UNITED STATES DEPARTMENT OF THE INTERIOR GEOLOGICAL SURVEY

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LITHIUM IN THE BRINES OF FISH LAKE VALLEY

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ABSTRACT

Analyses of waters from springs in Nevada have led to the identification of an area containing anomalous amounts of lithium northwest of the Clayton Valley area. Fish Lake Valley and Columbus Salt Marsh contain waters having relatively high lithium and potassium concentrations. At least a part of these waters is probably derived from the leaching of Tertiary rocks containing saline minerals. The high-lithium waters at Columbus Salt Marsh could be derived not only by the leaching of rocks with a high soluble lithium and potassium content but also by subsurface outflow from Fish Lake Valley.

INTRODUCTION

In the hydrologically closed basins of the western United States, those ions that commonly form soluble salts tend to accumulate in brines located on or beneath the floors of the basins. The controls on the chemistry of the waters in these basins has been discussed by many authors (Eugster, 1970; Garrels and Mackenzie, 1967; Hardie and Eugster, 1970; Jones, 1965; Smith and Drever, 1976; Tardy, 1971). Some constituents of the brines and/or their associated salts have been commercially produced. Sodium, chloride, boron, potassium, trona, and other ions and salts are now produced or have been produced from some of these brines. Most of the commercial production has been for the major constituents of the brine. However, a minor element, lithium, can also be produced economically from some brines. Although lithium (phosphate) had previously been produced as an economic by-product from the brines of Searles Lake, California, exploitation of the brines in Clayton Valley, Nevada, first demonstrated that production of lithium (carbonate) as the primary economic product of a brine was possible.

Since the commercial development of the Clayton Valley brines, other high-lithium brines have been sought in the western United States and elsewhere in the world. Other brines in the western hemisphere containing relatively high lithium concentrations have been identified, but lithium is not currently being produced. These brines include those at Great Salt Lake, Utah, in the Imperial Valley geothermal system, California, and in some of the salars of Chile and Bolivia.

Results of water sampling in Fish Lake Valley and Columbus Salt Marsh

Reconnaissance sampling of some of the cold springs in Nevada. in April 1976, let to the recognition of a lithium anomaly associated with some cold springs in the Fish Lake Valley area. The anomaly was identified by using the lithium-to-chloride ratio in springs to determine background (Smith, 1976). Two springs (samples 1 and 2 in figure 1 and table 1) contained anomalous amounts of lithium. In June 1976, ground-water samples from shallow holes dug around the edge of the playa (fig. 1) and two surface brine samples were collected (table 1). The ground water contained from 17 to 40 mg/llithium, and the two surface brine samples contained 200 and 350 mg/l lithium. In August 1976, after a period of rainfall and accumulation of water on the surface of the playa, another series of samples of the surface brine and shallow ground water of the Fish Lake Valley area was collected. During the same period, a series of reconnaissance samples from Columbus Salt Marsh was also taken. No lithium concentrations were greater than those previously obtained (table 1).

CHEMISTRY AND ORIGIN OF BRINE

The brines currently generated on the surface of Fish Lake Valley playa (table 1) are characterized by relatively high potassium, which varies from 5,400 to 24,000 mg/l, and low calcium and magnesium, which are less than 41 mg/1. The less concentrated brines, collected in auger holes dug less than 2 m deep around the edge of the playa, reflect, in their more variable compositions, the mixing of dilute ground waters derived from the surrounding hills with the brine currently generated on the playa surface. In contrast to the brines at Clayton Valley (Kunasz, 1970), the surface brines at Fish Lake Valley are characterized by somewhat lower lithium, somewhat higher potassium, and much lower calcium and magnesium. Kunasz (1970, 1974), in his study of the Clayton Valley lithium deposit, noted that some sediments of the Tertiary Esmeralda Formation contain a water-soluble fraction that is high in lithium, potassium, sodium, and chloride. Previously precipitated salts in the surrounding basin probably are the immediate source of the lithium and potassium in the Fish Lake Valley brines. The lithium concentration in the surface brine varies with time. In June 1976, the lithium concentration of the surface brine at the north end of the playa was 350 mg/l; by August 1976, a sample collected at the same place contained 180 mg/l lithium. The lithium concentration in the Fish Lake Valley brines has a correlation coefficient of +0.99 with the potassium concentration (figure 2). If potassium and lithium are not mainly removed from solution by authigenic silicates, they tend to persist in solution until precipitated

