

GEOCHEMICAL EVOLUTION OF BRINES IN THE SALAR OF UYUNI, BOLIVIA

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ABSTRACT

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Recent analyses of brines from the Salars of Uyuni and Coipasa have been compared with published chemical data for Lakes Titicaca and Poopo in order to evaluate solute compositional trends in these remnants of two large Pleistocene lakes once connected by overflow from the northern to the southern part of the Bolivian Altiplano. From Titicaca to Poopo the water chemistry shows an increase in concentration of Cl and Na somewhat greater than the total solutes, suggesting preferential inputs of these elements or significant losses of other constituents downstream from Lake Titicaca proper. In contrast, Ca and SO₄ increase to a lesser extent than do total dissolved solids, and carbonate species are relatively constant, suggesting solute losses most readily related to the precipitation of calcite and gypsum. Between Poopo and Coipasa the proportions of Ca, SO₄ and CO₃ continue to decrease. At Coipasa and Uyuni, the great salars frequently evaporate to halite saturation and widespread halite crystallization is accompanied by an increased proportion of K, Mg and SO₄ in residual brines.

Notably high concentrations of Li and B in brines from the south end of Uyuni, near the mouth of the Rio Grande de Lipez, are clearly in excess of that expected for the solute concentration trends for inflow from Coipasa and the northern Bolivian Altiplano, as shown by comparison with Mg and K. This supports other indications that the major source of Li and B are the recent rhyolitic volcanic rocks prevalent in the drainage of the Rio Grande.

INTRODUCTION

The Salar de Uyuni, in the southwestern corner of Bolivia (Fig. 1) is the largest of more than 75 salt pans or playas which lie in the closed basins of the central Andean Altiplano at altitudes of more than 3600 m. Uyuni, which has an area of about 9000 km², is in fact the largest salt flat in the world. Although for many years salt has been mined at Uyuni in sufficient quantities to supply all of Bolivia, only quite recently was there any scientific discussion of its brine resources (Ericksen et al., 1976, 1978; Risacher and Miranda, 1977). Ericksen et al. (1976) suggested that the Bolivian salars might contain a significant accumulation of Li. In September of 1976 a field party from



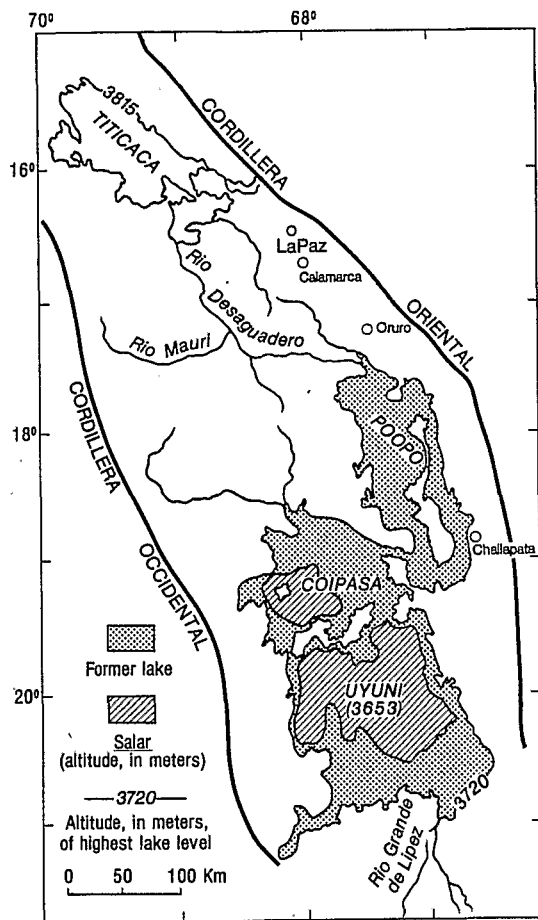


Fig. 1. Outline map of the Bolivian Altiplano showing areal extent of present and ancient lakes, and the principal inflow tributary to them.

