LITHIUM-RICH BRINES AT SALAR DE UYUNI AND NEARBY SALARS IN SOUTHWESTERN BOLIVIA

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The project report series present information resulting from various kinds of scientific, technical, or administrative studies. Reports may be preliminary in scope, provide interim results in advance of publication, or may be final documents.

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INTRODUCTION

In a recent summary of information about lithium resources in salars of the central Andes (Ericksen and others, 1976) it was concluded that Salar de Uyuni and Salar de Coipasa in southwestern Bolivia formed under conditions that were favorable to the accumulation of large amounts of lithium-rich brines. Unfortunately, the few known chemical analyses of brine from Bolivian salars had not determined lithium, so that the conclusion about lithium-rich brines at Uyuni and Coipasa could not be verified at the time of oral presentation of these conclusions at a symposium on "Lithium resources and requirements by the year 2000" in January, 1976 (Vine, 1976).

Verification did come in June, 1976, when two brine samples collected by W. D. Carter, U.S. Geological Survey, Reston, Va., and Raul Ballón, Servicio de Geológia and Minería de Bolivia (GEOBOL) from Salar de Uyuni were analyzed by Shirley L. Rettig, U. S. Geological Survey, and found to contain 490 ppm and 1,510 ppm Li, respectively. As a result of this initial discovery of lithium-rich brine at Salar de Uyuni, the cooperative study (between GEOBOL and the USGS) on which this report is based, was organized, and the field investigations carried out in September, 1976. These investigations have shown widespread lithium- and potassium-rich brines in Salar de Uyuni, and the presence, at least locally, of similar brines in the nearby salars of Coipasa and Empexa.

In the central Andes, lithium-rich brines are found chiefly in large basins of the interior drainage that have prevailed since early Pleistocene or late Tertiary time and in which there has been intense volcanic activity during late Tertiary and Quaternary time. Rhyolitic volcanic rocks of the central Andes have been shown to contain abundant water-soluble salts (Ericksen, 1961), which are selectively leached by circulating ground water and which may be a source of some of the lithium. Furthermore, thermal springs in this region, which may discharge water of volcanic origin as well as deeply circulating ground water, tend to be high in lithium and may be major sources of lithium in the salars. The link between volcanism and high-lithium brines has been noted elsewhere. White and others (1963) noted that geyser waters in volcanic areas tend to have very high Li/Na ratios that may indicate a high content of lithium in certain volcanic emanations. Bargar and others (1973) reported the lithium mineral lepidolite to have formed by deposition by a thermal spring in a geyser basin in Yellowstone National Park that has exceptionally high lithium to potassium ratios. Vine and others (1975) concluded that tectonism and volcanism provided the plumbing system and the heat for convective circulation of ground water needed to leach lithium from large volumes of rock.

Field investigation

Our field investigation in September, 1976, included reconnaissance of the regional geology and hydrology, the study of geomorphology and mineralogy of the salar crusts, and the sampling of salt crust and near-surface brines. Most of the brine samples were collected from 5-cm diameter, 50-cm deep holes that were drilled with a hand-held, gasoline-powered, four-horsepower chain saw motor that was modified to drive a specially designed drill stem equipped with tungsten carbide teeth.

The field party consisted of five geologists: Raul Ballón, Servico Geológico de Bolivia (GEOBOL), George E. Ericksen and James D. Vine, U. S. Geological Survey, Gerald Blanton, Lithium Corporation of America, and Ihor A. Kunasz, Foote Mineral Co. All five geologists participated in the study of Salar de Uyuni, after which Blanton and Kunasz returned to La Paz, and the study of Empexa and Coipasa was made by Ericksen, Vine, and Ballón. Travel was by two 4-wheel drive cars with chauffeurs furnished by GEOBOL.

Access to the interiors of the salars is difficult because they are surrounded by marshes, muddy flats, and ponds. Vehicles can enter at only a few places that are sufficiently dry to support a primitive roadway or dirt-filled causeway, and even these become impassable during and after periods of heavy rainfall. The principal access road to Salar de Uyuni extends onto the salar at the salt works west of Colchani (fig. 1). Access at other places include roads from Canquella and Llica, which connect to Salar de Coipasa and Salar de Empexa. It was possible to drive onto Salar de Coipasa from a road at its southern margin, but the interior of Salar de Empexa was not accessible by road at the time of our visit.

The salt crust of Salar de Uyuni is exceptionally flat and smooth so that it is possible to travel by automobile almost in any direction at high velocity. Roads do not exist on the salar--one navigates by sighting on distant mountains or by compass. Coipasa is less smooth and more subject to flooding during the dry season, and therefore less accessible than Uyuni.

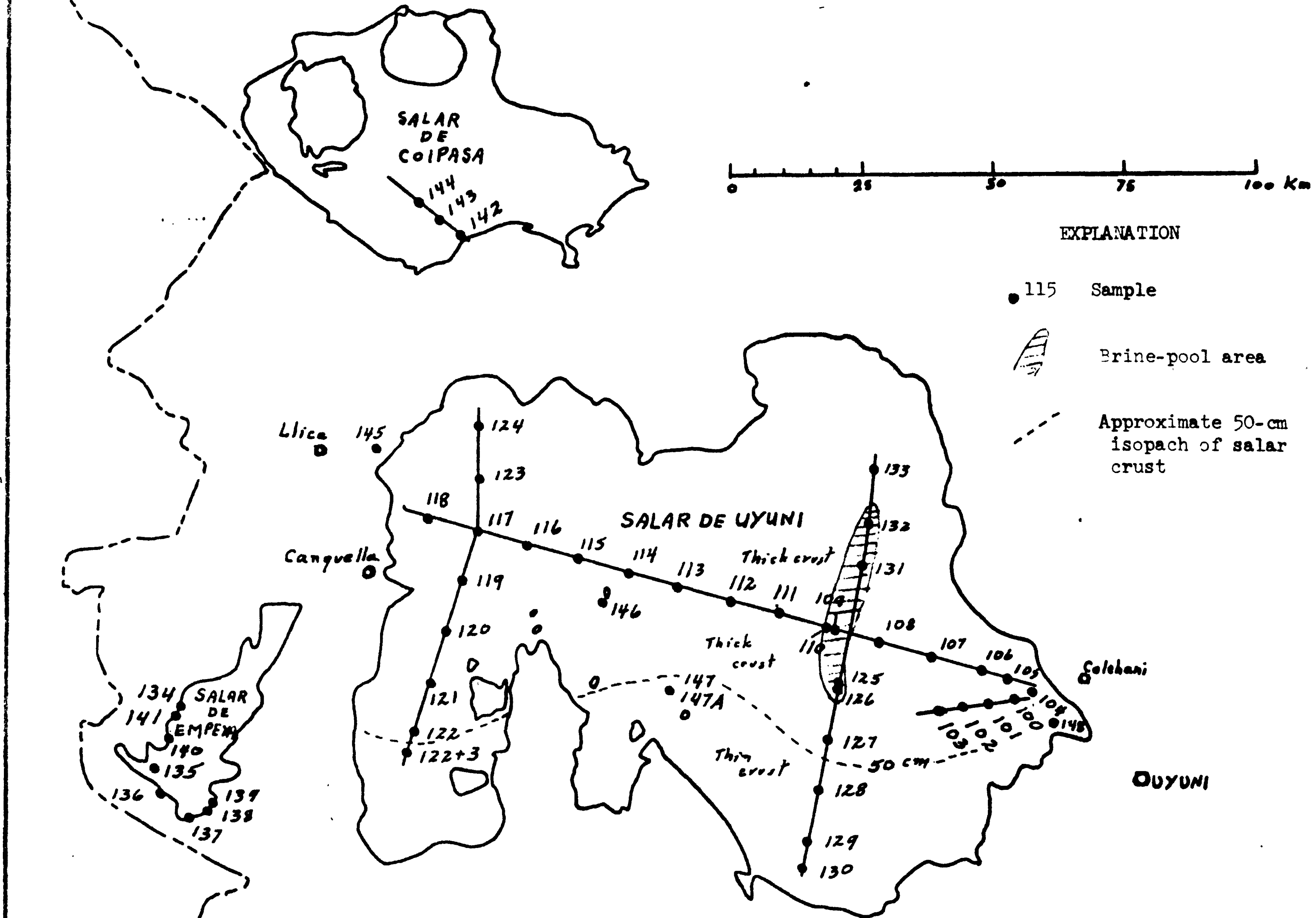

Figure 1.--Index map of Salar de Uyuni and nearby salars in southwestern Bolivia showing location samples.

Samples of brine were collected from 39 localities at Salar de Uyuni and 3 localities each at Salar de Coipasa and Salar de Empexa (fig. 1). An additional 5 samples were collected of saline springs at the west and southern margins of Empexa. The samples of brines for which partial analyses are shown in table 2 were collected as 250 ml plastic vials; duplicate large samples (2,000 ml) were collected at 20 of the same localities. The large samples, analyzed more completely and with greater precision than the 250 ml samples, are discussed in a separate report by Shirley L. Rettig and Blair F. Jones, USGS (Unpub. data). Partial chemical analyses of the saline crust from sample localities shown in figure 1 are listed in table 1.

Most of the brine samples from Salar de Uyuni were collected from drill holes at 10 km intervals along three major traverses, one crossing the salar in an east-west direction and the other two north-south. Samples also were taken along a shorter traverse in the southeastern part of the salar and at a few selected localities. Most of the drill holes were made with the gasoline-powered hand-held drill but a few samples were collected from hand auger holes 1.5 cm diameter and 40 cm deep, after a temporary breakdown of the motorized drill. Before sampling the drill holes, the brine was blown from the hole by a rubber tube to remove salt particles due to drilling, and to homogenize the brine in the hole. Thus, the samples represent the average brine that saturates the upper 40-50 cm of salt crust.

Samples at Empexa were collected from thermal springs and hand dug pits near the southern and western margins of the salar. The brine samples come from the marginal sulfate zone consisting chiefly of granular gypsum and gypseous soil. Brine samples from Coipasa were taken at 5 km intervals from 50-cm deep drill holes along a 10 km traverse in the southern part of the salar (fig. 1).

Acknowledgments

We wish to express our appreciation to personnel of GEOBOL and others for assistance in organizing and carrying out the investigation of salars in southwestern Bolivia. The Earth Resources Satellite Program of GEOBOL, referred to as ERTS-GEOBOL, paid the cost of international and in-country travel, and furnished logistical support for the actual field work. We are particularly grateful to Carlos Brockmann, Director, ERTS-GEOBOL, for his effective support of the investigation and for arranging the logistics. Our American geologist colleagues Gerald C. Blanton, Lithium Corporation of America, and Ihor A. Kunasz, Foote Mineral Co., contributed in many ways to make the work both pleasant and effective. Blanton and Kunasz made available to us the results of analyses of duplicate brine samples by their respective companies. We wish to thank John H. Curry, Regional Minerals Attache, American Embassy, La Paz, who furnished Embassy support for the investigation.

In the town of Uyuni, we were fortunate in being invited to stay at the guest house of the National Railroad Company (Ferrocariles Nacional del Estado), which was arranged by Ing. Gustavo Mendez, Gerente General, La Paz. Srs. Walter Alvarez, Luis Cespedes, and Waldemar Villafane of the National Railroad staff in Uyuni were most hospitable during our stay. People of the village of Canquella invited our group to "camp" in the school house during our 3-day stay while studying the salars of Coipasa and Empexa. We thank Sr. Abelino Ticona A., Corregidor of Canquella, and Prof. Nelle Saavedra de Morales, school teacher, for their assistance.

Several of our colleagues in the USGS aided in our study. Shirley L. Rettig made the first lithium analyses and analyzed the special large samples, which will furnish control data for the other analyses and for future work. Blair Jones contributed to the geochemical interpretation of the brine analyses. Preliminary brine and water analyses reported here (table 1) were made by Allen L. Meier. Rudolph Raspet and William E. Huff designed the core drill used in this study. William D. Carter, who collected our first samples at Salar de Uyuni, also furnished ERTS data about flooding of Salar de Uyuni.