as very soluble saline minerals. Redissolving previously formed saline minerals containing lithium and potassium could produce the observed strong correlation in figure 2. That saline minerals exist in the drainage area of Fish Lake Valley is indicated by the existence of borate prospects east of the playa in the Silver Peak Range (J. R. Davis, oral commun., 1976). The geographic variability of the lithium and potassium could reflect the relative amounts of the brine derived from leaching the saline-rich Tertiary formations versus that derived from leaching saline-poor rocks in the area. The proportion of water coming from the saline-rich rocks should change, depending on relative rain and snowfall intensity at various places in the basin. The higher lithium concentrations in the Fish Lake Valley brine and ground water tend to occur on the northern end of the playa.

At Columbus Salt Marsh reconnaissance sampling (figure 3) indicates anomalous amounts of lithium in the shallow ground waters of the southwestern part of the playa. The highest concentration of lithium in the ground-water samples is 64 mg/l. This sample contains 77,000 mg/l chloride. The relatively high lithium concentrations in this area could represent waters concentrated after leaching source rocks having high soluble lithium, similar to those present in the Fish Lake Valley area, or the high values may simply represent subsurface flow from Fish Lake Valley. Van Denburgh and Glancy (1970) found that the water budget for Columbus Salt Marsh indicated that subsurface flow through both the alluvium and volcanic and carbonate rocks from Fish Lake Valley could be as much as 3,000 acre-feet/year. Because of the small cross-sectional area of the alluvium in the pass between the two valleys and the low gradient for outflow from Fish Lake Valley through the alluvium, Rush and Katzer (1973) found the outflow through the alluvial material to be less than 200 acre-feet/ year. That this flow can occur is indicated by the calculated mixing curve of a spring (sample 31) in the Silver Peak Range with the surface brine containing 350 mg/l lithium (figure 4). On this curve the lithium concentration of the Gap Springs, springs in the bottom of the pass between the two valleys (sample 1), can be achieved by mixing less than 2 percent of the brine with a spring whose composition is that of sample 31. The close fit of the Gap-Spring point with the mixing curve is at least somewhat fortuitous because the composition of the spring group changes with time. A concentration

of 1.5 mg/l lithium and 900 mg/l chloride was found in earlier sampling as opposed to a value of 5.6 mg/l lithium found in 1976. This variability could result from either variation in flow from Fish Lake Valley--for example, the brine may make up less than 1 percent rather than 1.2 percent of the water discharging at the gap springs--or it may reflect the variability of the lithium concentration of the brine with time. If the standing brine under the salt crust containing 130 mg/l lithium (sample 13) is mixed with sample 31, the lower mixing curve in figure 4 is produced. The two Bap-Springs samples (figure 4), as well as the ground water collected from the auger holes on the northern and of the playa, fall between the two mixing curves and demonstrate that the change in composition of the Gap Springs can be achieved by mixing small amounts of a brine of changing composition with dilute ground water.

FURTHER EXPLORATION

The continuing search for high-lithium brines spurred an attempt to develop indirect geochemical techniques to identify high-lithium areas (Smith, 1976). The method uses hot springs because their deep circulation allows them to mix with brines that may be present at depth. As indicated in figure 4, if only small quantities of a highlithium brine, either hot or cold, are mixed with a dilute ground water, an anomaly will result. Although surface brines of relatively high lithium concentration are forming at Fish Lake Valley, nearsurface sampling of ambient-temperature waters will not indicate the existence of a brine at depth because of the shallow circulation of the waters. Subsurface exploration is necessary to determine that brines having lithium concentrations similar to those currently being generated in Fish Lake Valley were generated in the past and trapped.