GEOBOL^{*1} led by G.E. Ericksen and J.D. Vine made a brief systematic sampling of Uyuni and two nearby salars, Coipasa and Empexa. Over a similar period ORSTOM^{*2} (F. Risacher) sampled cross-sections in the area of the Rio Grande de Lipéz delta and adjacent salt crust on the south edge of the Salar de Uyuni, some samples of which were analyzed in U.S.G.S.^{*3} laboratories. This paper discusses the results and implications of the chemical analyses of these samples, and a few others collected subsequently from Uyuni and southern tributary drainage by GEOBOL, ORSTOM and USGS.

*1 GEOBOL: Servicio Geologico de Bolivia.

*2 ORSTOM: Office de la Recherche Scientifique et Technique Outre-Mer.

*3 USGS: U.S. Geological Survey.

HYDROLOGIC SETTING

According to Ahlfeld and Branisa (1960), in early Pleistocene times much of the Bolivian Altiplano was covered by two large lakes: Lake Ballivian, in the north, of which Lake Titicaca is a remnant, and Pre-Minchin in the south. The latter lake was succeeded in the late Pleistocene by Lake Minchin (3760 m, 15,000 yr. B.P.) and later by Lake Tauca (3720 m, 10,000 yr. B.P.), which is marked by well-developed terraces and deposits of algal limestone up to 75 m. above the level of the Salar de Uyuni at 3653 m (Servant and Fontes, 1978). Fig. 1 shows the extent of the ancient lakes and the system as it exists today.

The present area of Lake Titicaca is more than 8300 km² and its maximum depth exceeds 300 m. Outflow from Lake Titicaca now drains southward to Lake Poopo through the Rio Desaguadero, which was the connection between the Pleistocene lakes as well. According to Hueot (1908), Lake Poopo in 1905 covered an area of 3000 km² and had a total dissolved solids (TDS) content of $\sim 3.5 \cdot 10^4$ mg/l. Since that time it has fluctuated widely; in 1958 it was reported to be completely dry (Ahlfeld and Branisa, 1960) and since then its level has risen.

The water and solute budgets for Lakes Titicaca and Poopo have been evaluated for the period 1976–1977 by Carmouze et al. (1978). Using a chloride balance, they calculated that only 4.5% of the annual water loss from Titicaca was outflow to the Rio Desaguadero; 90% was lost to evaporation and the rest to groundwater infiltration. This has resulted in an approximately five-fold concentration from inflow to effluent. At the same time, the proportion of Na and Cl has increased to more than half of the major solutes at Lake Titicaca; according to Carmouze et al. (1978) the chemical composition of the lake over their period of intensive sampling has varied little from values obtained sporadically from 1956 to 1973. This can be attributed to a residence time of more than 600 years for the major cations (Na, K, Mg) and chloride.

In contrast to Titicaca, Lake Poopo has become a closed lake except for groundwater infiltration at its south end. Carmouze et al. (1978) suggested that 98% of the annual inflow to the lake was lost through evaporation during their period of study. At the time, the lake surface was estimated at 2500 km², with 60% of the area having a mean depth of ~ 1.5 m and the remainder of less than 0.5 m. Carmouze et al. (1978) showed that TDS concentrated by more than thirty times over Lake Titicaca, that the residence time for Na and Cl was just over 25 years, and that these solutes constituted 75% of the total dissolved ions.

The Salar of Coipasa was at one time apparently connected to Lake Poopo through an ephemeral drainage way to the east, now referred to as the Rio Lacajahuira, but the salar is not presently receiving any new material from that source. Coipasa is now supplied chiefly by several rivers from the north, creating a very shallow body of brine, highly variable in an area at the north end of the salar.

The Salar de Uyuni, ~ 7 m lower than Coipasa, apparently has been a closed basin since the last glacial period about 10,000 yr. B.P. Its only present surface-water inflow is from the Rio Grande de Lipez to the south and lesser drainages to the east. Uyuni is not as extensively flooded as Coipasa, but it contains a large body of brine enclosed in a very porous NaCl crust up to 10 m thick. During the rainy season the salar may be brine covered to a depth of about 25 cm, but during the dry season the brine usually evaporates to the salt surface or just below it. Evaporation from the brine "water table" in the dry season cements the upper crust pores. The annual flooding and evaporation gives Uyuni an exceptionally smooth surface with relief of only a few centimeters. The region is semi-arid with an average annual rainfall of about 30 cm, and for the last several thousand years hydrographic conditions appear to have been more or less stable.