PLEISTOCENE LAKES

Salar de Uyuni and nearby salars in southwestern Bolivia are remnants of a former large lake called Lago Minchin (fig. 2) that occupied the southern Bolivian Altiplano in late Pleistocene, and it seems probable that they contain most of the saline material that has been accumulating in lakes of the Altiplano since it first developed as a basin of interior drainage in late Pliocene or early Pleistocene time. The oldest lakes in the Altiplano, which are considered to be of early Pleistocene age (Ahlfeld and Branisa, 1960) include Lago Ballivian (fig. 2), considered to be the ancestral Lago Titicaca, and a large lake to the south that Ahlfeld and Branisa (1960) called Lago Pre-Minchin. Ahlfeld and Branisa (1960) reported the presence of well-developed terraces of Lago Ballivian in the vicinity of Lago Titicaca, extending upwards to about 100 m above present lake level to the north of the lake in Peru, but only to about 65 m in Bolivia to the south. These authors conclude that the different terrace levels of these two areas is the result of tectonic movement during Pleistocene. Terraces of Lago Pre-Minchin were observed by Ahlfeld and Branisa (1960) only in the region between Patacamaya and Viacha (fig. 2), so that the southern extension of this lake is not known. However, this lake may have extended over most of the area later covered by Minchin. Well-developed terraces of Lago Minchin are widespread in the southern Altiplano from near Oruro in the north to Ollagüe in the south (fig. 2).

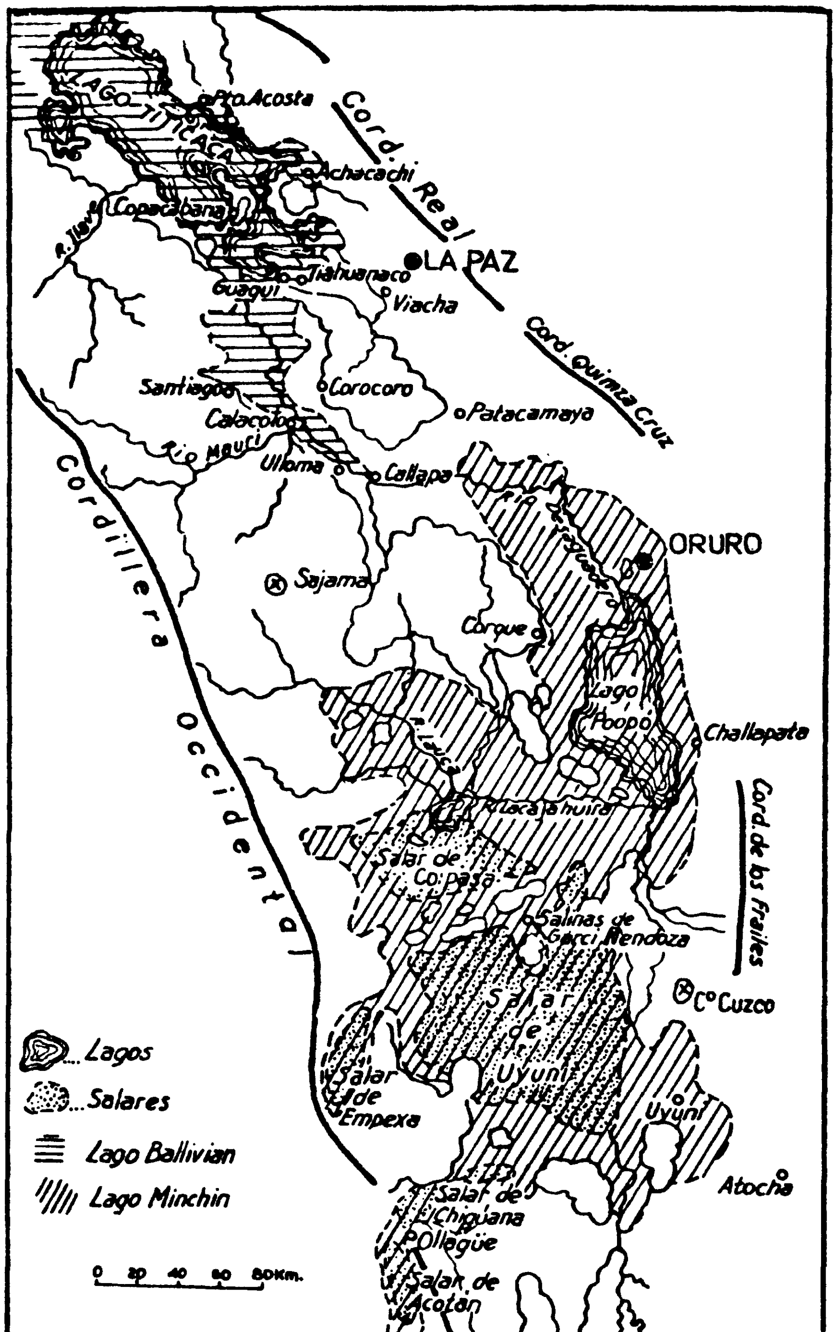

Figure 2.--Index map of the Bolivian Altiplano showing the location of present-day lakes and salars, and the former large lakes Lago Ballivian and Lago Minchin. After Troll and Ahlfeld <u>in</u> Ahlfeld and Branisa (1960).

Extensive deposits of algal limestone were formed in the shallow marginal waters of Lago Minchin, and clearly mark various terrace levels at many localities (fig. 3). Terraces and deposits of algal limestone are prominent in the vicinity of Salar de Uyuni where they show the former lake level was once at least 75 m above the present salar level, which is at an altitude of 3,653 m. Three or four prominent terraces may be distinguished at land-like hills in Salar de Uyuni and at hills marginal to the salar. Ahlfeld and Branisa (1960, p. 160) reported four distinct terraces in Cerro Llipillipi in the southeasternmost part of Salar de Uyuni, (fig. 2), at 75 m, 50 m, 25 m, and 20 m above the level of the salar. The town of Colchani, at the eastern margin of the salar (fig. 1), is on a fith terrace that corresponds to the lowest terrace shown in figure 3. The road north of Colchani, and within distance of 15 km, crosses 3 or 4 other prominent terraces that are marked by large algal heads as much as 3 m high (fig. 4).

The following chemical analysis of the algal limestone is cited by Ahlfeld and Branisa (1960):

	Percent
$CaCO_3$	92.40
$MgCO_3$	.98
SiO_2	4.64
Fe_2O_3	.46
Al_2O_3	.36
Organic material . . .	.15
H_2O	.85
Total	100.00

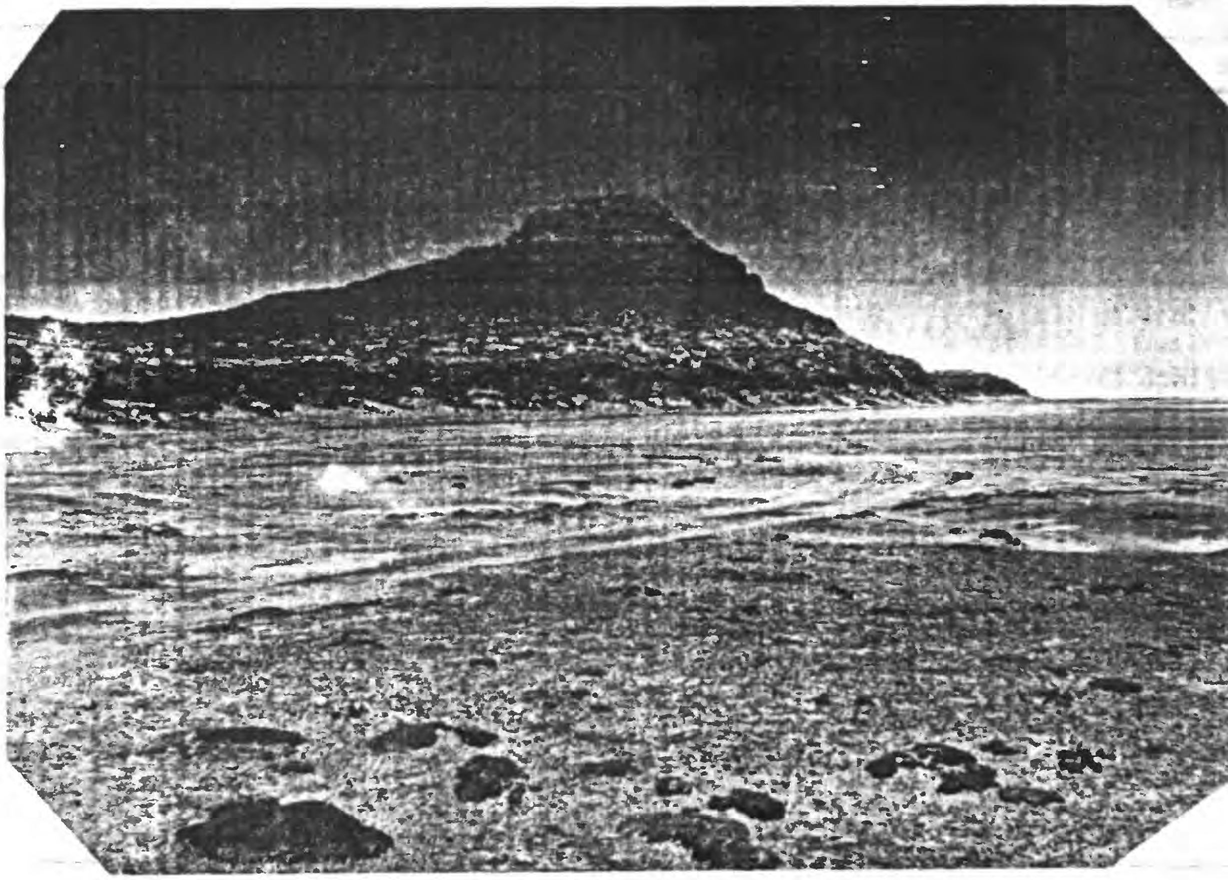

Figure 3.--Hill at eastern margin of Salar de Uyuni covered with algal limestone deposited in former Lago Minchin, and showing three distinct terraces (T). Silty salt flat in foreground is a fourth terrace that slopes gently upward from near the present salar margin. It is covered with discontinuous mats and flattened "heads" of algal limestone.

