Progress report on lithium-related geologic investigations in Bolivia

by

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Introduction

The lithium resource potential of the large salars (salt pans) in southwestern Bolivia was first recognized by Ericksen and others (1976). A few months after publication of the Ericksen article, two brine samples were collected from the Salar de Uyuni by W. D. Carter, U.S. Geological Survey (USGS) and Raul Ballón, Servicio Geologico de Bolovia (GEOBOL). Subsequent analysis of these samples by S. L. Rettig, USGS, indicated 1,510 and 490 ppm Li in the samples. These values were higher than brines produced for lithium extraction in Clayton Valley, Nevada (Barrett and O'Neill, 1970) and prompted the organization of a cooperative study between USGS and GEOBOL.

In September, 1976, a field party which included Ericksen and J. D. Vine of the USGS, Ballón of GEOBOL, Gerald Blanton of Lithium Corporation of America and Ihor A. Kunasz of Foote Mineral Company, made a systematic reconnaissance of the Salar de Uyuni and the nearby salars, Coipasa and Empexa. At approximately the same time, Francois Risacher of the French Office de la Reserche Scientifique et Technique Outre-Mer (ORSTOM) was conducting a field program which included sampling brines in the area of the Rio Grande de Lipez delta and the adjacent salt crust on the south edge of the Salar de Uyuni. Analyses of samples collected on these two field expeditions confirmed the existence of anomalously high lithium and potassium contents in the near-surface brines of the Salar de Uyuni and gave preliminary information concerning the geochemical evolution of the brines (Ericksen and others, 1978; Rettig and others, in press).

This data also encouraged the organization of GEOBOL-USGS-ORSTOM cooperative field party, which conducted research in southwestern Bolivia in September-November 1978. The purpose of this study was three-fold: 1) to continue the systematic sampling of the near-surface brines begun by Ericksen and others (1978), 2) to sample surface and ground waters in the drainage basin of the Salar de Uyuni to outline the source area of the lithium, and 3) to examine the rhyolitic ignimbrites in the basin as a possible lithium source. Analyses of the rocks and waters collected by this field party (fig. 1) are as yet incomplete, but are summarized below, pending more complete study by the participating scientists.

Lithium Distribution, Salar de Uyuni

The brine composition and the lithium distribution on the Salar de Uyuni can be explained, at least in part, by the hydrologic changes in the basin during late Quaternary time. Well-developed terraces and deposits of algal limestone up to 75 m above the salar indicate the existence of large lakes in the basin during the Pleistocene which extended more than 100 km north of the present drainage basin of the Salar de Uyuni. This Pleistocene basin included the present drainages of the Sālar de Coipasa and Lake Poopo (Servant and Fontes, 1978). Rettig and others (1980) studied the solute trends in the remnants of this Pleistocene lake, and showed how evaporative concentration of the lake waters and precipitation of evaporite minerals could account for the progressive changes in solute ratios observed on a transect from Lake Poopo to Coipasa to Uyuni. Between Lake Poopo and Salar de Coipasa, calcite and gypsum were precipitated as the Pleistocene lake receeded. At Salar de Coipasa, halite began to precipitate. Finally, halite and sylvite precipitated on the Salar de Uyuni as the Pleistocene lake waters continued to receed.

Uyuni is about 7 m lower than Coipasa and is the lowest point in the Pleistocene lake basin. At present, Uyuni receives surface water inflow only from the Rio Grande de Lipez, which drains a large area south of the salar, and from a few small drainage systems to the east. The salar surface is a very porous salt crust up to 10 m thick, and contains a large body of brine. During the rainy season, the salar may be partially flooded to a depth of about 25 cm, but during the dry season, the brine usually evaporates to a level just below the salt surface. Thus, whatever inflow waters reach the central salt crusts in the rainy season are quickly dominated in solute composition by re-solution of NaCl from the thick, pre-existing halite crust. As evaporation proceeds in the dry season, re-precipitation of NaCl results in enriching the magnesium and potassium content of the brines. These solute trends account for most of the sodium and chloride in the brines of the Salar de Uyuni by evaporative concentration of the Pleistocene lake waters, but the lithium in the brines follows different trends, suggesting a separate source.

