODUCTION (ORE AND COMMODITIES)

    ITEM    ACC  AMOUNT   THOUS.UNITS  YEAR    GRADE OR USE
  1  ORE
  3  BE
  4  U


CUMULATIVE PRODUCTION (ORE AND COMMODITIES)

    ITEM    ACC  AMOUNT   THOUS.UNITS  YEARS  GRADE OR USE
  8  F      ACC 00000144 TONS         1943-1962; 75% CAF2

SOURCE OF INFORMATION..  DASCH, 1964

PRODUCTION COMMENTS....  U FROM YELLOWCHIEF; BE BY BRUSH BERYLLIUM CO.; SMALL
  FLUORSPAR OPERATIONS CONTINUING FROM 1962 TO PRESENT.


RESERVES AND POTENTIAL RESOURCES

  ITEM          ACC  AMOUNT   THOUS.UNITS  GRADE OR USE
 1  CAF2        EST 00000362 TONS         40% CAF2
 2  BE          LGE                       LOW GRADE
 3  LI
 4  U           LGE                       LOW GRADE

  SOURCE OF INFORMATION..  DASCH, 1964

  COMMENTS...............  LARGE LOW GRADE  CAF2 (5%) ASSOC. WITH BE DEPOSITS.

GEOLOGY AND MINERALOGY

  HOST AND/OR COUNTRY ROCKS AND AGE..  LIMESTONE

  ASSOCIATED IGNEOUS ROCKS AND AGE...  DIKES

  AGE OF MINERALIZATION..............  TERTIARY

  GEOLOGICAL DESCRIPTIVE NOTES.......  FLUORITE IN IRREG PIPES AND VEINS IN
    LIMESTONE. FLUORITE (5%) IN WATER-LAID TUFF WITH BE, LI, AND MN OXIDES.


REFERENCES
  1) STAATZ, USGS PROF. PAPER 415
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to predict actual physical happenings in some way relevant to man, either by allowing him to anticipate future uncontrollable events or by demonstrating the possible consequences of various decisions. To date, many mineral resource models have been deficient in meeting this requirement.

Reasons for past deficiencies include misunderstandings between geologists and economists, inadequate resource data, and little research on certain fundamental relationships. Some of these deficiencies, however, may be resolved by working backwards from the policy questions to determine the type of information which is needed to answer the questions—the approach attempted here. This approach leads to an overview of the type of mineral resource data which should be gathered.

The purpose of resource estimates is to provide unbiased mineral resource information to decision makers, enabling them to make rational decisions which would insure the orderly supply of mineral materials without neglecting the proper use of land and the health and welfare of the people. Thus the need of the resource estimator to anticipate all future policy questions is im-

TABLE 65.—*An example of a printed output for a search for lithium deposits in the United States*

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                                        LITHIUM DEPOSITS IN THE UNITED STATES


                                                            ARIZONA

REC.ID.    DEPOSIT NAME                          LATITUDE  LONGITUDE  TWP RNG  SEC.    COMMODITIES                DEPOSIT  PROD.
                                                                                                                    TYPE
M003610                                                               11N 04W 02    LI                                     NO
M003554                                                               07N 03W 09    LI                                     NO
M003414                                                               08N 03W 29 31 LI                                     NO
M003396                                                               07N 03W 16    LI                                     NO
M003286                                                               07N 05W 26    LI                                     NO
M000983                                                               24S 16E 11    LI                                     NO
M000516                                                                             LI                                     NO
M000151                                                               17S 10E 25    LI                                     NO


                                                            COLORADO

REC.ID.    DEPOSIT NAME                          LATITUDE  LONGITUDE  TWP RNG  SEC.    COMMODITIES                DEPOSIT  PROD.
                                                                                                                    TYPE
DC01970 BIG BOULDER PROSPECT                                          07N 72W 36    BE  GEM FLD RAE MIC PER LI  PEGMATITE  YES
DC01934 COJADE                                                        05N 71W 36    BE  LI  NB  TA              PEGMATITE  YES
DC00688 COMET GROUP                                                   12S 84W 24    LI  BE  GEM                 PEGMATITE  NO
DC01960 KINGS KANYON                                                  07N 72W 21    MIC F   LI  BE              PEGMATITE  NO
DC01933 RATTLESNAKE PARK                                              05N 71W 36    BE  GEM LI                  PEGMATITE  YES