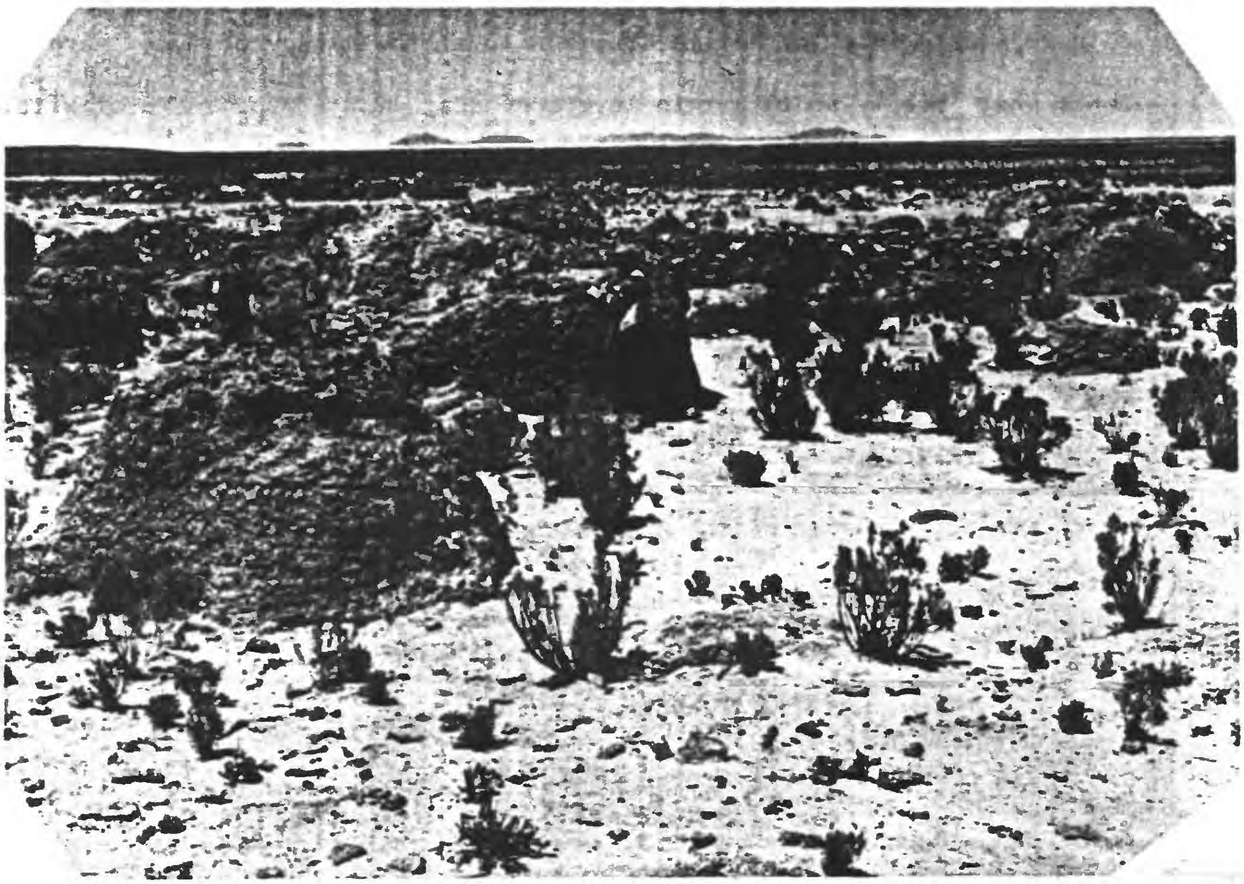

Figure 4.--Large algal "heads" near upper margin of broad terrace about 6 km northeast of Colchani, about 20 meters above present salar level.

CHARACTER OF THE SALAR CRUSTS

Each of the three salars discussed in this report has certain distinctive geologic and hydrologic features. Uyuni and Coipasa consist of hard, smooth, interior halite crusts with narrow marshy or muddy marginal zones that locally contain thin layers of soft impure gypsum and ulexite. During the rainy season of December-March the surfaces of these salars are extensively flooded (fig. 5), but during the ensuing dry season the brines evaporate and recede to the level of the salar crust while depositing a new layer of salt on the salar surface. During especially rainy years, the central part of Salar de Uyuni is said to be covered with brine to depths of 50-75 cm. At the time of our investigation in September, 1976, which was near the end of the dry season, we found that at most places the brine level was essentially at the surface or at depths of not more than a few centimeters. At a few sample sites the brine was encountered at depths of 10-30 cm. Because the brine level is at or near the surface over most of Salar de Uyuni, the salt at the surface remains slightly moist throughout the dry season. We found that local broad depressions, tens to hundreds of meters in width in the northeastern part of the salar, were covered with brine to depths of 5-20 cm at the time of our visit. In contrast, the western arm of the salar, which shows a complex pattern of flooding in figure 5, was dry at the time of our visit.

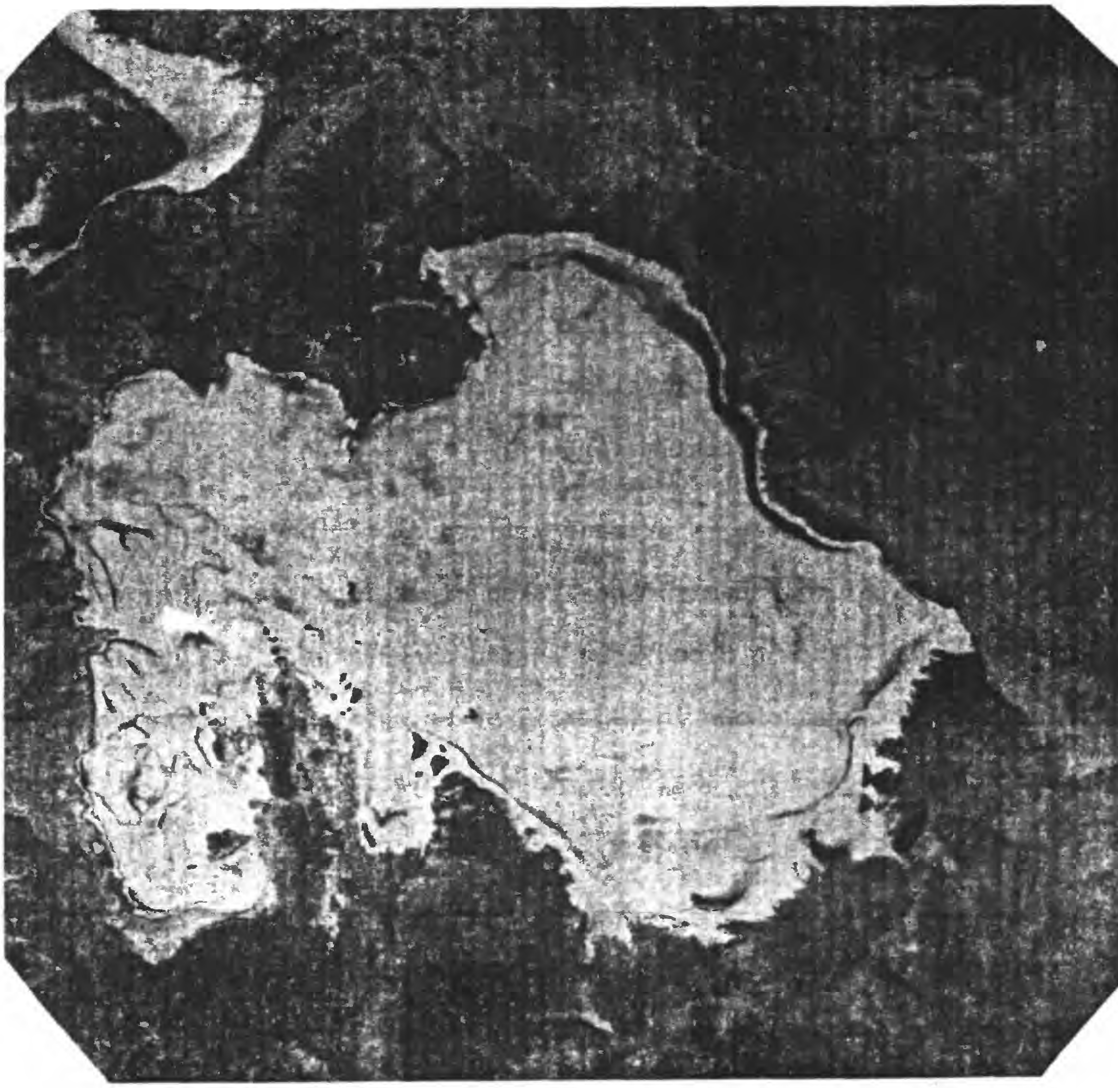

Figure 5.--Landsat image taken December 17, 1975, showing Salar de Uyuni and southeastern corner of Salar de Coipasa to the north. Dark patterns on salar surfaces show the distribution of shallow brine ponds. Maximum depth of brine in most of these ponds probably is a few tens of centimeters, but brine in the very dark areas near the northeastern margin of Uyuni and southeastern part of Coipasa may be a meter or more in depth.

As a consequence of salt being dissolved from the salar crust during flooding and precipitation of new salt as the surface brine evaporates, the crust of Salar de Uyuni is exceptionally smooth. Average maximum relief in most areas of the salar, due to clusters of halite crystals and upraised granular salt ridges or depressions at margins of desiccation polygons, is about a centimeter (figs. 6 and 7).

Salar de Coipasa is evidently flooded for longer periods of time than Salar de Uyuni. Landsat images taken at various times during the past several years show a broad area in the eastern part of Coipasa, which includes the area shown in figure 5 as being flooded during the dry season, and it is assumed that most of the rest of the salar is flooded during the rainy season as is Salar de Uyuni. The hard salt surface in the area that we sampled in the southern part of salar was covered with as much as 2 centimeters of brine at the time of our visit in September, 1976, near the end of the dry season when brine level would be expected to be at its' lowest. Because the brine does not evaporate to dryness in this area, the salt crust is somewhat different from that of Salar de Uyuni. The new salt surface is covered with flattened halite crystals and knobby large crystals (fig. 8), and desiccation polygons are lacking, an indication that the surface never dries out completely. Marginal marshy areas of Salar de Coipasa contain gypseous mud and locally have exploitable ulexite layers (Ahlfeld and Schneider-Scherbina, 1964).

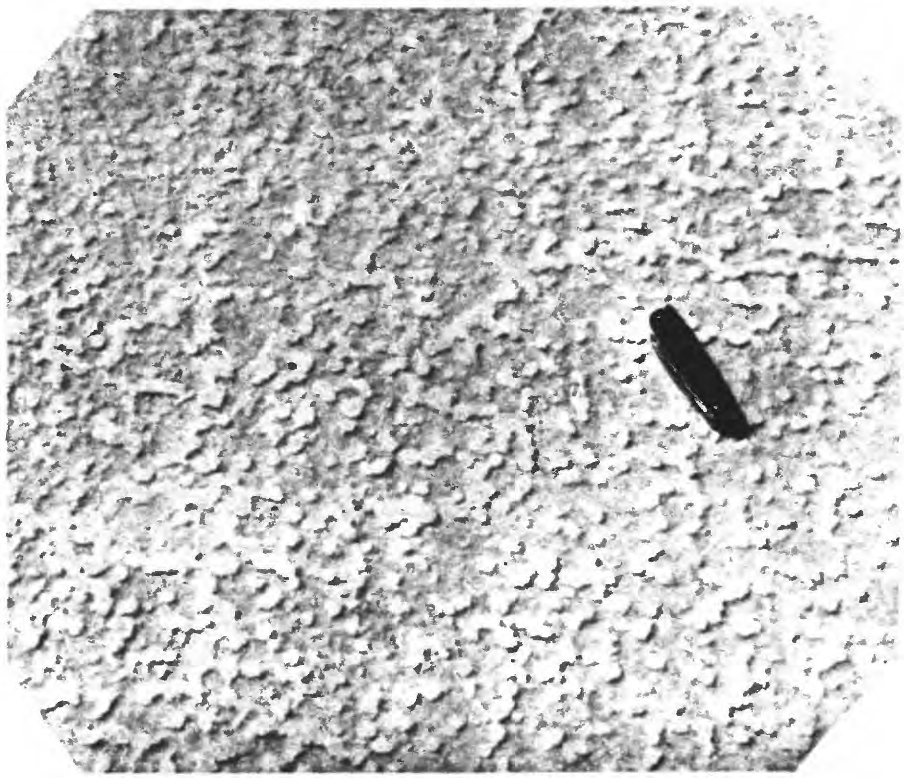

Figure 6.--Surface of Salar de Uyuni showing flattened clusters of halite crystals on the relative smooth salar surface. Pocket knife scale is 9 cm long. Crystal clusters average less than 1/2 cm in height.