Analyses of the first brine samples from the salar suggested that the east-central and southeastern parts of the salar contained the most lithium-enriched brine (Ericksen and others, 1978). Analyses of samples collected in 1978 has clarified the lithium anomaly, showing the highest concentrations west of the delta of the Rio Grande de Lipez in the southeastern portion of the salar (figs. 2 & 3). The location of the lithium anomaly in this area led to speculation concerning a lithium source in the drainage basin of the Rio Grande de Lipez (Rettig and others, 1980), and served as a guide for much of the later reconnaissance in that drainage basin, which is discussed below.

The addition of the most recent chemical data also delineates chemical trends which were not apparent from the earlier work. The most striking of these is a very linear, north-south lithium and Li:Cl anomaly (see figs. 2 and 3, respectively). The anomaly extends from the delta of the Rio Grande de Lipez to the northern margin of the salar, and the anomaly may be caused by dispersion of surface inflow from the Rio Grande. However, the eastern boundary of this anomaly is relatively abrupt, and may parallel pre-salar north trending faults in the region. The eastern edge of this anomaly also coincides with the location of brine pools described by Ericksen and others (1978). The lithium anomaly could be due to upwelling of a denser residual brine along fractures in the salt. This theory is supported by data which show that the brine from the two drill holes is normally density-stratified, and that the two brine pools are apparently mixed and contain a brine of intermediate density (Table 1).

In addition to the numerous 50-cm bore holes drilled for collection of brine samples in 1978, two 8 m bore holes were drilled for stratigraphic information. The two 8 m bore holes were drilled by the same hand-held, gasoline-powered drill used for the shallow holes. No core barrel was used, and the cores were extruded by hand from the unlined 6 cm and 3 cm drill pipe. Bore hole SU 209 was drilled in the area of thick salt crust, while SU 210 was drilled about 15 km to the southeast in the zone of thin salt crust (see Ericksen and others, 1978, fig. 2). The cores from the 50 cm bore holes and the logs from the two 8 m bore holes (Tables 2 and 3) generally confirm the description of the salt crust and its thickness as reported by Ericksen and others (1978). However, the log of SU 210 (Table 3) is more complex, both stratigraphically and chemically, than was anticipated, and suggests that the collection of larger-diameter, lined cores might be useful in developing the Quaternary stratigraphy of the Sălar de Uyuni.

Lithium Sources in the Andes

Much of the 1978 field season was dedicated to examining stream runoff, spring discharge and rock composition in the drainage basin of the Rio Grande de Lipez. The drainage basin of the Rio Grande de Lipez and its tributaries such as the Rio Salado and Rio Quentena covers more than 25,000 km^2 of rugged Andean volcanic terrain in southwestern Bolivia. This volcanic terrain is made up of an ignimbrite plateau at about 4300 m elevation which is breached by numerous composite volcanoes that attain heights of up to 6000 m elevation. Volcanism began in late Cretaceous or early Tertiary time with the extrusion of the Potoco Lavas, which are of alkaline, olivine-mugearite composition (Kussmaul and others, 1977). However, the Potoco Lavas have minor extent and differ considerably from the younger rocks, which are calc-alkaline in composition. Extrusion of these lavas and ignimbrites began in the Miocene and has continued to the Holocene, when the youngest strato-volcanoes in southwestern Bolivia were erupted (Kussmaul and others, 1977). Although Friedman and Heiken (1977) and Francis and

Baker (1978) had used SKYLAB and LANDSAT imagery to postulate large calderas as a source of the large ignimbrite sheets, they were originally thought to have erupted from fissures (Fernandez and others, 1973; Kussmaul and others , 1977). Our mapping clearly shows that these ignimbrites were erupted from very large calderas.

The ignimbrites in the study area include the Miocene Los Friales Formation in the northeast, parts of the Miocene Upper Quehua Formation in the east, and the Pliocene Ignimbrite Formation in the south and west (Ahlfeld, 1972). However, these stratigraphic divisions belie a more complex stratigraphy made possible by radiometric dates and field mapping of the caldera complexes. The ash-flow tuffs are associated with three clusters of calderas recognized so far: northeast, southeast, and southwest of the Salar de Uyuni. The ignimbrites generally decrease in age westward from about 20 m.y. at 66° W longitude to 3 to 7 m.y at 68° W.