                                                            CONNECTICUT

REC.ID.    DEPOSIT NAME                          LATITUDE  LONGITUDE  TWP RNG  SEC.    COMMODITIES                DEPOSIT  PROD.
                                                                                                                    TYPE
W000404 ANDERSON MICA MINES AND SWANSON LITHIA M 41-30-56N 072-31-16W               LI  MIC FLD                 PEGMATITE  YES
W001031 BRANCHVILLE MICA MINE                    41-16-04N 073-26-22W               MIC FLD QTZ BE  FE  LI  V   PEGMATITE  YES
W000945 GILLETTE GEM TOURMALINE, MINERAL SPECIME 41-29-34N 072-30-40W               GEM FLD MIC BE  F   LI      PEGMATITE  YES


                                                            MASSACHUSETTS

REC.ID.    DEPOSIT NAME                          LATITUDE  LONGITUDE  TWP RNG  SEC.    COMMODITIES                DEPOSIT  PROD.
                                                                                                                    TYPE
W000056 BARRUS PROPERTY LITHIA MINE              42-28-07N 072-50-25W               LI                          PEGMATITE  NO
W000060 CLARK LEDGE LITHIA MINE                  42-25-12N 072-52-25W               LI                                     YES
W000061 MAC COMBER LEDGE LITHIA MINE             42-25-50N 072-52-25W               LI                                     NO
W000058 MANNING LOCALITY LITHIA MINE             42-28-15N 072-48-45W               LI                                     NO
W000055 NORWICH LITHIA MINE                      42-19-07N 072-51-43W               LI                          PEGMATITE  YES
W000057 TAYLOR LEDGE LITHIA MINE                 42-28-10N 072-49-35W               LI                          PEGMATITE  YES
W000059 WEST CHESTERFIELD LITHIA MINE            42-24-20N 072-52-20W               LI                          PEGMATITE  YES


                                                            UTAH

REC.ID.    DEPOSIT NAME                          LATITUDE  LONGITUDE  TWP RNG  SEC.    COMMODITIES                DEPOSIT  PROD.
                                                                                                                    TYPE
W000026                                          39-43-00N 113-12-00W               F   BE  U   LI              PIPES, VEI YES

DC13199 ROADSIDE CLAIMS                                               012 012       BE  LI                                 NO


                                                            WYOMING

REC.ID.    DEPOSIT NAME                          LATITUDE  LONGITUDE  TWP RNG  SEC.    COMMODITIES                OEPOSIT  PROD.
                                                                                                                    TYPE
DC07602 BLACK MOUNTAIN SPODUMENE PROSPECT                             033 089 36    LI                          PEGMATITE  NO
DC06593 CARBONATE BELLE CLAIM                                                       AU  AG  TE  U   PB  LI  MN             NO
DC06594 PACIFIC LODE                                                                PB  SE  U   MN  LI                     NO