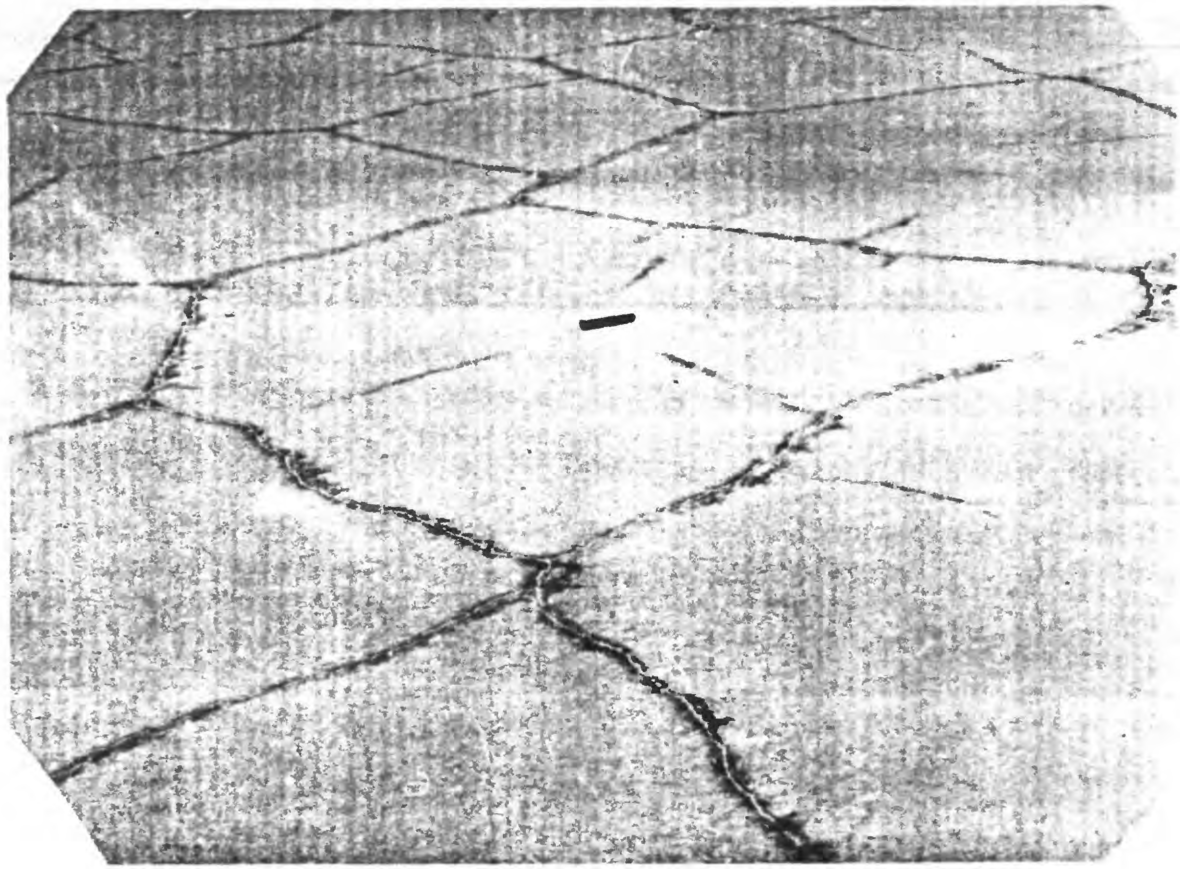

Figure 7.--Desiccation polygons in salt crust estimated to be 50-100 cm thick, southwestern arm of Salar de Uyuni. Margins of polygons are marked by organic-rich silt from within the salt crust and by veinlets of white granular salt that formed by evaporation of brine in the desiccation cracks.

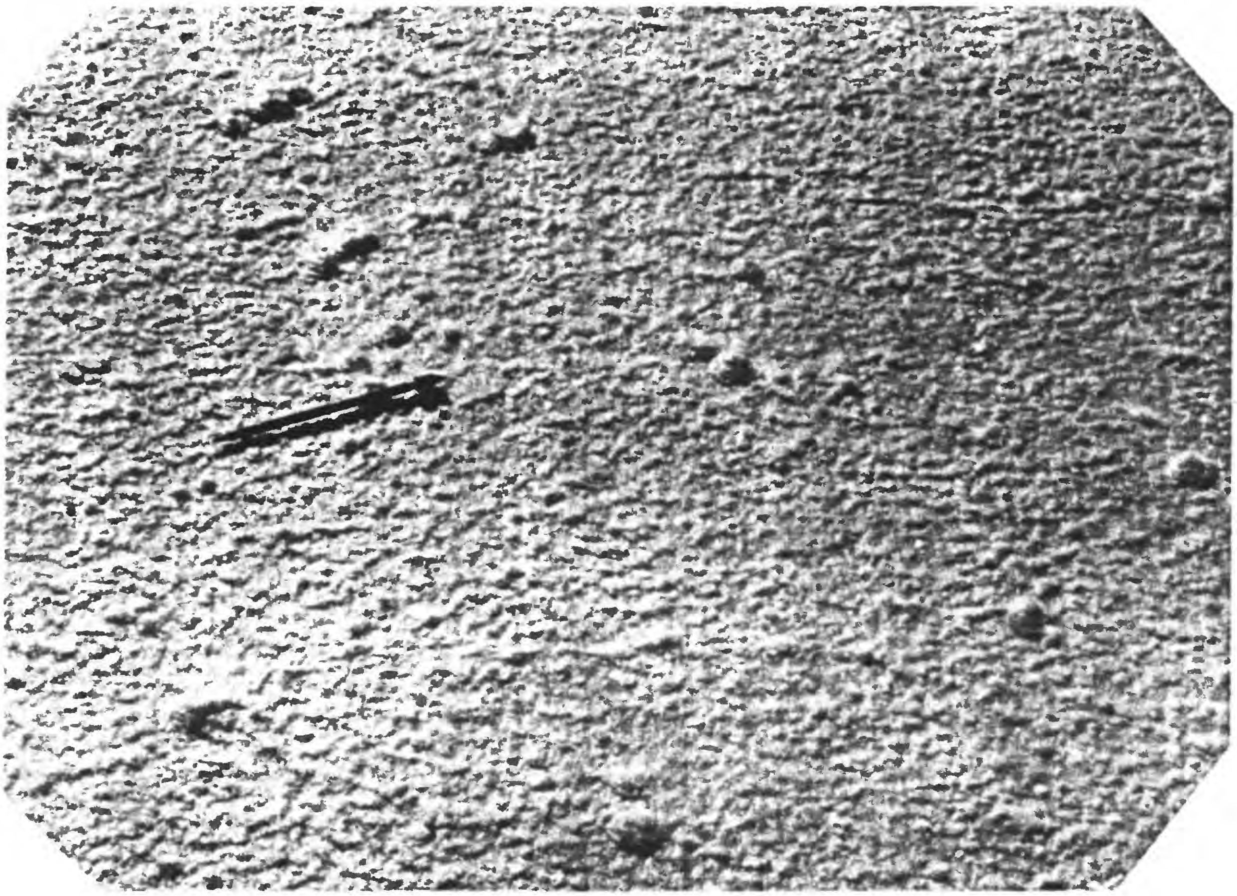

Figure 8.--Typical salt surface of Salar de Coipasa, which is flooded most of the year. Surface lacks desiccation polygons and is covered with flat halite crystals averaging about 1/2 cm in diameter and has scattered large halite crystals as much as 3 cm in diameter.

Salar de Empexa differs from Uyuni and Coipasa in consisting largely of a relatively thin, soft, granular, gypseous crust. When sampled in September, 1976, the brine along the western side of the salar was found to be 20-30 cm beneath the surface. Judging from the condition of roads and trails here and the presence of thin patches of halite crust, this area becomes flooded during the rainy season. The interior of the salar has a hard halite crust, which we saw only at one place near the western side of the salar where it is less than 10 cm thick. This halite crust is relatively smooth and evidently subject to annual flooding. Ahlfeld and Schneider-Scherbina (1964) reported that borate (ulexite) had been mined at the southern and northern ends of Salar de Empexa.

Very little is known about the maximum thickness and variations in thickness of the halite crusts of the three salars. Ahlfeld and Branisa (1960) reported the crust in the central part of Salar de Uyuni to be 2-8 m thick, but they do not mention how this was determined, although they state that the crust had not been drilled. According to data on file at GEOBOL in La Paz, a diamond drill hole near Isla de Pescado (near sample 146, fig. 1), where the salt crust would be expected to be relatively thick, penetrated about 15 m of salt crust beneath which were brine-saturated lacustrine sediments to the bottom of the 150-m deep hole. We found the salt crust to be thin in the southern part of the salar as indicated in figure 1.

The halite crust of both Uyuni and Coipasa is distinctly layered, consisting of alternating layers of coarse grained porous halite and generally thinner layers of finer-grained more dense halite. Individual layers generally range from about a centimeter to about 10 centimeters in thickness, and some are separated by thin films of organic-rich clay or layers of clay and muddy salt a few millimeters to several centimeters thick. Both clay and associated brine have a strong fetid odor. Permeability of the salt is high, and average porosity was estimated during field work to be on the order of 20-30 percent. Core segments shown in figure 9 give an idea of variations in porosity of the salt crust, although they do not show the most porous material that consists of a relatively incoherent meshwork of large halite crystals that was not recoverable as core. Of the cores shown in figure 9, sample 112 has an estimated porosity of 30-40 percent whereas the fine-grained relatively dense sample 108 averages less than 20 percent.

The main salar crusts of Uyuni and Coipasa are relatively pure halite. Ahlfeld and Schneider-Scherbina (1964) cited an analyses of salt from Salar de Uyuni as containing 95.1 percent NaCl, 0.34 percent Na_2SO_4, and 0.25 percent Na_2CO_3. Table 23 shows considerable variation in content of Li, K, and Mg in the salt, which in part reflects the presence of these elements in the brine that saturated the salt samples, as well as in the salt itself. Strontium is relatively constant.

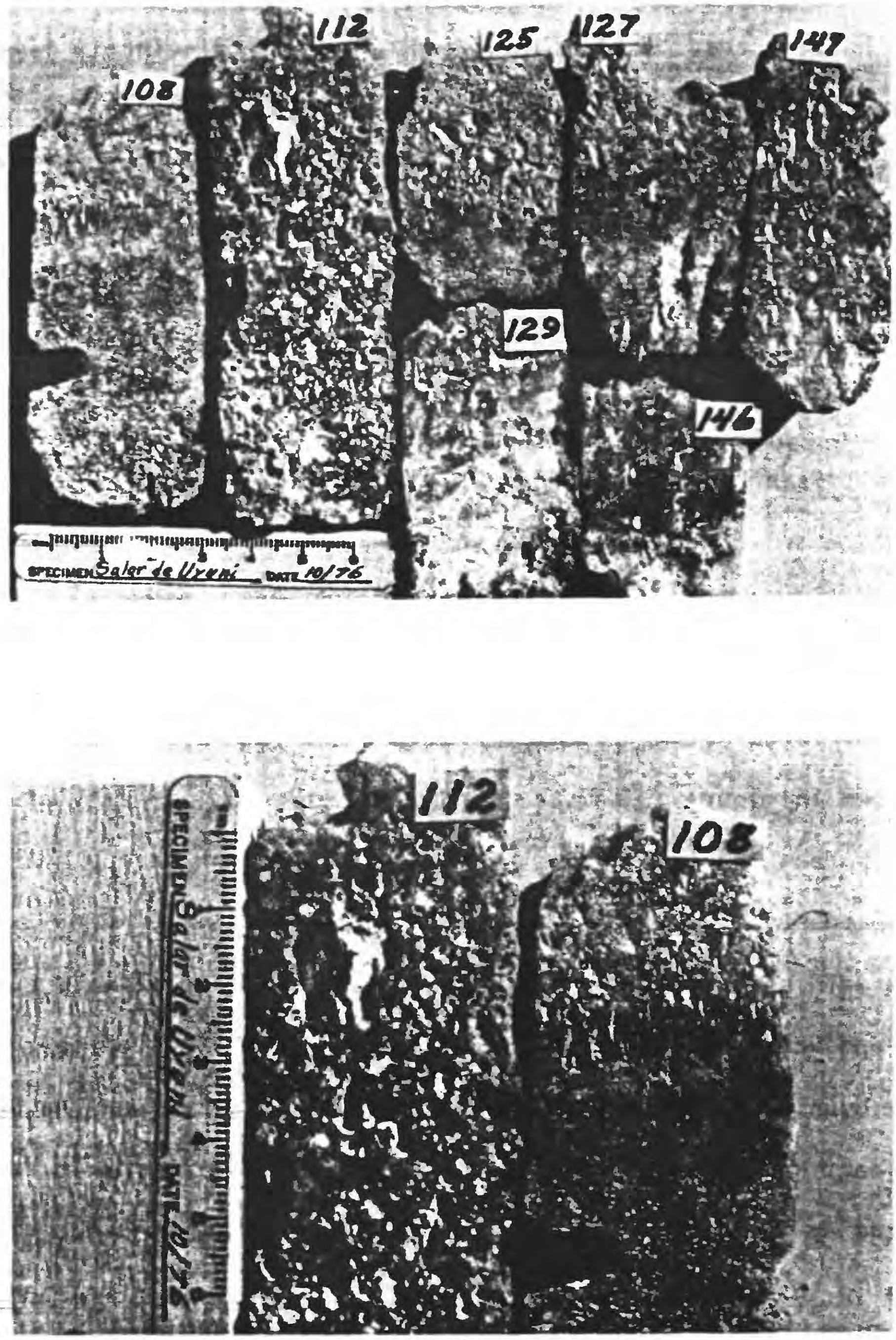

Figure 9.--Photographs of sections of salt core segments from shallow drill holes in Salar de Uyuni showing variations in porosity. Scale in centimeters. Sample numbers refer to localities shown in figure 1.