Southwest of the Salar de Uyuni near the Chilean border, ashflow tuffs of the Ignimbrite Formation are mostly uneroded and range from approximately 2 to 7 m.y. according to the unpublished K-Ar ages compiled by GEOBOL. Pink quartz phenocrysts are a common characteristic of these tuffs. Our mapping confirms that these tuffs are associated with two large resurgent calderas at Pastos Grandes and at Cerro Guacha that were suggested by Friedman and Heiken (1977). The Pastos Grandes caldera (67°50'W, 24°45' S.) is 45 km wide and has a resurgent dome 12 km across. We suspect that further to the southwest, Laguna Colorado may occupy another caldera, and suggest that other calderas associated with the Ignimbrite Foremation may also exist and be discovered by subsequent work.

Northeast of the Salar de Uyuni, on the east side of the Altiplano, lie upper Miocene (approximately 7 m.y.) ashflow tuffs of the Los Frailes Formation (Everden and others, 1977). Field reconnaissance and study of the orbital photographs indicate that these tuffs are sheets that surround several large calderas, including a 50 km wide resurgent caldera at Cerro Toro. Southeast of the Salar de Uyuni, slightly older ignimbrites (approximately 10 m.y.; Kussmaul and others, 1975) surround a caldera on the Argentine border near Laguna Arenal. This caldera was recognized by both Friedman and Heiken (1977) and Kussmaul and others (1977).

Older volcanic rocks form a belt even farther east. For example, northeast of the Laguna Arenal caldera, eroded stratovolcanoes and ash-flow tuffs are associated with one or two large eroded ring structures apparent on satellite images. These tuffs include some dated at 17 to 24 m.y. as part of the Upper Quehua Formation (Kussmaul and others, 1975) and are also present to the north near Potosi, where they occupy a similar easterly position relative to the upper Miocene Los Frailes - Arenal belt of calderas. We speculate that caldera associated with some of these rocks may be found near Potosi.

The composite volcanoes belong to the Strato-volcano Formation (Ahlfeld, 1972), and their eruptions were probably confined to the Quaternary. The youngest of the composite volcanoes show no evidence of glaciation, indicating that eruptions have continued into Holocene time. However, there is evidence of eroded composite volcanoes as old as Miocene (Kussmaul and others 1977). The ignimbrites and the lavas of the composite volcanoes are very similar chemically (see tables 1-4, Fernandez and others, 1973, and tables 1-3, Kussmaul and others, 1977). Kussmaul and others (1977) divided the lavas of the composite volcanoes into a calc-alkaline, average-potassium suite, and a calc-alkaline, high-potassium "shoshonite" suite, based on K_2O/Na_2O ratios. However, empirical criteria based on the An-Ab-Or plots of Irvine and Baragar (1971) show no potassium enrichment in the "shoshonite" lavas, and classifies most of the lavas of both suites as calc-alkaline, with average potassium saturation.

Based on plots of normative color index vs. normative plagioclase composition, (Irvine and Baragar, 1971), the ignimbrites are dacitic to andesitic in composition, with a few rocks being classed as rhyolitic. However, this classification scheme makes the ignimbrites seem more mafic than they would by most field criteria, because the normative plagioclase composition for many of the ignimbrites is greater than 40 percent anorthite, even though the color indices for the rocks are usually less than 10 and silica contents are greater than 65 percent by weight. Most of the ignimbrites are quartz and hypersthene normative, and mineralogically they are rich in phenocrysts of plagioclase, quartz, and biotite, with less abundant sanidine or hornblende. The lavas are generally andesitic, with a few rocks classed as dacites or basalts, and are also quartz and hypersthene normative. Mineralogically, the lavas contain plagioclase and hypersthene with quartz, biotite, and hornblende being less common.

The ignimbrites contain volcanic glass and apparently show more magmatic differentiation than the lavas of the composite volcanoes, and thus received most of our attention as potential sources of elements such as lithium. Lithium becomes concentrated in the late phases of an igneous melt due to fractional crystallization or other processes, and volcanic glass may provide an especially good source of lithium because lithium is so readily leached from glass. Preliminary analyses of ignimbrite samples (Table 4) show average Li concentrations relative to a number of ignimbrite analyses from North America, and give some suggestion that lithium is depleted during weathering and tafoni formation. The leaching of lithium from volcanic glass and the formation of tafoni are discussed in more detail elsewhere (Davis, in preparation).