        28 LITHIUM RECORDS PRINTED
```

plicit, but of course, this need cannot be fulfilled in many cases.

There are certain policy questions involving mineral commodities that have been prevalent in the past, and we may expect them to recur. Some of these questions, as they relate to resource estimates, are: What would be the change in reserves with a change in the price of the commodity? Should some particular area be excluded from mineral development? How much additional material would be available as a result of a technological breakthrough in some process or mining method? Where are the alternative sources of the commodity? Is it worthwhile to encourage domestic exploration for some mineral? Which mineral resources might be minable if improvements were made in highways and related facilities? Should we have a mineral stockpile?

Perhaps the objectives of resource estimates can be better defined after considering the following question: How much of each commodity is avilable under all conceivable future conditions? This new question may appear open-ended and unanswerable, and to some extent it is. Not all future mineral supply problems can be anticipated and, as a result, a broad base of resource information is needed to even attempt an answer. It is pertinent to discuss what type of information is required.

Suppose a robot were developed which could mine underground; many resource estimates based on today's technology would become useless. The point of this example is that, although resource estimates should be based on economics, technology, and geology, economics and technology should not be included explicitly in the data since they are subject to change over relatively short periods of time.

What should be specified in the raw data are estimates of the quality and quantity of the resources available with respect to the factors which economics and technology could affect. These variables would include the usual grade and tonnage estimates; the physical, chemical, and mineralogic features of the ore which could affect its metallurgical treatment and recovery; the thickness of the deposit; the geographical location; the geologic structure and hydrologic conditions; and the spatial distribution of the mineralization and the overburden. Recording such information for known mineral depsoits, updating the records when major changes occur within deposits, would provide a firm foundation from which the effects of changes in economics and technology could be estimated. This type of data base is hereafter described as "disaggregated."

Desposits which have not yet been found present other problems. Most people are reluctant to predict the occurrence of a rare event such as an unfound deposit. Although single rare events are unpredictable, the statistical averages of large numbers of them are highly regular and predictable. Thus for the lead-zinc, porphyry copper, and sandstone uranium deposit types, for which there may be a large number of unfound deposits, the statistics of the known deposits of the same type provide an adequate predictive model. Resource estimates made by such statistical models must be tempered, of course, by the geological extrapolation which provides estimates of the numbers of the unfound deposits and by the extrapolated conditions such as depth, general location, ground water, and legal status, which could adversely affect the economics of recovery. Additionally, due to the nature of mineral searches, not all the deposits may be found. The effects of the search should be estimated separately from the resource estimates because of changes in the technology and economics of the search itself.

The precision of each estimate should also be estimated and expressed explicitly because of the probability that the actual resources amount to a quantity other than the expected value; this difference could have important implications for some policy decisions. An even more serious problem with present resource estimates is the tendency of estimators to be conservative, and, therefore, biased. The main reason for this appears to be a fear that the increasingly large numbers will tend to have proportionately less precision when they are extrapolated from reserve figures to unfound resources. Thus analysts have reacted by presenting lower estimates in which they have more confidence. Including confidence intervals with unbiased estimates would obviously alleviate much of this problem. Biased resource estimates cannot be tolerated in light of the possible adverse effects on policy decisions.

The major question that remains is: What would be the exact configuration of resource model that could generate resource estimates applicable to decision making? A general model for such analyses has been developed by the U.S. Geological Survey and is presented in figure 85.