The region of the great Altiplano salars themselves is underlain by Pliocene and Quaternary volcanic rocks, including thick rhyolitic ash-flow tuffs, especially to the south. Extinct or dormant volcanoes dot the area, and there are a number of saline thermal springs. In times of greater volcanic activity, the thermal springs were probably more numerous.

GEOCHEMICAL EVOLUTION OF WATERS FROM THE NORTHERN ALTIPLANO

Because the entire region has functioned as a single closed basin intermittently through the Pleistocene, we have begun with the premise that the geochemical evolution of waters on the Bolivian Altiplano can be compared to that expected from the stepwise evaporative concentration of a single water mass. The assumption that the chemistry of the major surface water bodies of the southern Altiplano has a singular origin is inspired by consideration of the total area (at least 43,000 km²) covered by Pleistocene lake (see Servant and Fontes, figs. 8 and 9). Fig. 2 shows the major solutes plotted against TDS on a log-log scale for the waters of Lakes Titicaca and Poopo and the most concentrated brines of the Salars of Coipasa and Uyuni, as compared to the 1:1 slope expected for evaporative concentration if the total solute concentration is conserved. The values used for Lakes Titicaca and Poopo and the Rio Desaguadero were recalculated from the average analyses of Carmouze et al. (1978). The plots show that between the waters of Lake Titicaca, the Rio Desaguadero, and Lake Poopo, there is an increase in dissolved Cl and Na greater than the total dissolved solids content. On the other hand, Ca, Mg and SO₄ do not increase as rapidly as the TDS concentration. Without widespread and detailed analyses of lacustrine sediments from the area, it is not possible to estimate how much of the apparent constituent gain or loss is due to varying inflow composition, ion exchange, sorption, or mineral precipitation. Nevertheless, some attractive suggestions can be made.

Indications from the data of Carmouze et al. (1978) were that changes in solute proportions due to different compositions of inflow waters to Lake Poopo other than the Rio Desaguadero are minor. However, more recent