In Columbus Salt Marsh the relatively high lithium waters in the southeastern part of the playa do not make, at this time, a significant contribution to the lithium concentration of the near-surface brine. The interstitial water was squeezed from a still-wet surface mud collected near the center of the playa (sample 56). Despite a chloride concentration of 165,000 mg/l, the sample contained only 2.3 mg/l lithium. There is a possibility that the high-lithium waters from the southwestern part of the playa are mixed with and diluted by low-lithium waters derived from elsewhere in the drainage basin. Subsurface exploration will be necessary to determine if a lithium-rich brine exists at depth.

CONCLUSIONS

A surface brine of relatively high lithium concentration is being formed at Fish Lake Valley. The lithium and potassium in this brine are probably derived from the leaching of Tertiary rocks that have a high content of water-soluble lithium and potassium (Kunasz, 1970). Because of the restriction of high-lithium waters to the southwestern part of Columbus Salt Marsh, it is possible that much, if not all, of the high-lithium water in this area is derived from sub-surface cutflow from Fish Lake Valley. Mixing of a brine of high but variable lithium concentration with ground water derived from the Silver Peak Range could produce most of the high-lithium waters of the northern part of Fish Lake Valley and of the southwestern part of Columbus Salt Marsh.

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| Sample Number | Description | Li | K | Ca | Mg | C1 |
|------------------|--|-----------|------------|-------------|---------|---------|
| | Fish Lake Va | lley, sa | mpled Apr | 11 . 1976 . | .`` | |
| 1 | Gap Springs | 5.6 | 154 | 73.3 | 65 | 2,020 |
| 2 | Seep-standing water | 10.9 | 323 | 153 . | 97.5 | 5,000 |
| | Fish Lake V | alley, s | ampled Jur | ne 1976 | | |
| 3 | Auger hole | 29 | - | 110 GB | | - |
| 4 | Surface brine | 350 | 24,000 | 10 | 7 | 142,000 |
| 5 | Auger hole | 40 | | 5 | 28 | 30,400 |
| 6 | Auger hole | 36 | | | | |
| 7 | Auger hole | 17 | | - | | |
| 8 | Auger hole | 22 | | ~ ~ | 60° 400 | |
| 9 | Auger hole | 18 | | | | |
| 10 | Surface brine | 200 | | 40 | . 4 | 157,000 |
| | Fish Lal | ke Valley | , sampled | August | 1976 | |
| 11 | Surface brine | 180 | 13,000 | 9 | 10 | 145,000 |
| 12 | Auger hole | 35 | 3,500 | 9 | 7 | 46,000 |
| 13 | -Surface brine under salt crust | 130 | 10,000 | 6 | 7 | 135,000 |
| 14 | Surface brine | 37 | 3,500 | 9 | 10 | 52,000 |
| 15 | Shallow depression in prospect pit in alluvium where rain collected | 1 | 60 | 21 | 2 | 2,600 |
| 16 | Surface brine | 160 | 10,000 | 12 | 6 | 140,000 |

Table I. Partial chemical analyses of waters from Fish Lake Valley and Columbus Salt Marsh (in mg/l). [Leaders mean not determined.]