Although figure 85 is extremely simplified in terms of both the amount of data required and the effort involved in developing such a model, it does provide a basic framework within which a resource estimate can be created. Such a model simultaneously allows for updating of the individual elements of the model and provides for a feedback of information as the data are generated. The initial phase of the model is an occurrence model for the resource, and it therefore provides the total quantity of the resource by aggregation. However, because the development of a resource is contingent upon first discovering its existence, the resource estimate should be revised to show that portion of the total that will be ultimately discovered. Therefore, aggrega-

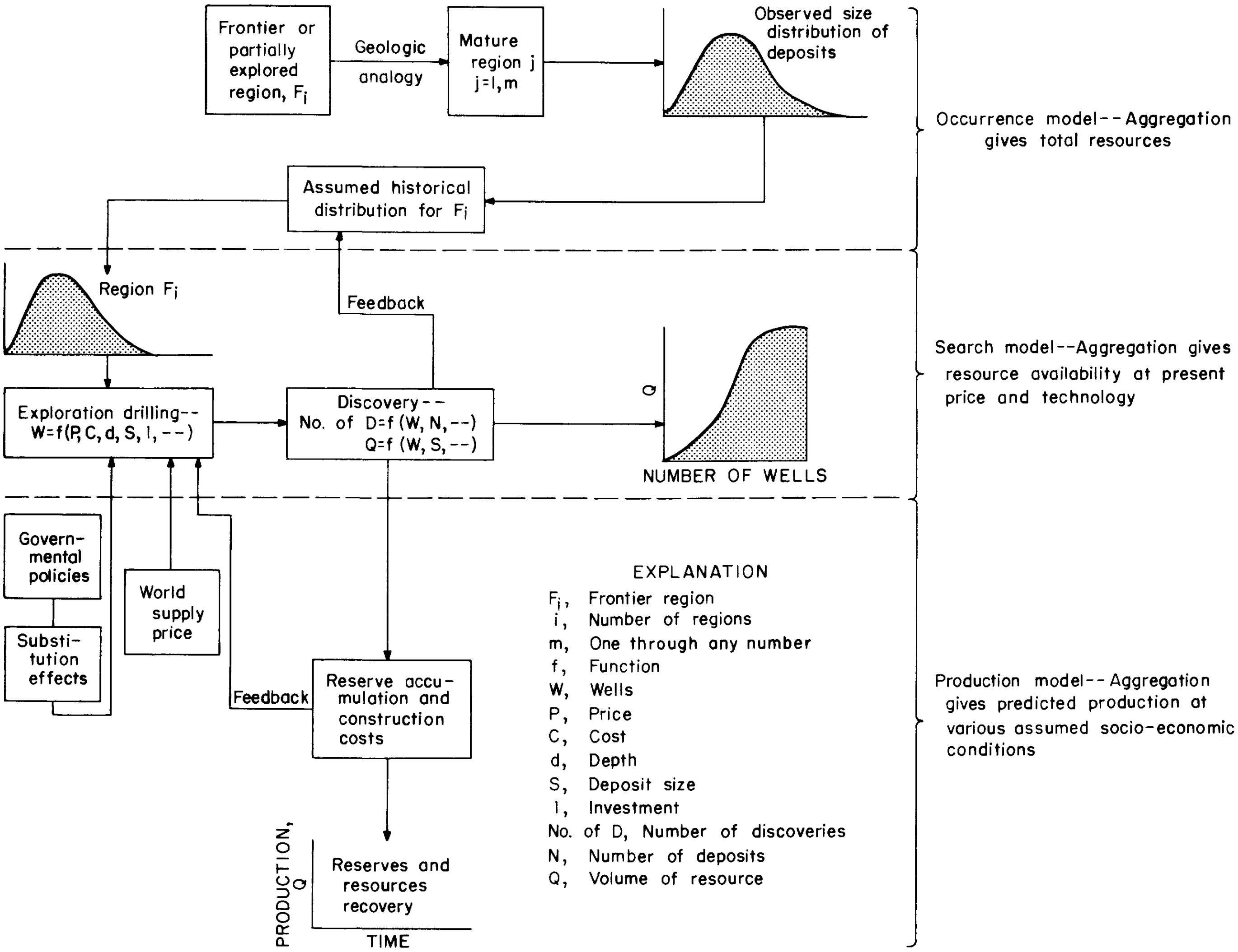

FIGURE 85.—General model for estimating resource availability.

tion of the data from the search-model portion of the model (fig. 85) gives the resource availability at present price and technology.

Finally, it is necessary to introduce the econometric model in order to devise a time-dependent production model. This aspect of the model is normally outside the expertise of the U.S. Geological Survey but must be integrated with the data from the search and occurrence submodels in order to develop a long-term supply model for use by decision makers.

In summary, decisions on mineral resource policy should reflect the major factors which affect the availability of resource commodities: (1) geological availability, (2) technological availability, (3) economic availability, and (4) alternate sources of supply. Reliable information on these factors should be developed through research on quantitative resource occurrence models, models of the exploration process, mineral economics models, and gathering of resource data at a disaggregated level. Systems design and software development in progress should allow users without computer experience to use the system. Update procedures, along with retrieval and display capabilities should be provided for in the software being developed.

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ANALYTICAL METHODS AND PROBLEMS OF LITHIUM DETERMINATION IN ROCKS, SEDIMENTS, AND BRINES

By Allen L. Meier, U.S. Geological Survey, Denver, CO

ABSTRACT

Exploration for lithium resources involves reliance on geochemical methods. In turn, the precision and accuracy of the analytical procedures determine the usefulness of the resultant data for exploration. Two published analytical methods and an experimental technique were applied to a variety of rocks, sediments, and brines to determine their relative precision and accuracy. The method used for analysis of brine showed good precision and accuracy. Improved precision and accuracy were obtained on rocks and sediments by an experimental technique that uses boric acid when compared to a method that does not use boric acid.

INTRODUCTION

Potential lithium deposits are not easily recognized by physical evidence alone. Chemical analysis must be used to detect and determine the distribution of the element. The success of lithium exploration depends on the ability of the analytical technique to provide the data necessary to recognize and evaluate a potential resource.

The most frequently asked question of an analyst is, "What is the precision and accuracy of the method used?" Precision and accuracy do not mean the same thing but are mistakenly used interchangeably.

Precision is a measurement of reproducibility when replicate analysis or measurements are made. Precision can be determined by repeating an analysis and examining the variability. Variability is usually expressed as standard deviation, relative standard deviation, confidence intervals, or range.

Accuracy is the nearness of a value to the true value. Comparison of a value obtained to an accepted value for a sample determines accuracy. A percentage of the true value is an expression of accuracy. A true or accepted value for the material under study is often unknown. Accuracy can be determined in this case, however, by the addition of a known amount of the element to the previously analyzed sample. The percent recovered in the re-analysis is an indication of the accuracy (Fletcher and Collins, 1974).

Precision and accuracy are difficult to determine in analysis of geologic material for the following reasons:

1. Each sample is unique.
2. Variability within the sample is unknown.
3. The matrix of each sample is different.
4. Interaction of the elements present is often unknown.
5. The element of interest normally occurs in trace amounts.

Therefore, an analytical technique that works well on one sample type may not work on another.

In this work the precision and accuracy of two published analytical methods and an experimental technique were studied. Several representative samples of different types were analyzed for lithium. They included clays, tuffs, carbonates, water, and brine.

PROCEDURES

Atomic absorption was used for the determination of lithium in each of the methods.