Many of the surface and spring waters in the ignimbrite terrain are enriched in lithium (Table 5). The lithium-enriched surface waters include most of the major tributaries of the Rio Grande de Lipez which drain large expanses of ignimbrites, and the thermal ground waters of the region also appear to be enriched in lithium. It is suggested that a single source for the lithium in the Salar de Uyuni does not exist, and that leaching of lithium from ignimbrites throughout the drainage basin may be the source of lithium in the Salar de Uyuni.

References cited

Ahlfeld, F., 1972, Geologia de Bolivia, Los Amigos del Libro, La Paz, 190 p.

Barrett, W. T., and O'Neill, B. J., Jr., 1970, Recovery of lithium from saline brines using solar evaporation, in Rau, J. L., and Dellwig, L. E., eds., Third symposium on salt: Northern Ohio Geological Society, v. 2, p. 47-50.

Ericksen, G. E., Chong, G., and Vila, T., 1976, Lithium resources of salars in the central Indes, in Vine, J. D., ed., Lithium resources and requirements by the year 2000: U.S. Geological Survey Professional Paper 1005, p. 66-74.

Ericksen, G. E., Vine, J. D., and Ballon, R., 1978, Chemical composition and distribution of lithium-rich brines in Salar de Uuyni and nearby salars in southwestern Bolivia: Energy, v. 3, p. 355-363.

Everden, J. F., Kriz, S. J., and Cherroni, C., 1977, Potassium-Argon ages of some Bolivian rocks: Economic Geology, V. 72, p. 1042-1061.

Fernandez, A., Hormann, P. K., Kussmaul, S., Meave, J., Pichler, H., and Subieta, T., 1973, First petrologic data on young volcanic rocks of SW-Bolivia: Tschermaks Mineralogische und Petrographische Mittelilungen, v. 19, p. 149-172.

Francis, P. W., and Baker, M. C. W., 1978, Sources of two large ignimbrites in the Central Andes: Some LANDSAT evidence; Journal of Volcanology and Geothermal Research, v. 4, p. 81-87.

Friedman, J. D., and Heiken, Grant, 1977, Volcanoes anf volcanic landforms, in SKYLAB explores the Earth: National Aeronatuical Space Administration, SP-380, p. 137-171.

Irvine, T. N., and Baragar, W. R. A., 1971, A guide to the chemical classification of the common volcanic rocks: Canadian Journal of Earth Sciences, v. 8, p. 523-548.

Kussmaul, S., Hormann, P. K., Ploskonka, E., and Subieta, T., 1977, Volcanism and structure of southwestern Bolivia, Journal Volcanology and Geothermal Research, v. 2, p. 73-111.

Kussmaul, S., Jordan, L., and Ploskonka, E., 1975, Isotopic ages of Tertiary volcanic rocks of SW- Bolivia: Geologisches Jahrbuch, Reihe B, Heft 14, p. 111-120.

Rettig, S. L., Jones, B. F., and Risacher, F., 1980, Geochemical evolution of brines in the Salar de Uyuni, Bolivia: Chemical Geology, v. 30, p. 57-79.

Servant, M. and Fontes, J. C., 1978, Les lacs quaternaires des hauts plateaux des Andes boliviennes, Premieres interpretations paleoclimatiques: Cahiers O.R.S.T.O.M., Serie Geologie, v. 10, n. 1, p. 9-23.

Table I. Variation of brine composition with depth, Salar de Uyuni.

[Cations determined by atomic absorption spectrometry and Cl determined spectrophotometrically.

Analyzed by P. Briggs, J. Crock, and C. Gent, U.S. Geological Survey, Denver, Colorado, and S. Rettig, U.S. Geological Survey, Reston, Virginia.]