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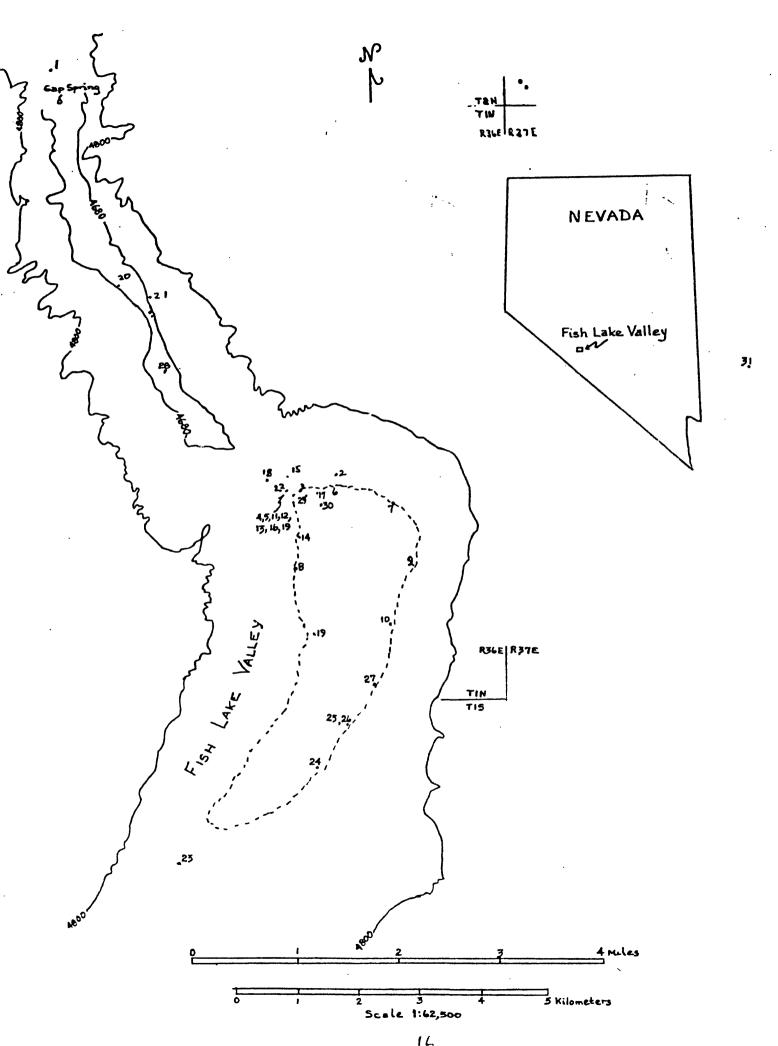
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| Sample Number | Description | Li | K | Ca | Mg | CI |
|------------------|------------------------------|-----------|-------------|-----------|----------|---------|
| | Fish Lake Valley, | sampled / | ugust 19 | 76 (conti | inued) | |
| 17 | Standing brine | 160 | 12,000 | 12 | 6 | 140,000 |
| 18 | Auger hole in wash | 32 | 1,400 | 21 | 83 | 12,000 |
| 19 | Auger hole | 22 | 2,800 | 23 | 17 | 44,000 |
| 20 | Mining shaft in alluvium | 3.5 | 190 | 18 | <u>5</u> | 1,700 |
| 21 | Auger hole in wash | 2.1 | 110 | 14 | 5 | 1,400 |
| 22 | Auger hole in wash | 22 | 91 0 | 640 | 95 | 9,600 |
| 23 | Standing water in ditch | 2.0 | 77 | 26 | 39 | 7,000 |
| 24 | Auger hole | 8.1 | 860 | 9 | 2 | 21,000 |
| 25 | Standing brine | 55 | 5,400 | 6 | 2 | 64,000 |
| 26 | Auger hole | 10 | 000 ș | 5 | 1 | 21,000 |
| 27 | Auger hole | 25 | 1,000 | 920 | 620 | 41,000 |
| 28 | Auger hole in wash | 22 | 1,300 | 13 | 3 | 19,500 |
| 29 | Standing brine | 190 | 13,000 | 9 | . 3 | 148,000 |
| 30 | Interstitial brine- 0.6 m | 130 | | 19 | 4 | 118,000 |
| | Silver Pe | ak, sampl | ed June 1 | 976 | | |
| 31 | Spring | 0.13 | 0.2 | 29 0.26 | 0.54 | 1.3 |
| | Columbus Salt I | March, sa | mpled Aug | just 1976 | | |
| 32 | Flowing well | 1.0 | 126 | 8 | 2 | 2,300 |
| 33 | Well | 2.0 | 38 | 82 | 6 | 1,250 |
| 34 | Well | 1.8 | 157 | 8 | 2 | 4,600 |