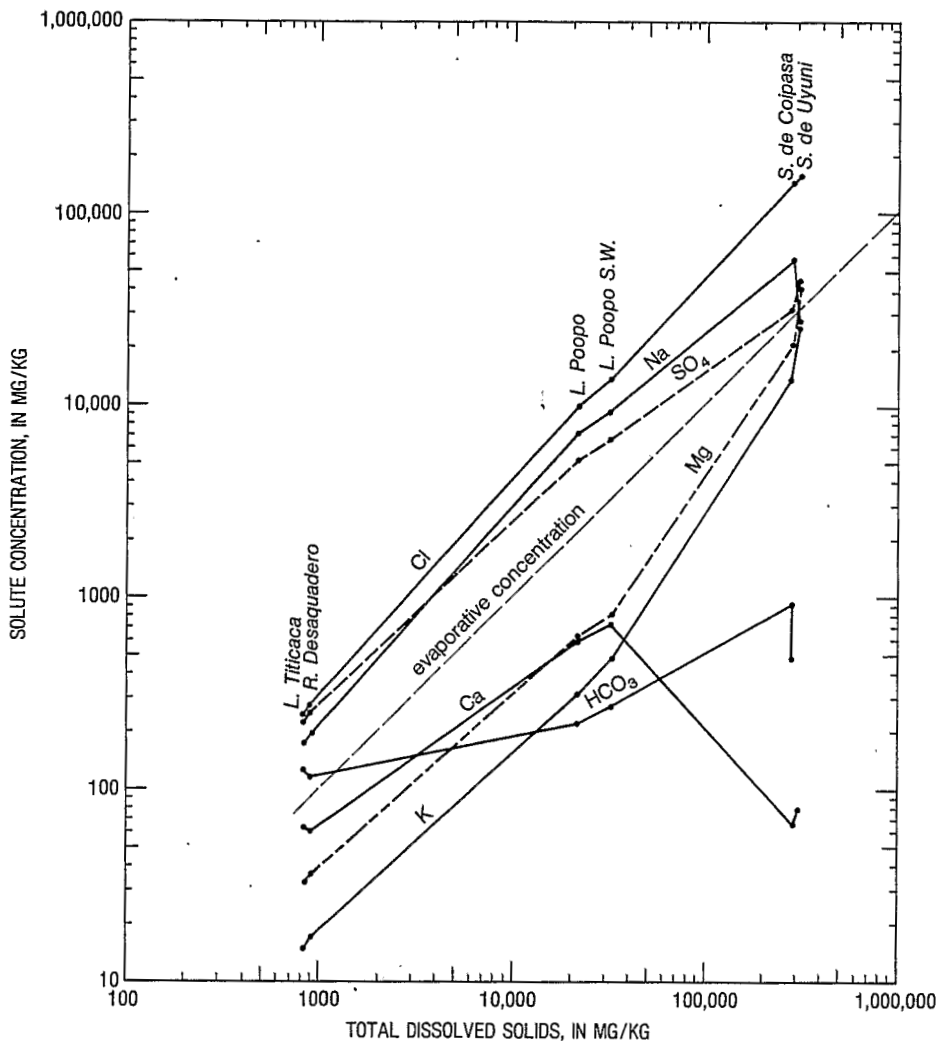


Fig. 2. Concentration of major constituents relative to total dissolved solids in waters from the Bolivian Altiplano from Lake Titicaca to Salar de Uyuni.

observations (J.P. Carmouze, pers. commun., 1979) indicate that the discharge of the Rio Desaguadero downstream from about midway between Lake Titicaca and Lake Poopo is presently dominated by inflow from the Rio Mauri, which drains largely ignimbrite terrane of the Cordillera Occidental to the west. Also, analyses made in 1976 of some hot springs* in the region of Calamarca, Oruro, and Challapata (Fig. 1) show primarily Na-HCO₃ and

* Sampled by W.D. Carter, USGS.

Na-Cl waters. Increased inflow from these springs in the past would have caused Na and chloride to constitute a larger share of the total solute composition of the lakes.

Despite inflow variations, the most obvious explanation for apparent loss of dissolved carbonate and sulfate over the concentration range of the Altiplano lake waters would be the precipitation of calcite and gypsum. The similar slopes of the Ca, Mg and SO_4 increases between Titicaca and Poopo actually reflect continuous loss relative to conservative total solute content. The relative decrease in HCO_3 content is to be expected when waters already saturated with respect to calcium carbonate receive added input of Ca from other sources. Indeed, Boulangé et al. (1978) report up to 30% carbonate in the sediments of central Lake Poopo, apparently a low-Mg calcite. Further loss of Mg from solution may be associated with smectite clays or precipitation of diatomaceous silica (Jones and Van Denburgh, 1966; Eugster and Jones, 1979).

The fundamental importance of calcite and gypsum precipitation to the subsequent geochemical evolution of saline waters on the Altiplano has been discussed previously (Risacher, 1978). Inasmuch as the northern Altiplano region is an area of calcareous sedimentary rocks, molar Ca concentrations in inflow of the area generally have exceeded carbonate, and the constant ion-activity product accompanying calcite precipitation should be maintained by relative Ca increase as HCO_3 is lost, until gypsum saturation is reached. Thereafter, calcium is rapidly depleted as sulfate increases at constant $a_{\text{Ca}} \cdot a_{\text{SO}_4}$. The result is the trend toward Na-(Mg)-Cl- SO_4 brines predicted by calculations (Risacher, 1978) on the freshwater compositions of the northern Altiplano.

Besides the trends in major solute composition relative to total dissolved solids content shown in Fig. 2, changes in individual solute concentrations can be shown with respect to chloride, which is normally conserved in solution over the complete concentration range of natural waters up to halite saturation [for application to other hydrologically closed basins, see Eugster and Jones (1979)]. Computations of the change in major solute matrix over the drainage basin of Lakes Titicaca and Poopo, based on the data of Carmouze et al. (1978), are given in Table I.