Sample locality	Depth meters	Na percent	K percent	Li ppm	Cl percent	density
Station 209	0.4	8.36	1.64	553	13.80	1.21
	4.0	7.62	1.97	733	13.93	1.22
	8.0	7.60	2.70	787	14.92	1.22
Station 210	0.4	8.51	1.79	607	12.81	1.21
	1.0	8.19	1.79	607	12.81	1.21
	2.0	8.07	2.43	663	13.74	1.23
	4.0	7.83	2.54	735	12.85	1.23
	4.2	7.68	2.56	756	13.57	1.23
	5.0	7.78	2.56	756	10.49	1.23
	6.2	7.73	2.59	756	12.84	1.23
Brine pool near	0.2	9.10	1.64	426	11.97	1.22
Station 211	5.2	9.26	1.66	434	12.13	1.22
Brine pool	5.8	6.74	1.04	384	12.83	1.216
sampled by	7.3	6.72	1.04	391	12.83	1.216
Rettig						

Table 2. Lithologic log of bore hole SU 209. Locality shown in figure 2.

Core description	depth, in meters
Hard, dense halite	0.0-0.3
Halite crystals, some mud	0.3-0.4
Hard, dense halite	0.4-0.5
No recovery; lithology inferred to be primarily halite.	0.5-3.0
No recovery; lithology inferred to be primarily halite. Drill stem stained black from reducing waters	3.0-8.0
Hard, dense zone of halite or calcite(?)	8.0-8.2
Mud and halite crystals	8.2-8.4
Mud and fecal pellets	8.4-8.5
Mud and gypsum crystals	8.5-8.6
Mud and halite crystals	8.6-8.8

Table 3. Lithologic log of bore hole SU 210. Locality shown in figure 2.

Core description	depth, in meters
Hard, dense halite	0.0-0.1
Mud and halite crystals	0.1-0.25
Halite crystals and mud	0.25-0.45
Saline mud	0.45-0.60
Hard dense halite	0.60-0.65
Hard black halite(?)	0.65-0.70
Black mud and gypsum crystals	0.70-0.83
Black halite	0.83-0.85
Black mud, with halite and gypsum crystals	0.85-1.17
Halite crystals and yellow gypsum crystals in black mud matrix	1.17-1.40
Gray gypsum and mud	1.4-1.6
Gray halite and mud	1.6-2.0
Gypsum	2.0-2.1
Thin beds (2-5 cm) of halite alternating with halite crystals in a gypsum matrix	2.1-3.2
Halite crystals in a gypsum matrix	3.2-4.35
Light gray mud, with gypsum and halite	4.35-4.38
Halite in gypsum matrix	4.38-6.03
Halite	6.03-6.18
Mud and gypsum	6.18-6.20
Halite and mud	6.20-6.46
No recovery	6.46-6.67
Halite	6.67-6.82
Hard calcite crust	6.82-6.83
Brown oolitic mud	6.83-6.85
Soft, green, calcareous mud with gypsum and minor mirabilite	6.88-7.50
Interbedded calcareous mud and gypsum	7.80-8.3
Hard, dense gypsum	8.3-8.5

Table 4. Preliminary trace-element distributions, in parts per million, of selected ignimbrites, southwestern Bolivia. [Li, Rb, and Sr determined by atomic absorption spectrometry; Cl determined spectrophotometrically. Analyses by R. More, A. Neuville, and F. O. Simon, U. S. Geological Survey, Reston, Virginia.]

	Latitude	Longitude	Li	Rb	Sr	Cl
Ignimbrite Formation, well developed tafoni	22°20'S	67°21'W	16	120	340	510
Ignimbrite Formation, no tafoni	21°56'S	67°21'W	65	170	270	880
Los Friales Formation	19°51'S	66°07'W	35	180	540	620
Los Friales Formation	19°04'S	66°13'W	43	180	480	500
Los Friales Formation	19°30'S	66°52'W	36	260	250	550
Unnamed tuff sheet	20°13'S	68°28'W	17	130	430	540

Table 5. Partial list of lithium-enriched inflow waters in the Salar de Uyuni drainage basin. [Li determined by atomic absorption spectrometry, Cl determined spectrophotometrically. Analyses by P. Briggs, J. Crock, C. Gent, and F. E. Lichte, U.S. Geological Survey, Denver, Colorado, and S. Rettig, U. S. Geological Survey, Reston Virginia.]