Table 1.--Analyses of samples of saline (s) material from salars in southwestern Bolivia (in ppm).

Sample No.	Li	K	Mg	Sr
		Salt samples		
SU-100s	15	450	580	610
101s	12	420	530	660
102s	14	560	610	610
103s	5	310	460	610
105s	12	290	440	620
106s	15	510	570	590
107s	16	520	580	620
108s	12	370	490	620
111s	10	370	470	640
112s	9	390	500	610
114s	15	560	610	590
115s	16	540	610	670
116s	22	640	710	610
117s	14	520	630	610
118s	4	380	560	650
119s	60	1600	1300	660
120s	31	820	850	650
121s	19	600	660	640
122s	48	1200	1100	690
123s	6	370	660	680
124s	1	300	510	660
125s	13	700	640	650

Table 1 (cont'd).--Analyses of samples of saline (s) material from salars in southwestern Bolivia (in ppm).

Sample No.	Li	K	Mg	Sr
		Salt samples		
SU-126s	15	500	640	680
127s	18	730	730	690
128s	65	2700	2700	680
129s	16	700	800	660
130s	51	3900	1200	660
131s	22	630	740	530
132s	10	410	560	550
SE-140s	24	740	1200	940
SC-142s	40	1700	1600	610
143s	11	610	710	650
144s	5	490	560	630
SU-146s	10	370	490	630
147s	24	850	830	640

The accumulation of relatively thick and pure halite crusts, which are characteristic of many salars in the central Andes, is due to fractional crystallization in saline lakes that formerly occupied the basins of interior drainage that now contain the salars, and to further separation of salines of differing solubilities by partial solution of saline material by rainwater and during seasonal or periodic flooding followed by seasonal evaporation and precipitation of new crust. Huge amounts of calcium carbonate ($CaCO_3$) were deposited in Lago Minchin when it was of maximum size and during the time it slowly dried to the level of Salar de Uyuni. As the result of the removal of $CaCO_3$ the waters of Lago Minchin became progressively enriched in the more soluble saline components such as chlorides and sulfates. It is probably that the lacustrine sediments beneath the saline crusts of Uyuni, Coipasa, and Empexa also contain admixed $CaCO_3$, as do sediments in better known salars in Chile. Calcium sulfate separated as gypsum ($CaSO_4 \cdot 2H_2O$) from saline waters to form the extensive gypseous zone of Salar de Empexa and gypseous muds that occur in marginal areas of Uyuni and Coipasa. Gypsum probably also is abundant in the lacustrine sediments beneath the saline crusts of these salars. At places, gypseous marginal zones of the salar also contain layers and scattered nodules of the borate mineral ulexite ($NaCaB_5O_9 \cdot 8H_2O$), which in times past have been exploited as a source of boron. Separation of carbonate, sulfate, and calcium during primary evaporation of saline lake water and selective leaching of saline deposits thus formed, ultimately resulted in a concentrated chloride brine that formed the high-purity halite crusts, and which became enriched in lithium and potassium.

Most of the saline material in Salars Uyuni, Coipasa, and Empexa were probably deposited during final drying of Lago Minchin, probably not more than a few thousand to a few tens of thousands of years ago. A sample of organic-rich mud collected by W. D. Carter from Salar de Uyuni about 35 km west of Colchani gave a radiocarbon date of 3,520 ± 600 years (W.D. Carter, oral communication). This sample came from a depth of 15 cm beneath the surface of the salt crust in an area where the crust is relatively thick, perhaps 10 m or more. The apparent rate of accumulation of salt here has been about 4 mm per hundred years since deposition of the mud layer. A rate of deposition of this order of magnitude probably has prevailed since drying of Lago Minchin.

The surface of Salar de Uyuni shows several features that are indicative of processes that tend to modify the characteristically flat, smooth surface caused by annual flooding and drying. Broad areas in the northern part of the salar, which are flooded to maximum depths of about 20 cm during the dry season, are thought to be due to differential warping of the salt crust. Shallow water courses are present at places where they evidently were etched by shallow "streams" of unsaturated brine. These channels may be several meters wide but are extremely shallow--maximum depths commonly are not more than 2 or 3 cm. Solution along margins of desiccation polygons may leave the polygons standing in relief as shown in figure 10. Brine pools (fig. 11) along our eastern north-south traverse (fig. 1) evidently formed by dissolution of the salt crust by spring water or unsaturated brine from beneath the crust. The pools form at the margins of desiccation polygons and one can observe all stages of their development from the earliest brine filled fissure-like openings to irregular pools as much as 2 m long and 50 cm wide. Depths of as much as 2 m were observed, but total depths could not be determined because of the irregular shape of the pools. It is assumed that they extend to the bottom of the salt crust. Thin films of brine around the pools at the time of our visit in late September, 1976, indicated a weak flow of brine from the pools. At this same time it was noted that thin salt crusts and large halite crystals (as much as 5 cm across the face) were being deposited on the sides of some of the pools, indicating that the brine was saturated or even super-saturated at this time of the year, perhaps because of a reduction in flow of spring water at the end of the dry season.

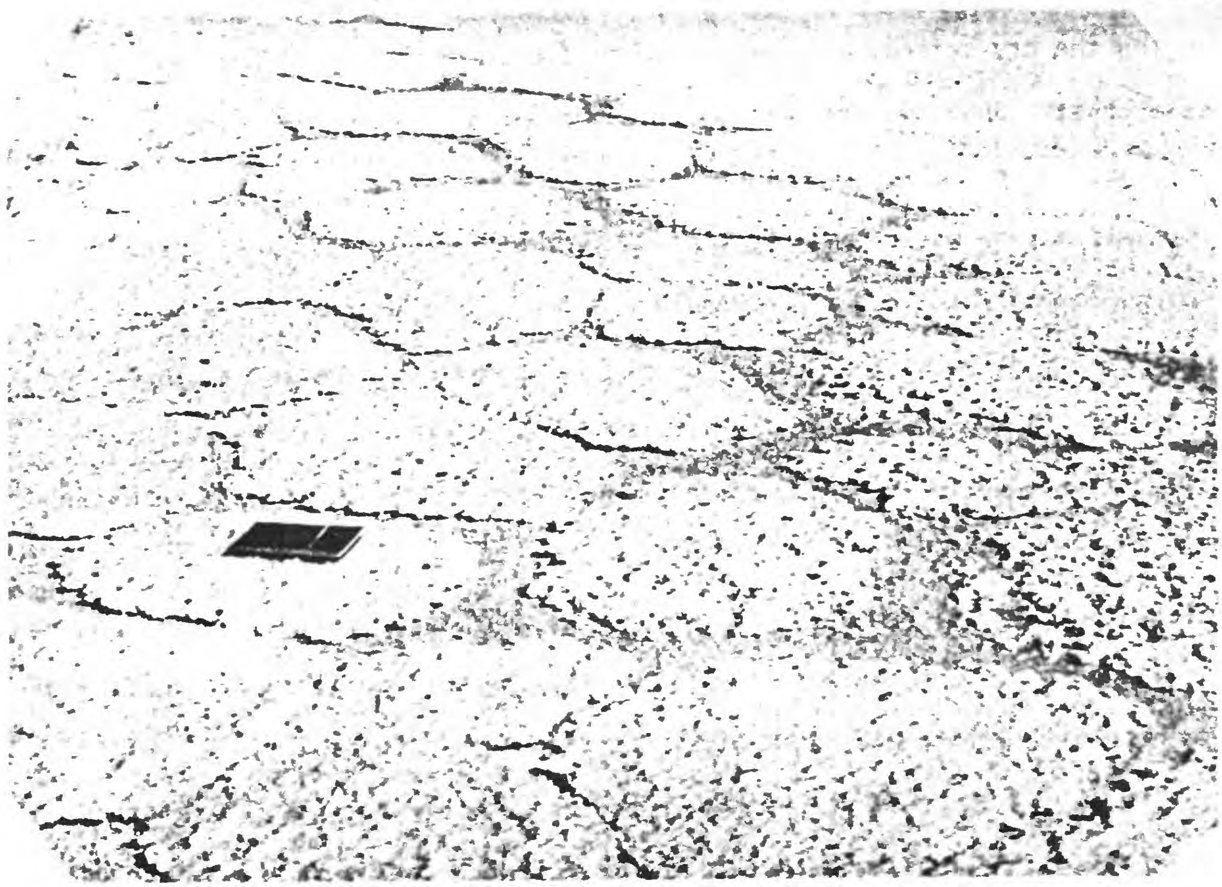

Figure 10.--Eroded desiccation polygons on surface of thick salt crust (probably >5 m) in center of Salar de Uyuni, where a narrow depression is a water course for rainwater.

Figure 11.--Small brine pool in salt crust in eastern part of Salar de Uyuni (fig. 1). Pool is irregular in vertical and horizontal section, and here is at least 2 m deep. Clear brine fills the pool to the level of the salar surface. Pool probably is due to inflow of unsaturated spring water from lacustrine sediments below salt crust. Moist areas around pool indicate only a slight flow at end of 1976 dry season when photograph was taken. A newly deposited thin salt crust at the margin of this salt pool shows brine to be saturated or super-saturated at this time of year.

The relatively small size of the brine pools in Salar de Uyuni indicate either a very slow rate of inflow of fresh water or that dissolution is by a brine that is only slightly below saturation. Brine pools first reported from salars in Chile (Stoertz and Ericksen, 1974) where moderate inflows of fresh water formed pools in halite crusts as much as 7 m in diameter and 7-10 m deep. Springs in the brine pool area of Salar de Uyuni may be related to a north-trending recent fault that crosses the salar in this area (W. D. Carter, unpublished data, 1975).

Wind-generated currents in surface waters during periods of deep flooding of the salars and windblown spray and sheets of shallow surface water tend to cause widespread mixing of brines and the development of erosional and depositional features in the salar surfaces. Local inhabitants have observed strong wind-generated currents in the flood waters of the rainy season in the interior of Salar de Uyuni. At some places in Salar de Uyuni we observed a delicate grooving of the salar surface that evidently was the result of corrosion of the halite by wind-blown rain and unsaturated brine spray or surface brine films. Crescent-shaped (fig. 12) to oval-shaped mounds consisting of granular halite and solidified saline froth, which we refer to as froth mounds, are widespread on the surface of Salar de Uyuni, where they have formed by deposition from spray and wind-driven shallow surface water. These froth mounds form at an obstruction such as a rock or salt fragment that someone has placed on the salar, or some natural irregularity such as a cluster of halite crystals or upraised margin of a desiccation polygon. They range from a centimeter to about 15 cm in maximum height and about 50 cm to 8 m in longest dimension. Although in

Figure 12.--Froth mound on surface of Salar de Uyuni. Consists of a dry, well cemented mass of halite fragments and crystals and salt froth that was deposited from wind-driven shallow water and spray at an obstruction on the salar surface. Felt tip marking pencil is at position of natural obstruction around which mound has accumulated. Mound is about a meter long and maximum height is about / cm.

plan the froth mounds are shaped like miniature sand dunes; the process by which they grow is different. Fragments of salt and froth that are carried along by very shallow wind-blown brine and spray builds up in front of the obstruction and then trails off to the sides to form the typical streamlined half moon shape of the barchan dune. Continued deposition results in enlargement on the windward side of the obstruction as the leeward arms coalesce. The final shape, typical of the larger mounds, is oval, and the obstruction where the mound first started to accumulate is near the middle.