From Table I, it is immediately apparent that Na in the northern Altiplano waters is as conservative as chloride, and this suggests that the two solutes have a similar source. At the same time, Ca and HCO_3 are the principal cation and anion, respectively, lost in the compositional evolution from north to south, as expected from calcite precipitation. The loss of proportionally more HCO_3 than Ca at Lake Poopo may be related to alkalinity loss accompanying cation sorption with increasing salinity. Decrease in proportion of sulfate is significant in the Lake Titicaca system at concentration levels below gypsum saturation, whereas Mg proportions are notably decreased only on inflow to Lake Poopo. The most unexpected figures of Table I are those for K. The proportion of K lost on inflow to Lake Titicaca is nearly regained in outflow, and almost 20% of the K proportion lost on inflow to Lake Poopo is regained in the more con-

TABLE I

Chemistry of waters from the Bolivian Altiplano compared to model compositions based on conservation of chloride in solution during evaporative concentration [analyses of waters from L. Titicaca and L. Poopo drainages taken from Carmouze et al. (1978)]

	Concentration (mmol/l)							Total (mg/l)
	HCO ₃	SO ₄	Cl	Ca	Mg	Na	K	
Inflow to L. Titicaca	1.21	0.66	1.46	0.90	0.28	1.54	0.08	280
inflow × 4.92	5.95	3.25	7.19	4.43	1.38	7.58	0.41	1,380
L. Titicaca	2.05	2.43	7.19	1.58	1.36	7.58	0.39	895
% difference	-66	-25		-64	-1.5	0.	-6	-35
Outflow from L. Titicaca	1.90	2.65	7.95	1.53	1.50	8.40	0.45	957
L. Titicaca × 1.11	2.27	2.68	7.95	1.74	1.51	8.39	0.43	990
% difference	-16	-1		-12	-1	0	+5	-3.3
Inflow to L. Poopo	1.87	3.11	9.61	1.85	1.46	10.3	0.40	1,120
inflow × 30.59	57.1	95.1	294	56.6	44.7	315	12.2	34,300
L. Poopo	3.60	54.0	294	15.0	25.0	315	8.85	24,500
% difference	-94	-43		-74	-44	0.	-28	-29
Southwest L. Poopo	4.46	70.5	395	18.8	33.1	422	12.5	32,600
L. Poopo × 1.34	4.84	72.6	395	20.2	33.6	423	11.9	46,100
% difference	-8	-3		-7	-1.5	0.	+5	-29
S. de Coipasa No. 143	11.1	209	4260	4.83	375	3630	183	436,000
Southwest L. Poopo × 10.8	48.1	760	4260	202	357	4550	135	352,000
% difference	-77	-72.5		-97	+4.8	-20	+26	+19

centrated waters to the southwest. This is probably related to organic uptake and release on decay or to concentration-dependent ion exchange with fine-grained particulates.

Between Lake Poopo and the Salar de Coipasa the compositional trend for the most saline waters continues toward chloride dominance (Fig. 2). Ca has been decreased markedly, and SO_4 , though it continues to increase, does so by a factor notably less than that for total solutes. The extent of the precipitation of calcite and gypsum has become readily apparent in the abundant gypsum crystals in the muds at the margin of the salar and deposits of algal limestone along terraces of old lake levels. The proportional increase of Mg and K at Coipasa is enhanced by the loss of Na to initial halite precipitation.

Between Coipasa and the Salar de Uyuni, solute compositional trends are discontinuous like the present drainage and, though illustrating diverse changes in individual constituents relative to the Lake Poopo chemistry, the TDS concentrations are very similar. From the limited data, Coipasa brines appear to be proportionally higher in Na and lower in Mg and K— SO_4 than the brines from Salar de Uyuni. Na is definitely depleted in the most concentrated liquors from both salars, whereas Mg, K and, to a lesser extent, SO_4 are decidedly enriched relative to the TDS concentration. Such trends are consistent with the precipitation of halite from a solute matrix dominated by chloride [see solute concentration trends for marine brines given by Carpenter (1978)].