Ambient Runoff	Latitude	Longitude	Li ppm	Cl ppm
Rio Grande de Lipez	20°55'S	67°00'W	3.0	780
Rio Viscachillas	21°25'S	67°38'W	0.23	42
Rio Chajra Wayhko	21°25'S	67°38'W	0.86	140
Rio Hondo	22°35'S	66°33'W	2.3	310
Rio Quetena	21°42'S	67°21'W	5.8	890
Rio Quetena	22°17'S	67°24'W	0.03	16
Rio San Antonio	22°17'S	67°22'W	1.5	360
Rio San Antonio	22°11'S	67°17'W	1.7	380
Rio Viscachillas	22°20'S	67°25'W	0.04	14
Rio Salado	20°04'S	66°53'W	5.8	1400
Rio Salado	21°33'S	67°07'W	7.3	1300
Rio Soniquera	21°50'S	67°23'W	0.05	92
Thermal Springs:				
Horsu Spring (30°C)	22°45'S	67°40'W	3.8	560
Spring near Pastos Grandes (30°C)	21°37'S	67°54'W	4.6	580
Unnamed spring-fed stream (30°C)	21°25'S	67°38'W	0.42	88

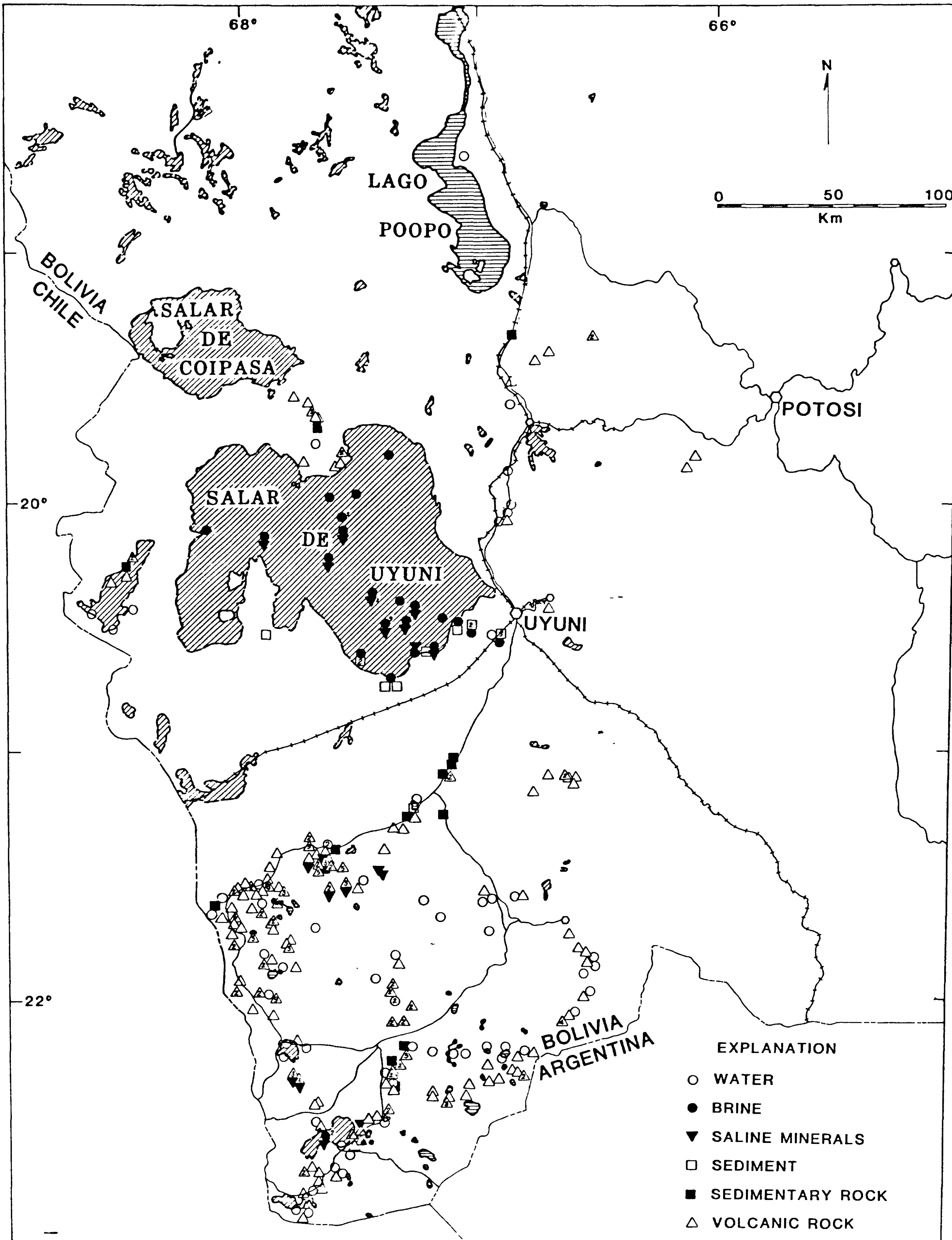

Figure 1. Location of samples collected in SW Bolivia during 1978 field season.