NATURE OF THE BRINES

Temperatures and densities

In addition to variations in chemical composition, the brines from shallow drill holes and salt pools in Salar de Uyuni show variations in temperature and density. Brine in drill holes in the halite crust in the interior of the salar has an average temperature of 5°-$6^{\circ}C$ and a density chiefly of 1.20-1.21 (measured in the laboratory at $25^{\circ}C$, as are all following densities). The brine in the brine pools in the eastern part of the salar (fig. 1) tends to be higher in temperature and denser. Several pools were found to have temperatures of 9°-$12^{\circ}C$, which were the highest brine temperatures encountered in Salar de Uyuni. These abnormally high temperatures are probably the result of an inflow of warmer spring water from beneath the salar crust in this area. Of the three samples of brines collected from these pools, two (SU-109 and SU-126, table 1) were found to have densities of about 1.22, whereas the third sample (SU-131) has a density of 1.21. The two samples having the highest densities also are high in magnesium and potassium (table 1). Two brine samples (SU-129 and SU-130) from the southeastern part of the salar were collected from shallow pits in brine-saturated lacustrine sediments beneath a thin salt crust. They show the highest densities (1.22-1.23) of the brines collected in the salar, and also are highest in lithium, potassium, and magnesium (table 1). Analyses of duplicate samples supplied by the Lithium Corporation of America show these 4 samples of high density as also having high sulfate (SO_4) (1.57-2.14 percent), which is on the order of twice the value of sulfate in the lower density brines from elsewhere in this salar.

Brines from Coipasa and Empexa are somewhat different. Samples from shallow drill holes in Coipasa show a temperature of 10°C and densities of 1.22 (samples SC-143 and SC-144) and 1.25 (sample SC-142). The brine samples from Empexa, which were collected from 30-40 cm deep pits in gypseous material show temperatures of 5°-6°C; sample SE-135 shows a density of 1.16, which indicates an unsaturated brine. Thermal springs at the western and southern margin of Salar de Empexa show temperatures ranging from 13° to 24°C. Inasmuch as the spring waters are only slightly saline, densities are near 1.0.

Chemical composition

As can be seen in table 2, the concentration of lithium in the brines of the three salars, which are basically saturated chloride solutions, ranges from about 80 ppm to 1,150 ppm. A sample collected previously from a surface pond on the interior of Salar de Uyuni near SU-146 (fig. 1) was found to contain 1,510 ppm Li (Ericksen and others, 1976). The concentrations of lithium vary directly with the concentrations of potassium and magnesium, which show ranges of 0.11-2.0 percent (1,100-20,000 ppm) and 0.15-2.4 percent (1,500-24,000 ppm), respectively. The ratios between these constituents are relatively constant--averages for both Li/K and Li/Mg in the brines from Salar de Uyuni show a mean value of 0.050. In contrast, the median values of these ratios, which are the midpoint values in the data set represented by the analyses, are 0.047 for Li/K and 0.051 for Li/Mg. These median values, which are not biased by a few exceptionally high and low values, are probably nearer the average for the brines than are the mean values. The values for brines from Salar de Coipasa and Salar de Empexa, based on far fewer samples, are Li/K = 0.028 and Li/Mg = 0.025 for Coipasa, and Li/K = 0.043 and Li/Mg = 0.030 for Empexa. Saline spring water from Salar de Empexa (samples SE-136, SE-137, and SE-138), which have relatively low values for Li, K, and Mg, still show ratios of these three elements (Li/K = 0.039-0.068 and Li/Mg = 0.024-0.059) that are not significantly different from the brines.

Lithium values in brines of Salar de Uyuni, which tend to be highest in the middle and southeastern parts of the salar (fig. 13), are due, at least in part, to major drainage patterns within the salar crust and to wind-generated currents in surface brines during periods of flooding, as previously discussed. Maximum values are chiefly in the range of 300-600 ppm. The highest values encountered in this study are those of the two southernmost samples of brine (SU-129 and SU-130, fig. 1), which contain 740 and 1,150 ppm Li. This is an area of very thin halite crust, and the samples of brine were collected from the mud beneath this crust. It seems likely that these brines move only slowly in the relatively impermeable mud in contrast to brines in the highly porous and relatively permeable thick salt crust in the central and northern part of the salar. On the other hand, the samples from brine pools in the eastern part of Salar de Uyuni (SU-109, SU-126, and SU-131, fig. 1) are somewhat higher in lithium than are nearby samples collected from shallow (40-50 cm) drill holes (SU-110, SU-125, and SU-132). It seems likely that this is an indication of density stratification of brine within and perhaps beneath the salar crust, and that a small inflow of unsaturated spring water from beneath the crust mixes with the relatively dense lithium-rich brine in the lower crust, and then flows

Table 2.--Partial chemical analyses of brine and water samples from salars in southern Bolivia (in ppm, or wt percent)[1/] [Samples were collected from holes drilled 40 to 50 cm into the salt crust of the salar with the exception of those marked as follows: bp = brine pool; sp = spring water; sw = surface water; dh = dug hole, excavated by hand in soft sediment].

Sample number	Li ppm	Na percent	K percent	Ca ppm	Mg percent	Cl percent
			Salar de Uyuni			
SU-100	90	10.5	.23	310	.18	13.9
101	140	9.2	.36	450	.30	13.7
102	130	8.6	.32	400	.29	14.3
103	80	9.0	.18	490	.15	13.7
104sw	240	8.4	.58	660	.53	14.3
105	110	8.4	.23	380	.23	13.3
106	240	8.1	.74	400	.45	14.3
107	190	8.5	.43	470	.36	14.0
108	240	9.0	.51	490	.48	14.3
109bp	580	6.9	1.2	310	1.2	14.4
110	420	7.5	1.0	400	.83	14.3
111	230	8.8	.53	720	.42	14.9
112	420	7.3	.85	480	.81	14.7
113	350	7.4	.75	470	.66	14.4
114	300	7.8	.66	470	.61	15.1

1/ Original analyses reported weight per unit volume have been recalculated to ppm or wt. percent on basis of density measurements; ppm values have been rounded to nearest 10 ppm. The analyses vary slightly from analyses of duplicate samples by Foote Mineral Co. and Lithium Corporation of America. Precise analyses by Shirley Rettig, USGS, of large duplicate samples, will be reported separately.

Table 2 Cont'd

Sample number	Li ppm	Na percent	K percent	Ca ppm	Mg percent	Cl percent
Salar de Uyuni (cont'd)						
SU-115	140	9.9	.24	590	.27	14.7
116	130	9.7	.25	540	.27	14.9
117	160	9.6	.29	530	.32	14.4
118	180	9.1	.41	560	.36	14.3
119	250	8.4	.56	490	.50	14.5
120	360	8.3	.75	400	.68	14.5
121	160	9.6	.31	670	.29	14.4
122	310	8.9	.45	440	.58	14.2
122+3	120	9.3	.20	750	.23	14.7
123	100	9.0	.11	410	.19	14.3
124	120	8.9	.19	460	.25	14.2
125	390	8.5	.66	410	.76	14.5
126bp	670	6.8	.92	220	1.33	15.3
127	570	6.9	.91	290	1.16	15.5
128	480	7.7	1.1	360	.92	15.5
129	740	6.5	1.6	260	1.4	14.7
130dh	1150	5.7	2.0	200	2.4	15.6
131bp	310	8.5	.77	510	.60	15.8
132	180	8.7	.44	530	.38	15.0
133	230	8.6	.54	530	.43	14.7
145sw	620	6.5	1.3	380	1.4	17.1
146	420	7.4	1.0	370	.73	16.7

Table 2 Cont'd

Sample number	Li ppm	Na percent	K percent	Ca ppm	Mg percent	Cl percent
			Salar de Uyuni (cont'd)			
SU-147	580	6.8	1.3	350	1.1	16.0
147A	520	6.8	1.2	380	1.0	16.5
148	180	7.6	.45	690	.37	15.5
			Salar de Empexa			
SE-134sp	6	.96	.016	590	.020	.34
135dh	170	5.4	.38	380	.71	11.8
136sp	6	.18	.010	230	.0210	.32
137sp	4	.06	.009	350	.0140	.16
138sw	30	.3	.04	980	.0460	1.6
140dh	220	7.5	.51	480	.83	16.7
141dh	370	7.1	.83	370	.93	15.8
			Salar de Coipasa			
SC-142	580	5.6	2.0	170	2.3	16.3
143	210	7.9	.77	260	.85	16.2
144	240	7.8	.85	250	.93	16.9

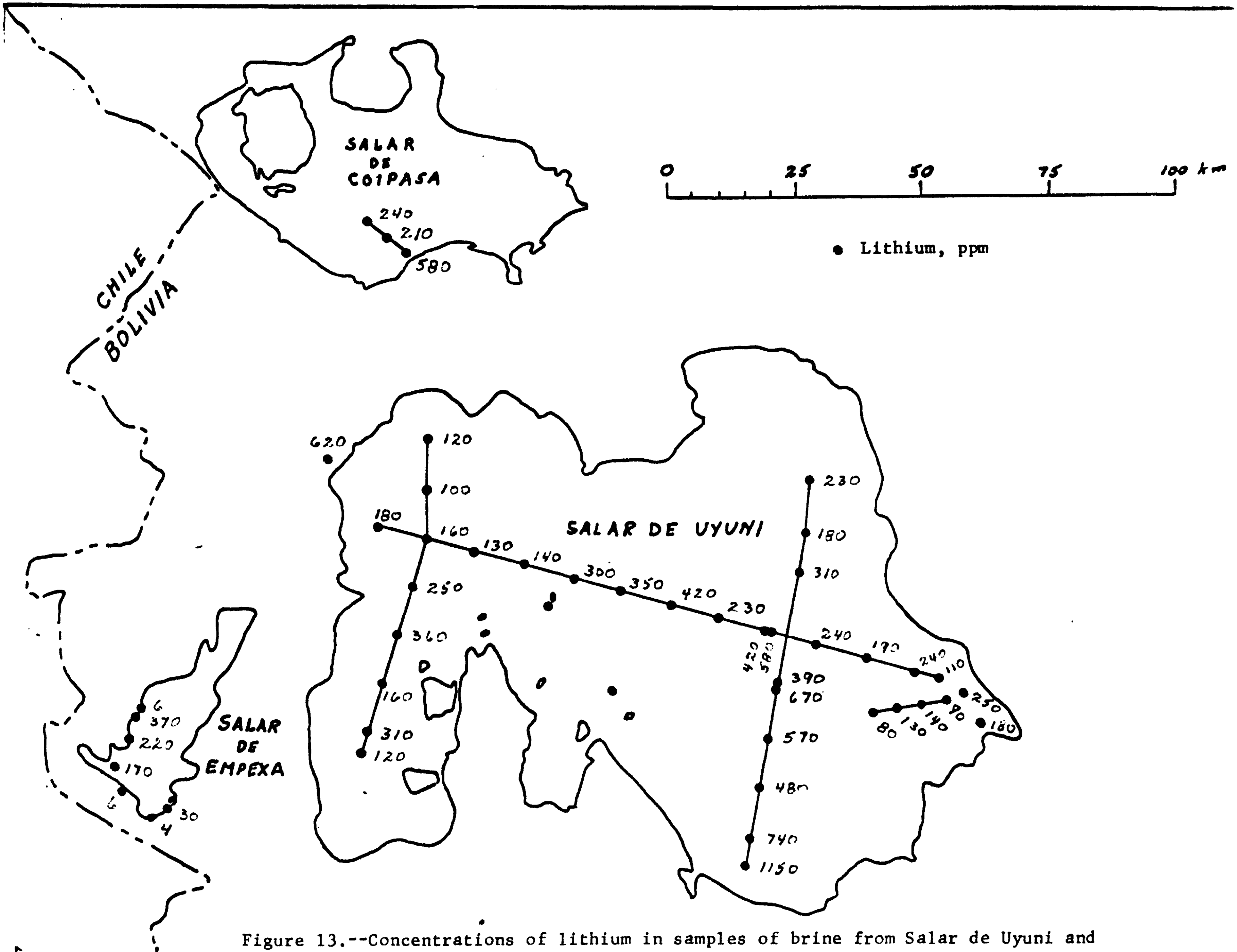

Figure 13.--Concentrations of lithium in samples of brine from Salar de Uyuni and nearby salars in southwestern Bolivia.

upward, slowly dissolving salt to form these brine pools. If this interpretation is correct, lithium concentrations may be expected to be greater at depth within thick salt crust and in the underlying lacustrine sediments than they are at or near the surface.