CHEMICAL ANALYSES OF BRINES FROM THE GREAT SALARS

Table II is a compilation of the chemical analyses of brine samples: 18 from central Salar de Uyuni, 15 from the Rio Grande de Lipez delta area, and 3 from Salar de Coipasa. Fig. 3 is a map of the area showing sample locations. All brines with a density greater than 1.2 g/cm^3 were essentially saturated in halite. The solutes remaining were largely SO_4 , K and Mg.

Analytical methods were based on those of Rainwater and Thatcher (1960) and Skougstad et al. (1979), subject to some of the same considerations noted by Jones et al. (1977). Samples were diluted by a factor of 10 prior to determination of the major constituents. Chloride was determined gravimetrically, and sulfate was determined turbidimetrically by stabilizing the BaSO_4 suspension with gelatin as proposed by Tabatabai (1974). The major cations were analyzed by atomic absorption spectrophotometry. Ca was analyzed in a nitrous oxide—acetylene flame with the addition of K, and Mg was determined in an air—acetylene flame with the addition of La. To allow for the matrix effects in the analysis of K, Na was added to the standards to match the concentration of the samples. Li was determined by standard addition. It should be noted that the values reported for bromide, analyzed by oxidation with hypochlorite, have not been corrected for iodide, which we have considered to be negligible. Because chloride is conserved in solution only to the point of halite saturation, the various constituents were initially considered with respect to increasing density to explore trends in individual solute content with the TDS concentration.

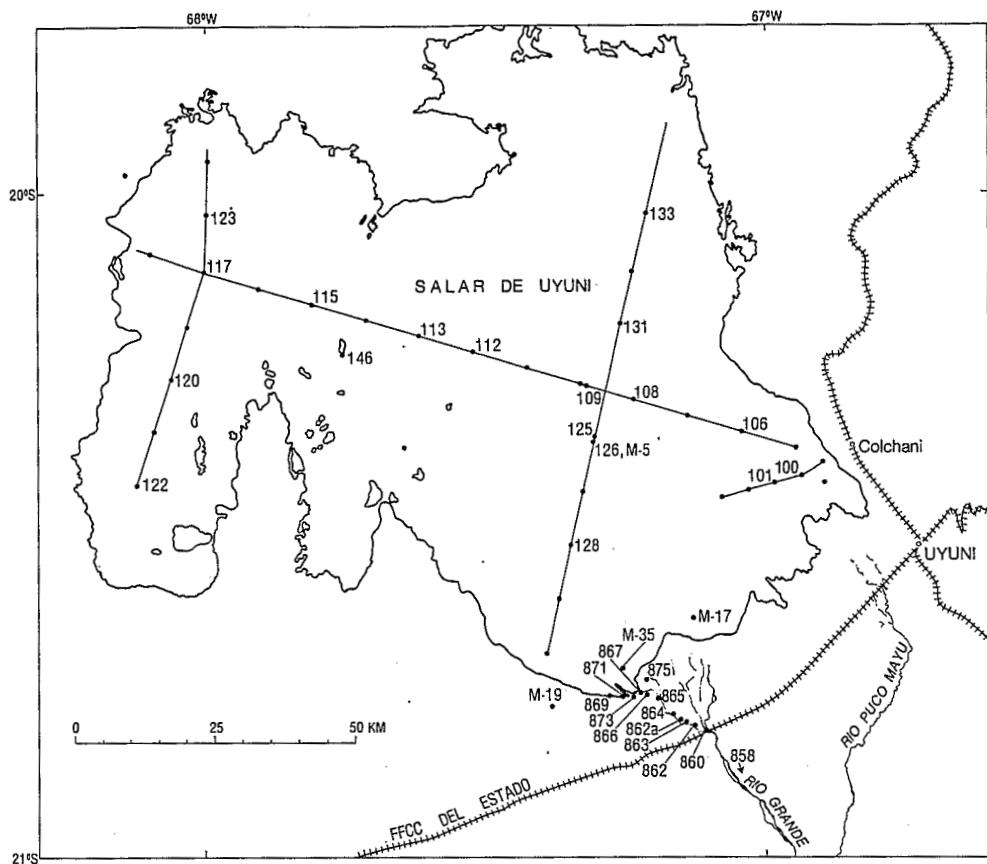


Fig. 3. Map of the Salar de Uyuni illustrating the location of brine sample traverses and individual brine sample collections.