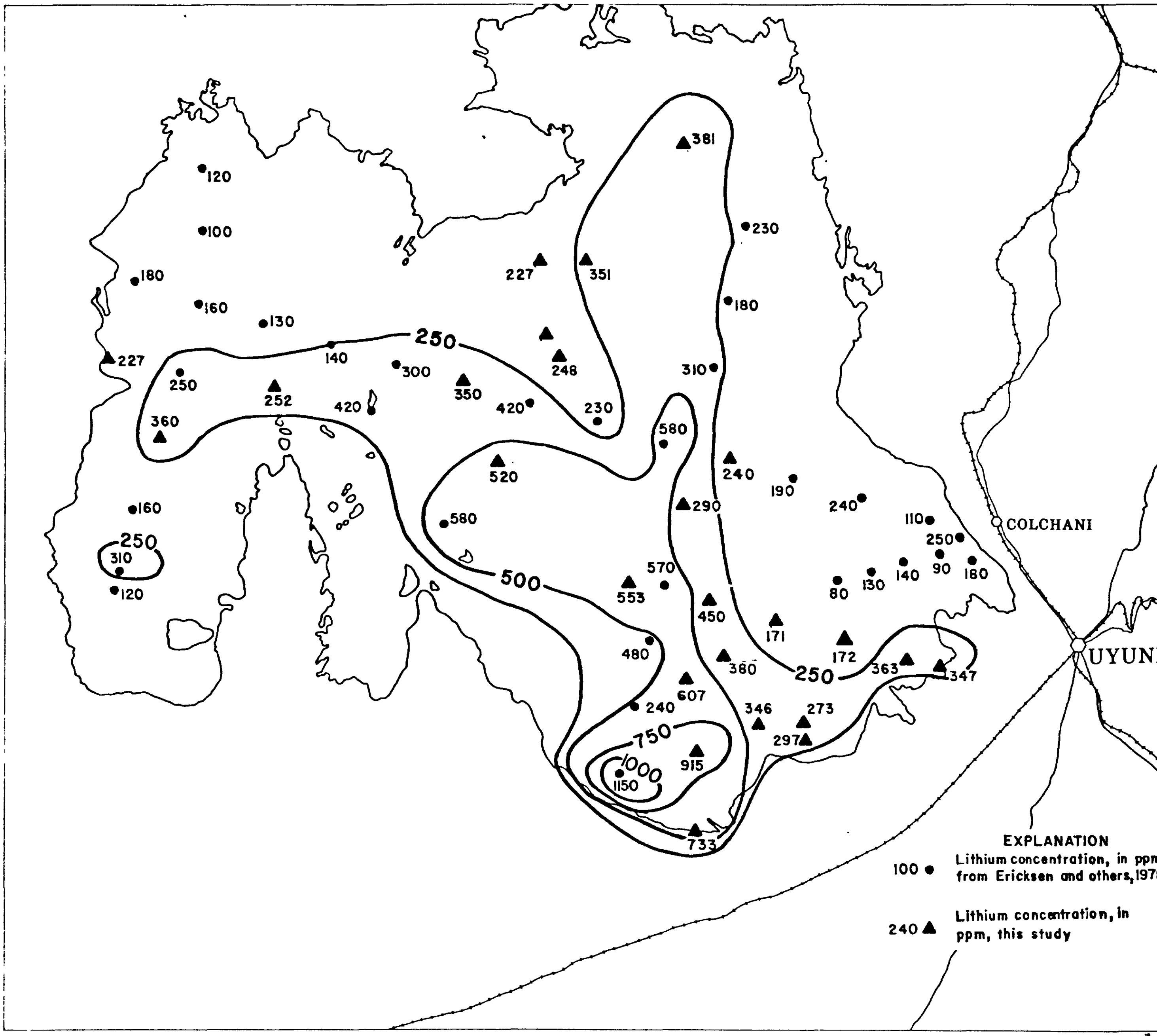

Figure 2. Lithium isopleths in ppm, Salar de Uyuni.