| Sample Number | Description | Li | K . | Ca | | C1 |
|------------------|-------------------------------------|-----------|------------|---------|-----------|-----------------|
| | Columbus Salt Marsh, | sampled | August | 1976.(c | ontinued) | |
| 35 | Brine in prospect pi | t 3.2 | 4,700 | 8 | 3 | 166,000 |
| 36 | Brine in prospect pi | t 14 | 3,600 | 12 | 3 | 83,000 |
| 37 | Brine in prospect pi | t 3.3 | 5,200 | 5 | 2 | 172,000 |
| 38 | Well | 5.7 | 1,400 | 6 | 3 | 52,000 |
| 39 | Auger hole | 13 | 2,900 | 550 | 80 | 140,000 |
| 40 | Brine in prospect pi | t.6 | 130 | 16 | 3 | 6,000 |
| 41 | Brine in prospect pi | t 40 | 3,500 | 13 | 2 | 115,000 |
| 42 | Pond | 48 | 4,300 | 220 | 50 | 77,000 |
| 43 | Auger hole | 64 | 3,800 | 380 | 90 | 77 ,0 00 |
| 44 | Auger hole | 37 | 2,900 | 1,000 | 70 | 46,000 |
| 45 | Pond | 150 | 7,700 | 610 | 110 | 180,000 |
| 46 | Pond | 170 | 11,000 | 450 | 150 | 170,000 |
| 47 | Auger hole | 12 | 740 | 45 | 9 | 17,500 |
| 48 | Auger hole | 42 | 2,100 | 280 | 50 | 55,000 |
| 49 | Auger hole | 23 | 2,000 | 40 | 15 - | 62,000 |
| 50 | Auger hole | 6 | | | | 85,000 |
| 51 | Auger hole | 19 | 4,400 | 80 | 26 | 110,000 |
| 52 | Auger hole | 5.8 | 2,500 | 10 | 5 | 140,0 00 |
| 53 | Auger hole | 12 | 920 | 32 | 12 | 23,000 |
| 54 | Auger hole | 18 | 860 | 370 | 15 | 16,400 |
| 55 | Auger hole | 39 | 1,500 | 300 | 54 | 31,000 |
| 56 | Interstitial water from surface mud | 2.3 | 1,500 | 6 | 3 | 165,000 |

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Figure 1. Sample distribution at Fish Lake Valley, Nevada. The sample numbers are those listed in table 1. The solid lines are contour lines in thet. The dashed line indicates the playa outline. Base from U.S. Geological Survey, 1:62,500 series, Rhyolite Ridge quadrangle.