The relationship of chloride, Na, K, Mg and SO_4 content to density indicate that for brines denser than 1.20 g/cm^3 , chloride was nearly constant, with a decrease of Na being balanced by increases in K, Mg and SO_4 . The chloride contents of the few Coipasa brines obtained were slightly less than those from Uyuni, even though their density was higher and the Na/K ratio at comparable total solute content was greater. These compositional differences can be explained in part by the inflow history and present hydrologic balance of the two salars. Uyuni is now a completely closed basin. It presumably has been isolated from the Pleistocene lake systems for some time longer than Coipasa. Inflow is now principally from the Rio Grande de Lipez with minor contributions from other small drainage basins to the south, and from groundwater flow, none of which can be expected to contribute the major discharge or

TABLE II

Analyses (in mg/kg, unfiltered; S.L. Rettig, analyst) of brines from the salt crust of Salar de Uyuni, Rio Grande de Lippez delta area, and Salar de Coipasa, Bolivia

	pH	Density (g/cm ³)	HCO ₃	SO ₄	Cl	F	Br	Ca	Mg
<i>Salar de Uyuni Central Traverse:</i>									
100	7.40	1.204	106	3,270	158,000	5.8	17	329	1,910
101	7.34	1.207	159	5,080	157,000	5.8	27	489	3,080
106	7.23	1.210	263	7,720	157,000	7.4	49	468	5,300
108	7.29	1.210	329	7,000	157,000	7.4	50	512	5,330
109	7.03	1.221	570	15,000	157,000	12	86	341	11,500
113	7.22	1.213	482	7,420	158,000	9.1	55	517	7,310
115	7.41	1.205	162	4,930	157,000	9.1	15	647	2,560
117	7.34	1.207	178	5,910	157,000	8.3	14	585	3,480
120	7.24	1.213	354	9,150	156,000	12	47	451	7,380
122	7.39	1.211	264	8,520	157,000	14	34	484	6,250
126	7.05	1.224	515	19,100	155,000	9.8	90	183	13,800
129	7.13	1.214	488	10,100	158,000	12	75	380	9,720
131	7.24	1.211	376	8,420	158,000	11	66	558	6,410
133	7.35	1.208	240	5,430	157,000	9.9	43	609	4,620
146	7.12	1.213	511	10,700	157,000	13	64	393	8,750
<i>SE crustal margins:</i>									
M-5	7.07	1.216	633	13,400	157,000	8.0	69	366	9,530
M-17	5.99	1.279	—	46,500	160,000	26	291	80	41,300
M-19	7.16	1.131	270	5,850	103,000	3.0	40	1,550	5,480
M-35	7.48	1.035	300	959	30,600	2.0	18	679	502
Colchani Salt Works	6.37	1.256	1,800	32,600	161,000	17	210	0	36,200
Isla de los Pescadores	6.69	1.224	735	18,100	155,000	4.0	96	133	12,300
<i>Rio Grande de Lippez Delta:</i>									
858	8.07	1.000	225	300	875	1.0	<10	161	45
860	7.83	1.000	303	600	3,380	1.3	<10	429	197
862	7.83	1.019	326	2,360	12,300	4.9	<10	1,180	554
862A	7.00	1.093	448	4,680	72,600	6.4	34	1,780	4,270
863	7.56	1.050	589	5,430	38,200	6.7	19	807	3,240
864	7.05	1.143	610	3,150	113,000	7.0	45	2,340	7,570
865	7.13	1.151	800	4,950	117,000	6.1	64	1,440	8,190
866	7.57	1.164	1,100	6,570	126,000	8.6	79	1,070	9,830
867	7.32	1.213	816	10,500	157,000	6.6	91	418	8,660
869	7.30	1.210	744	9,180	157,000	9.9	72	467	8,420
871	7.21	1.198	893	13,000	143,000	10	96	382	11,300
873	7.10	1.215	1,000	13,000	156,000	13	123	321	9,350
876	7.34	1.211	566	8,430	157,000	12	79	491	6,880
<i>S. de Coipasa:</i>									
142	6.97	1.247	922	33,300	150,000	30	221	67	21,800
143	7.37	1.224	678	20,100	151,000	19	88	193	8,990
144	7.34	1.223	642	20,500	152,000	20	116	207	9,910