The water and brine samples were analyzed by a procedure described by Brown, Skougstad, and Fishman (1970). Water samples were analyzed directly without dilution. Brine samples were diluted to concentrations of less than 15,000 mg/l total dissolved solids. (Results are given in table 66.)

Rock and sediment samples were analyzed by a modified method reported by Ward, Nakagawa, Harms, and VanSickle (1969). Decomposition was accomplished by a mixture of nitric and hydrofluoric acids. The use of perchloric acid was eliminated from the procedure for exploration and field use. Samples were taken to dryness on a hotplate, redissolved in 6-normal hydrochloric acid, and diluted. (Results are given in table 67.)

Rock and sediment samples were also analyzed by an experimental technique using boric acid. The method is essentially the same as the one previously described, except that 5 ml of a saturated boric acid solution was added after decomposition. (Results are given in table 67; see columns that refer to boric acid method.)

To study precision, each sample was analyzed five times by each method. The mean and confidence limits at the 95 percent level, and the percent relative standard deviation are reported (tables 66 and 67).

Accuracy was determined by adding a known amount of lithium to each of the rock and sediment samples before the decomposition step. Percent recovery was calculated by using the mean of five replicate determinations of each sample with the addition and the mean of the sample as previously determined by each of the methods (Fletcher and Collins, 1974) (tables 66 and 67).

RESULTS AND DISCUSSION

Results obtained on the water and brine samples show both good precision and accuracy by the method studied (table 66). Sample number MAF 810 has poorer preci-

TABLE 66.—*Precision and accuracy of lithium determinations on brine and water samples*

Sample No.	Sample type	Specific conductance (micromhos)	Range (mg/l) Low	Range (mg/l) High	Mean and confidence limits at 95 percent level (mg/l)	Relative standard deviation (percent)	Accuracy (percent recovery)
MAF 109	Water	6,800	0.99	1.03	1.01±0.02	1.5	97
115	Brine	58,300	6.8	7.2	7 ± .2	2.2	99
810	do	180,000	10	12	11 ±1	7.7	109
797	do	160,000	65	68	67 ±1	1.7	98
798	do	160,000	68	69	68 ±1	1.9	100
MAI 095	do	190,000	300	310	308 ±6	1.5	98

TABLE 67.—*Comparison of precision and accuracy determinations on rock and sediment samples using a method without boric acid and a method with boric acid*

		Method without boric acid			Method with boric acid		
Sample No.	Sample type	Mean and confidence limits at 95 percent level (ppm)	Relative standard deviation (percent)	Accuracy (percent recovery)	Mean and confidence limits at 95 percent level (ppm)	Relative standard deviation (percent)	Accuracy (percent recovery)
MAI 180	Clay	384± 56	11.7	66	815±25	3.0	100
MAI 177	do	73± 7	7.2	95	74± 6	6.3	106
MAI 445	do	272± 47	13.9	80	420±22	5.0	99
MAF 432	Tuff	642±182	22.7	71	1233±54	4.2	95
MAF 593	do	1620± 56	2.8	95	1705±42	2.3	98
MAH 429	do	338±127	30.1	48	700±18	2.4	99
MAG 754	Carbonate	252± 27	8.6	62	588±20	2.8	96
MAG 886	do	448± 20	3.7	100	456±24	4.3	97
MAG 714	do	1210±494	21.7	108	1467±54	3.5	100

sion and accuracy than the other samples, because of the high ratio of salinity to lithium concentration in the sample. Dilution was necessary to reduce the dissolved-solids concentration for atomic absorption determination. The lithium concentration was also reduced by this dilution to near the detection limit. The precision and accuracy normally decrease as the detection limit is approached.

A comparison of the results obtained by the two methods for rocks and sediments indicates that the method using boric acid has better precision and accuracy than the method without boric acid (table 67). The mean values obtained by the boric acid technique are higher than the mean values obtained by the method without boric acid. Stable fluoride compounds can be formed when hydrofluoric acid is used for decomposition (Dolezal and others, 1968). Boric acid can be used to complex residual fluoride (Bernas, 1969). These factors explain the lower recoveries using the technique without boric acid and the higher recoveries with the use of boric acid.

CONCLUSIONS

The method used in this study for water and brine samples shows adequate precision and accuracy to be useful for exploration for lithium. An improved technique for the determination of low concentrations of lithium in concentrated brines would be useful.

The poor accuracy of the method without boric acid indicates low recovery of lithium for some samples. The greater recovery observed for these samples using the method with boric acid suggests that the formation of stable fluorides does occur when hydrofluoric acid is used for dissolution. Boric acid inhibits this formation and improves the recovery. The use of boric acid with hydrofluoric acid is under study at the present time.

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