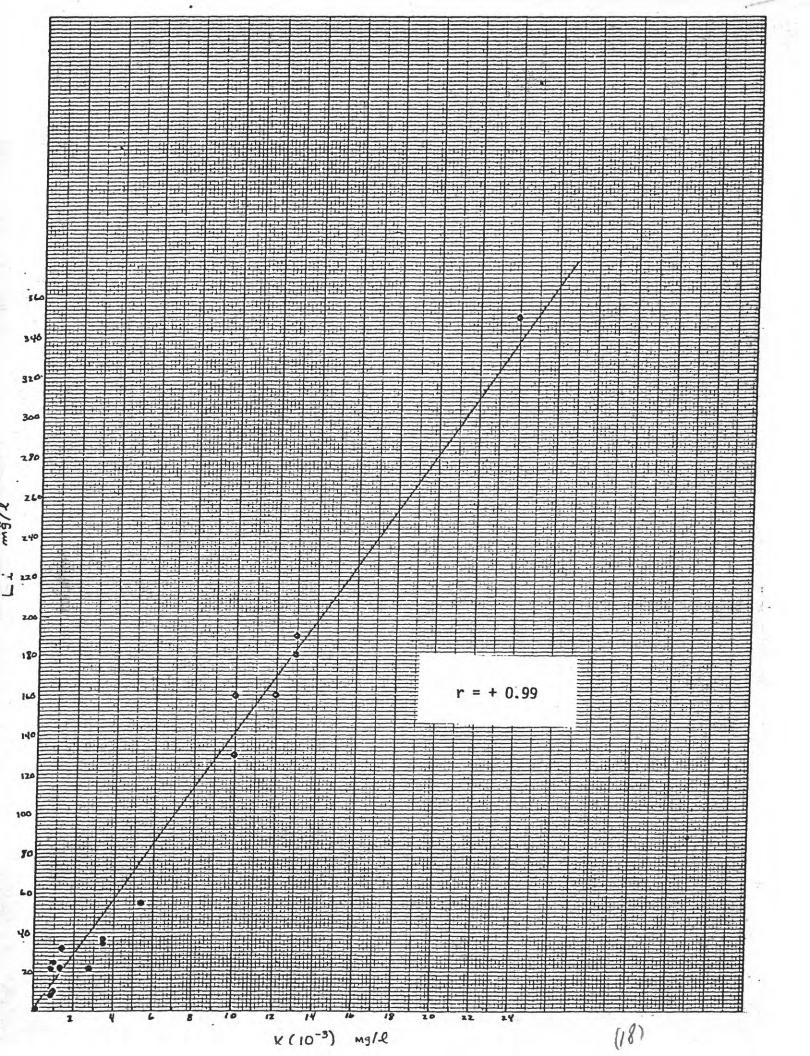


Figure 2. Variation of potassium with lithium in water samples from Fish Lake Valley; r is the correlation coefficient.

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Figure 3. Sample distribution at Columbus Salt Marsh, Nevada. The sample numbers are those listed in table 1. The solid lines are contour lines in feet. The dashed lines indicate the playa outline. Base from U.S. Geological Survey 1:200,000 Mineral Investigations Field Studies Map MF-298.

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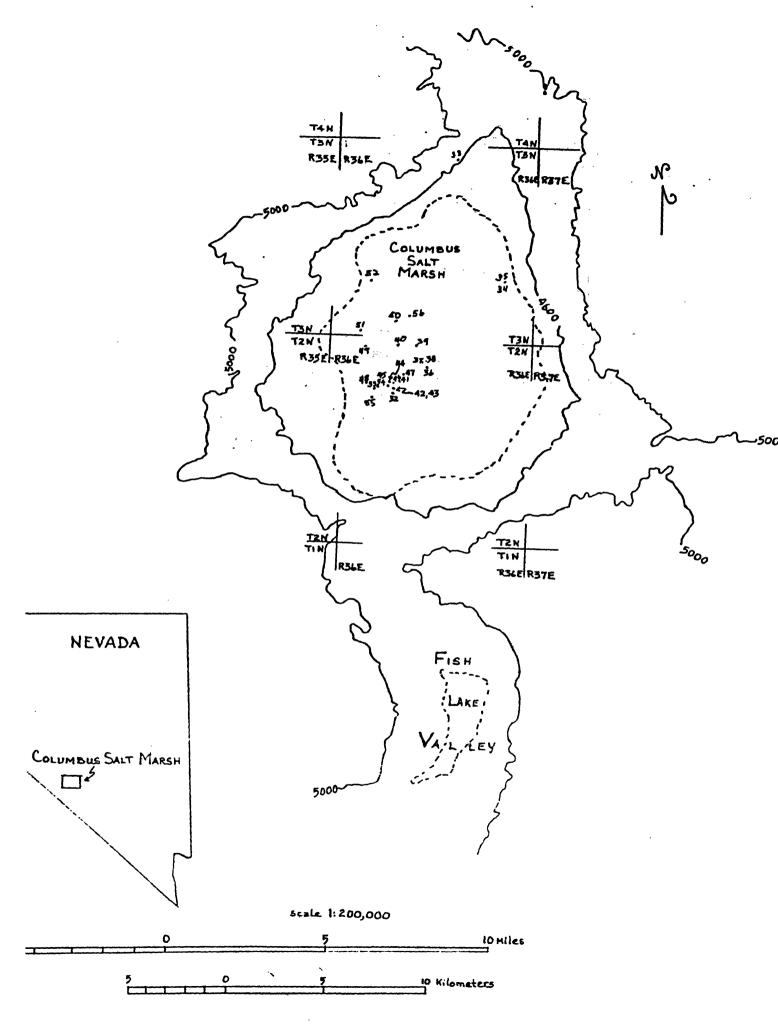


Figure 4. Mixing curves for high-lithium brines with a ground water in the Silver Peak Range. Samples are represented by black dots. Sample numbers associated with the black dots are those listed in table 1. The numbers associated with the two mixing curves give the percent of the dilute ground water (31) mixed with high-lithium brine (4 and 13). The sample point, labeled Gap Spring, is a sample collected in 1957 and not listed in table 1. The diagonal line represents the upper level of background lithium concentration in hot springs (from Smith, 1976). Points above the line are considered to contain anomalous amounts of lithium.