The variations in values of potassium and magnesium in brines of Salar de Uyuni show distributions similar to those of lithium (figs. 14 and 15). Potassium shows values of 0.25-1.0 percent (2,500-10,000 ppm) at most places in the northern and western part of the salar, but exceptionally high values of 0.91-2.0 percent (9,100-20,000 ppm) in the southeastern arm of the salar. Magnesium values are similar to those of potassium north and middle, but reach a maximum of 2.4 percent (24,000 ppm) in the southeastern part of the salar.

The brines in all three salars are high in chloride but low in sulfate, carbonate, and bicarbonate. Values for chlorine and sodium, which are the dominant ions in the brines, are shown in table 2, and distribution of these values are shown in figure 16 and 17. As can be seen in the table, chlorine in brine from Salar de Uyuni ranges from 14.2 to 17.1 percent (142,000-171,000 ppm) whereas sodium is 5.7 to 9.9 percent (57,000-99,000 ppm). Chlorine does not show any significant variation in the distribution of low and high values (fig. 16). Sodium tends to show an inverse relationship with lithium, potassium, and magnesium, which is due to saturation and selective precipitation of NaCl, being lowest in the center and southern part of the salar where these elements are high and highest in the northern and western parts where they are low (fig. 17).

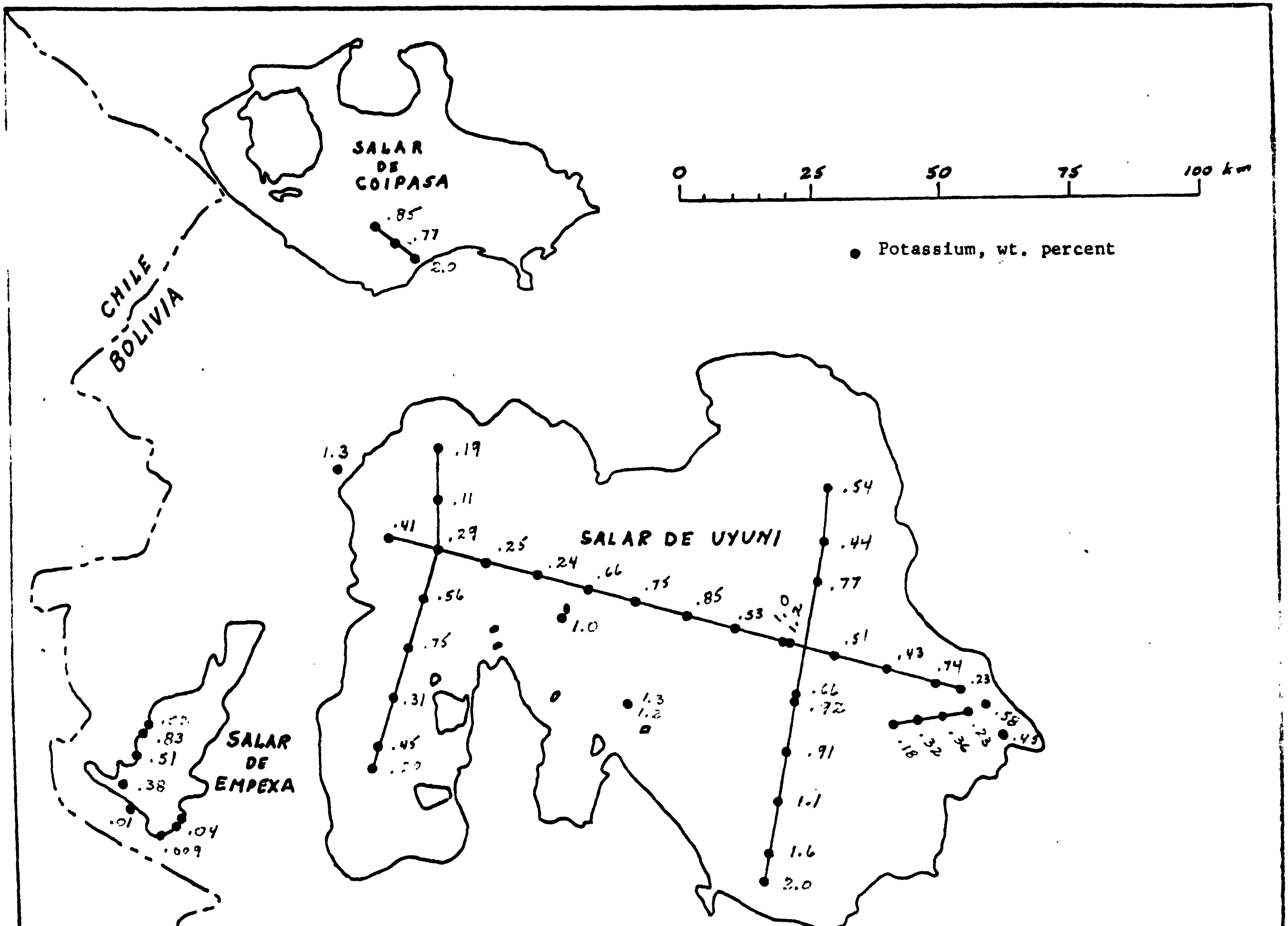

Figure 14.--Concentrations of potassium in samples of brine from Salar de Uyuni and nearby salars in southwestern Bolivia.

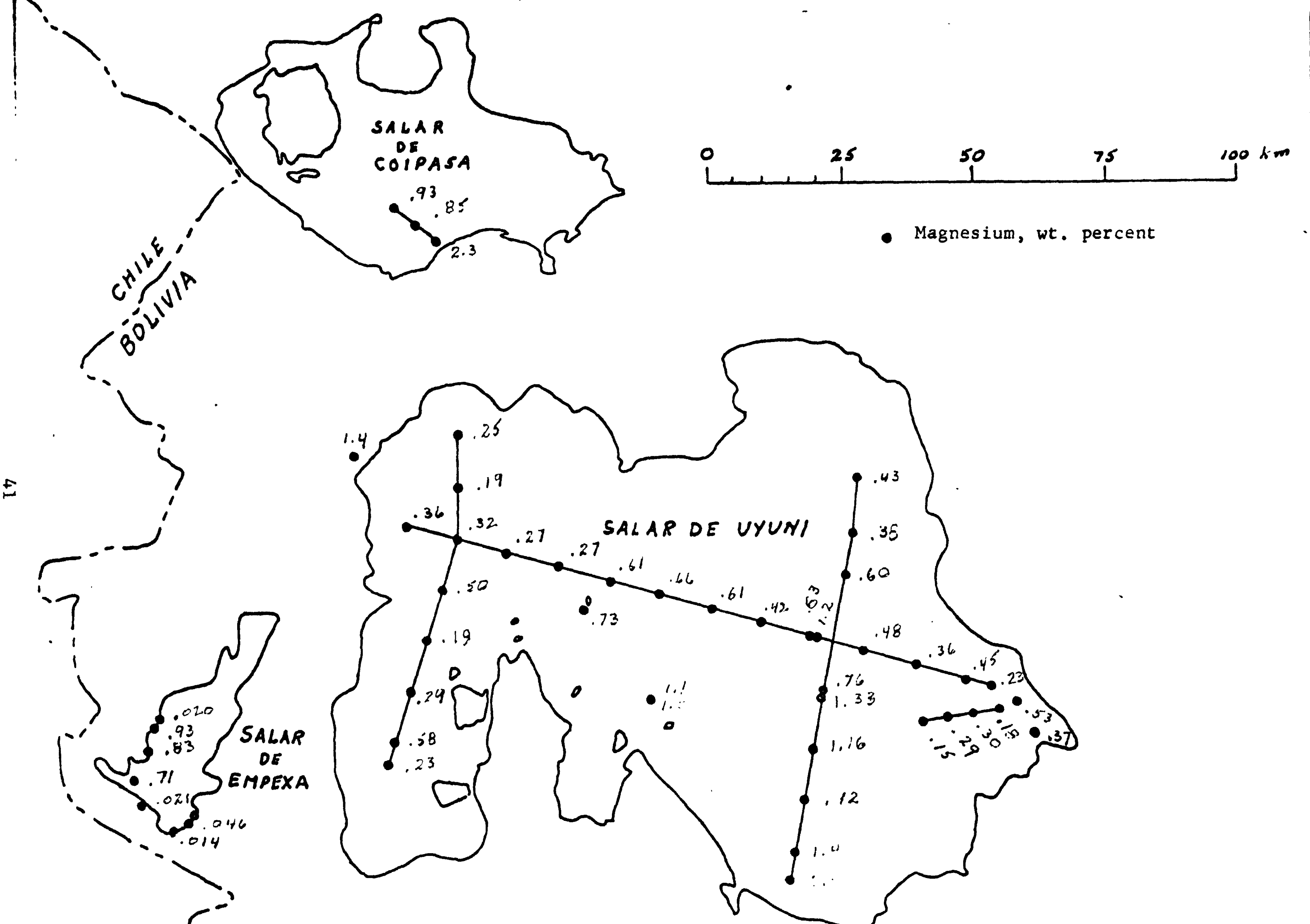

Figure 15.--Concentrations of magnesium in samples of brine from Salar de Uyuni and nearby salars in southwestern Bolivia.