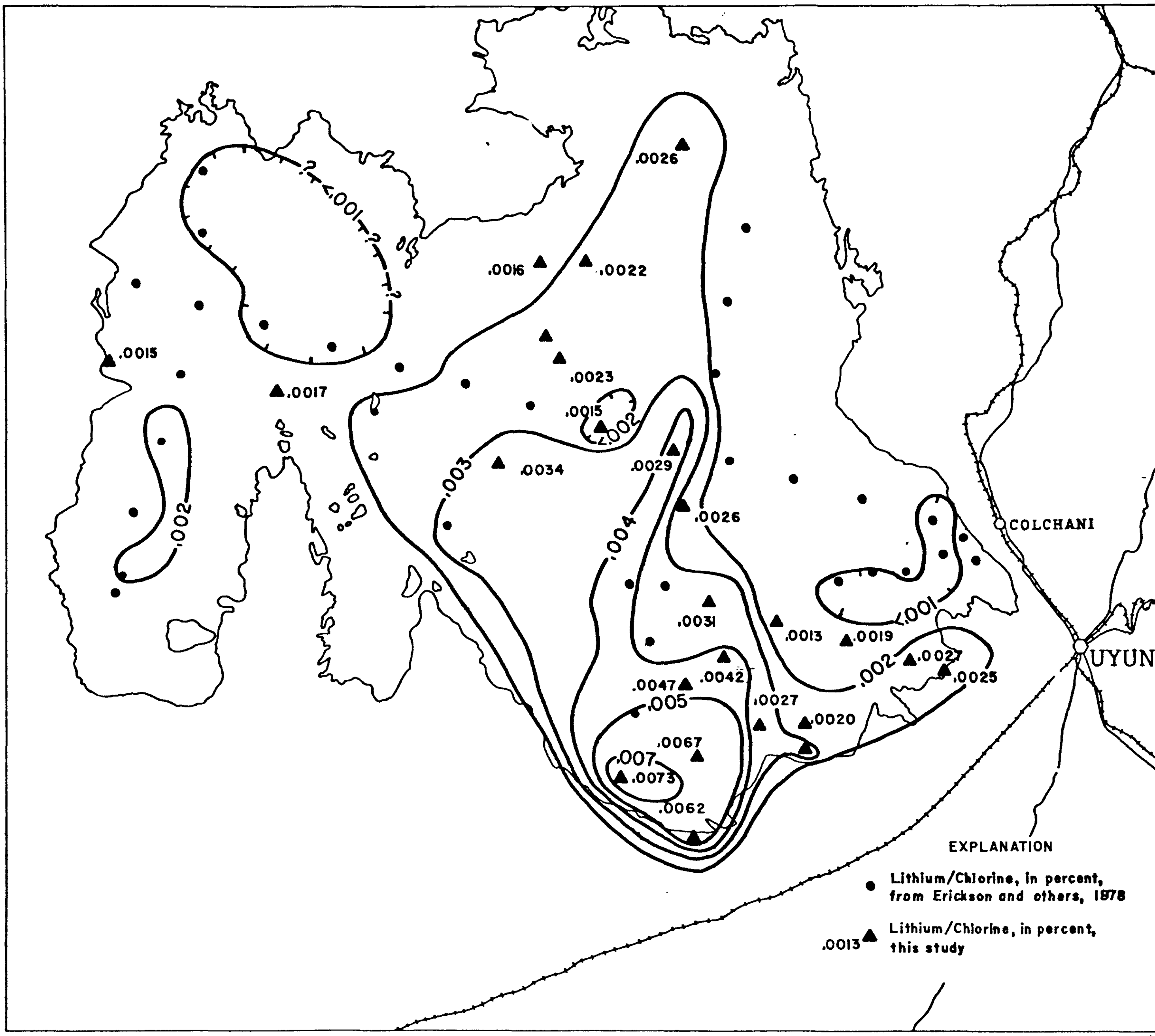

Figure 3. Li/Cl isopleths, Salar de Ununi.