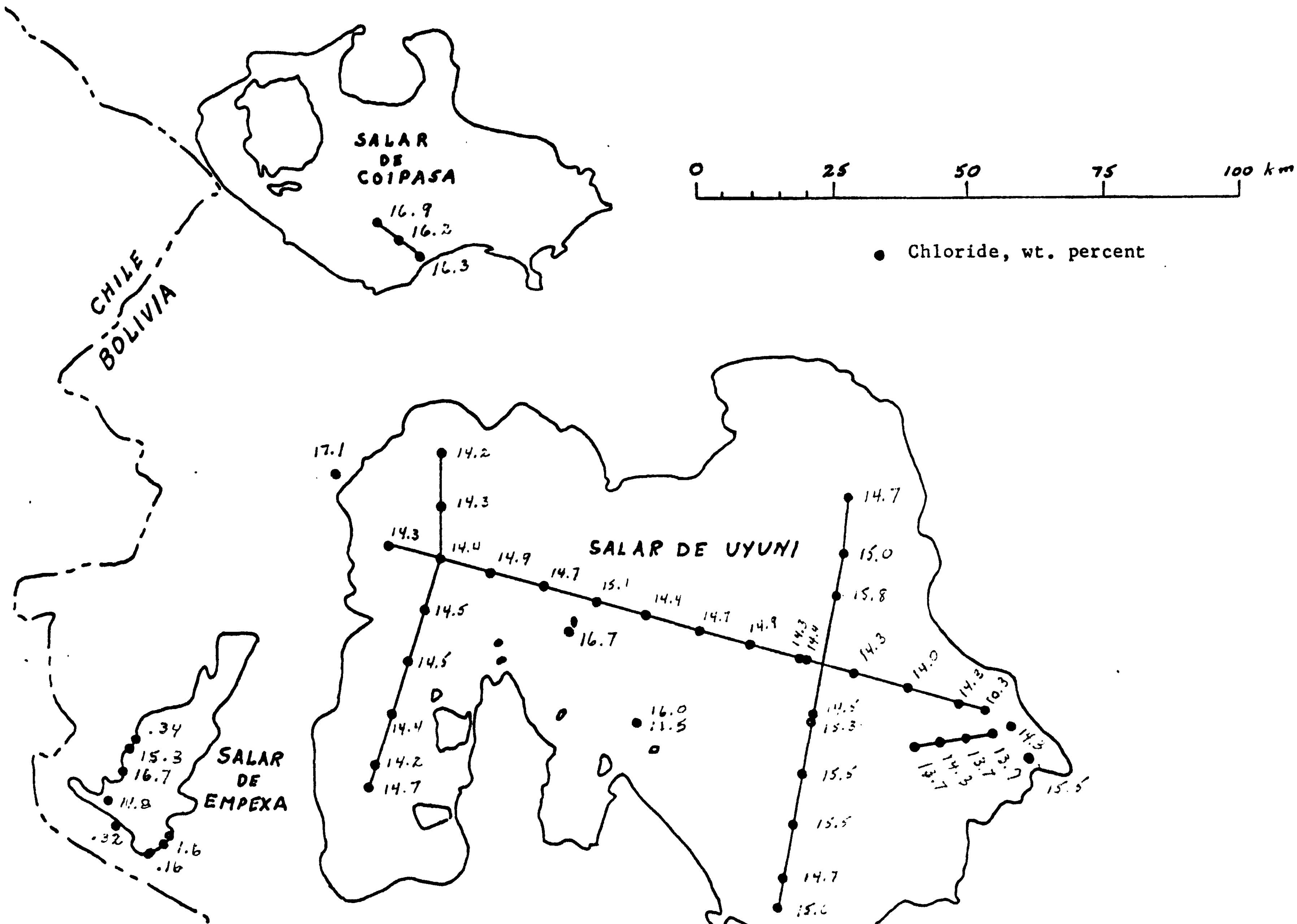

Figure 16.--Concentrations of chloride in samples of brine from Salar de Uyuni and nearby salars in southwestern Bolivia.

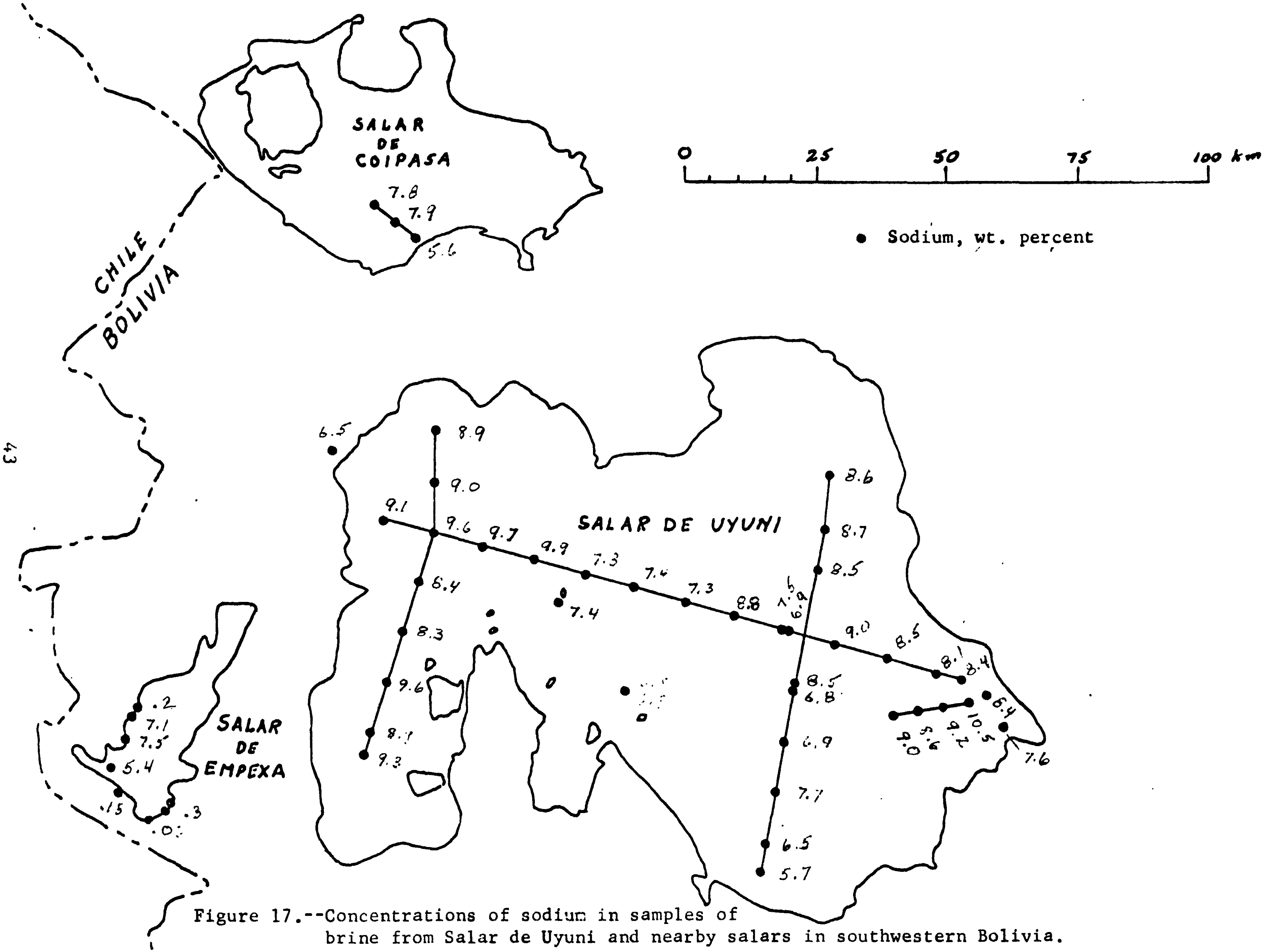

Figure 17.--Concentrations of sodium in samples of brine from Salar de Uyuni and nearby salars in southwestern Bolivia.

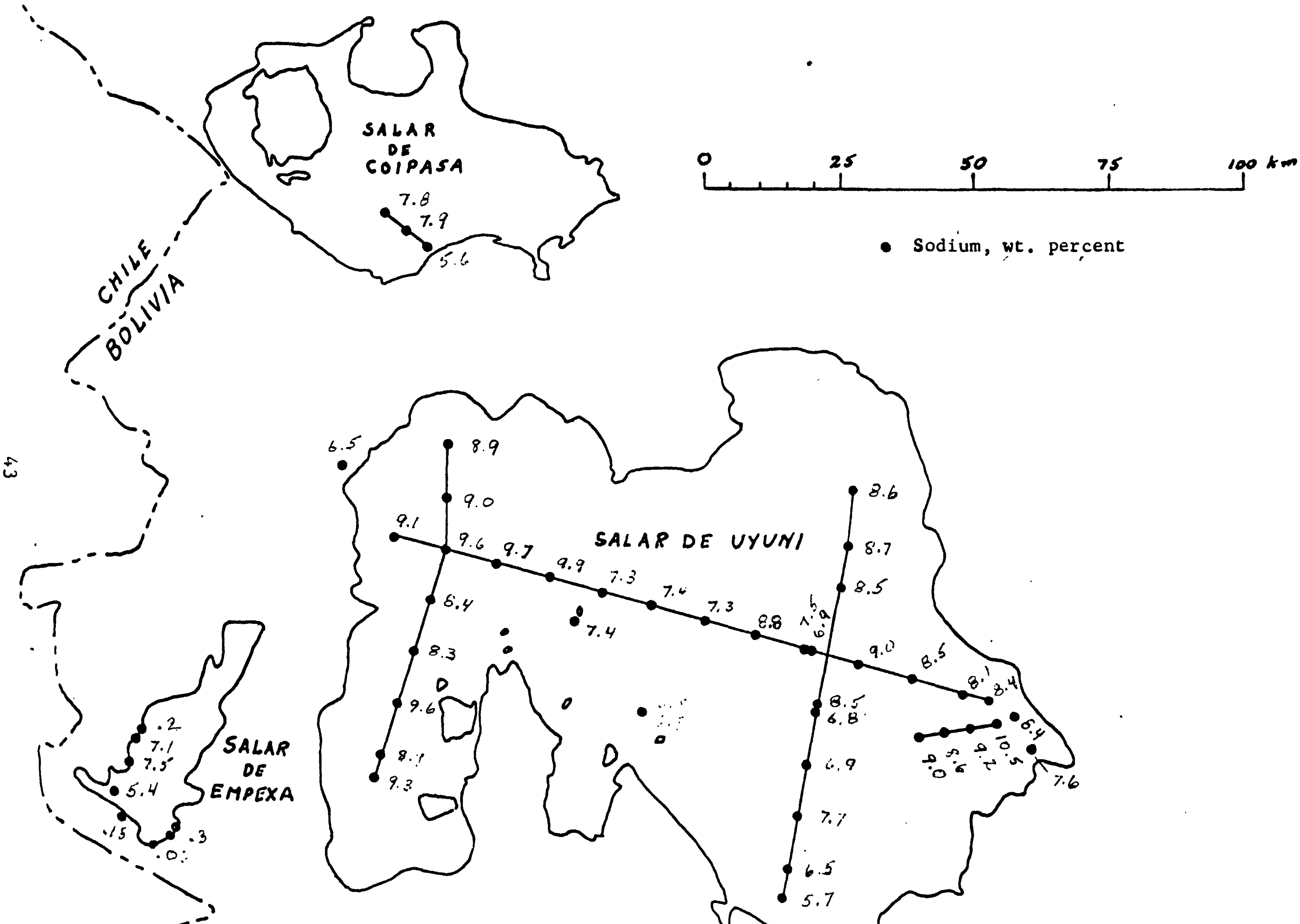

Figure 17.--Concentrations of sodium in samples of brine from Salar de Uyuni and nearby salars in southwestern Bolivia.

CONCLUSIONS AND RECOMMENDATIONS

Preliminary sampling of brines at Salar de Uyuni indicates the presence of widespread near-surface brines containing 200 to 1,500 ppm lithium and 0.5-2.0 percent (5,000-20,000 ppm) potassium, both of which are potentially economically recoverable at the present time. Potential new energy-related uses for lithium in the industrial nations suggest that it may have significant value in the export trade, whereas potassium for fertilizer should be of value in both the domestic and export markets. Brines in extensive areas of the salar have average lithium values greater than lithium-rich brines now being exploited at Clayton Valley, Nevada, which have been reported as averaging about 300 ppm lithium (Kunasz, 1975). The brines of Clayton Valley are exploited only for lithium; other saline components of the brines are not recovered. Concentrated brine at Searles Lake, California, where lithium is one of several saline components being recovered, averages about 70 ppm lithium (Smith and Irwin, 1966).

Salar de Coipasa also may contain abundant lithium-rich brines as indicated by the three samples having 240-580 ppm lithium, which were collected in the southern part of the salar, but more study is needed to determine the distribution of such brine. Additional study is needed of the distribution of lithium-rich brine in Salar de Empexa where three samples of brine collected in this study show lithium concentrations of 170-370 ppm.

Now that the presence of lithium-rich brine has been confirmed in the salars of Uyuni, Coipasa, and Empexa, additional exploration is needed to complete sampling of the near-surface brine, which was initiated in the investigation leading to this report, and start a drilling program to determine the distribution and concentration of lithium- and potassium-rich brine at greater depth in the salt crusts of these salars and in the lacustrine sediments beneath the crusts. It is recommended that this exploration be carried out first in Salar de Uyuni, which appears to be the most favorable of the three salars for having very large amounts of readily accessible lithium- and potassium-rich brine.

In addition to detailed studies of these salars, reconnaissance exploration of other salars and saline lakes of southwestern Bolivia should be carried out as soon as possible. This study will give an idea of the distribution and potential resources of lithium and potassium as well as other potentially recoverable salines such as sodium carbonate, sodium sulfate, and boron compounds that might be concentrated in brines or in associated saline crusts.

In order to carry out the investigation of the saline resources of Bolivia it will be necessary to build and staff a laboratory capable of analyzing the brines and salt samples collected. Such a laboratory does not exist in Bolivia at present.

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