*Though no particulate contamination was noted visually, lack of filtration suggests these values be considered semi-quantitative.

quantities of dissolved material appropriate to the size of the salt crust. Whatever inflow waters reach the central salt crusts of the salar are quickly dominated in solute composition by re-resolution of NaCl from thick pre-existing halite. As evaporation proceeds, any carbonate or sulfate is precipitated as calcite, gypsum, or sodium sulfate, and on reprecipitation of NaCl, Mg and K are enriched in the resulting chloride liquors. Therefore Uyuni has apparently reached a final stage of development, and any future changes in its final brine

Na	K	Sr	Li	B	PO ₄	SiO ₂ *
97,700	1,950	7.8	104	75	0.38	6.2
94,400	3,340	11	134	115	0.68	5.5
90,300	5,830	18	215	178	0.67	5.9
91,100	10,000	12	303	169	1.3	6.1
77,400	11,600	8.2	512	351	1.1	6.5
85,500	7,480	22	441	238	1.1	6.5
96,100	2,790	11	139	82	0.73	7.4
94,400	3,620	14	193	109	0.66	7.6
87,000	7,760	13	354	195	0.91	7.5
88,700	6,660	16	351	174	0.76	7.7
71,700	14,800	3.6	817	492	1.4	7.5
78,200	11,100	18	577	291	1.7	7.2
85,800	7,210	19	343	199	0.71	9.7
89,700	4,730	18	246	123	0.41	8.3
80,500	8,860	15	511	270	0.98	9.2
82,300	10,900	5.1	469	337	2.0	4.4
28,500	27,400	0.5	2,060	1,090	5.9	20
57,500	3,760	7.3	221	93	0.9	15
18,100	1,450	27	232	108	8.0	61
40,600	24,100	<50	1,510	722	6.4	18
80,400	10,600	<50	490	527	0.88	7.9
515	27	2.5	3.1	10	0.66	47
1,550	80	5.8	10	21	0.51	51
6,530	294	23	26	31	0.54	60
36,400	2,930	32	217	229	0.23	43
18,700	1,710	21	142	110	2.2	61
54,000	5,380	37	503	421	2.8	29
56,500	6,340	21	548	727	7.6	12
59,500	6,790	12	579	469	3.3	1.9
82,400	8,570	9.1	459	317	1.7	14
80,600	8,680	9.5	445	304	1.4	5.4
68,400	10,400	6.1	611	423	2.0	1.8
78,800	9,050	3.4	521	516	2.1	1.8
83,000	6,940	9.5	353	235	1.2	14
59,600	18,300	18	524	1,300	13	20
83,500	7,140	14	251	497	6.1	4.9
82,100	7,420	18	276	561	7.7	5.6

composition will be an increase in Mg and K at the expense of Na. On the other hand, Coipasa has continued to receive inflow (presumably high in Na) from Lake Poopo for a longer period during the desiccation of the Pleistocene lakes, and thus has not proceeded as far in its geochemical evolution. In addition, recent satellite observation suggests surficial brine levels are presently sustained by discharge of inflow from the north. Eventually Coipasa might be expected to achieve brine compositions similar to those in central Uyuni.

SOLUTE CHEMISTRY vs. CONCENTRATION

Because the relation between the TDS content and density varies as a function of the solution composition, the effect of evaporative concentration on individual constituents in solution must be examined by reference to a conservative solute.

Chloride and bromide

Chloride is normally appropriate for such purposes (Hanor, 1977; Jones et al., 1977; Eugster and Jones, 1979), but in view of the halite predominance in the Altiplano salars, another element must be considered. Experience with bromide as a reference in marine evaporites (Braitsch, 1971) suggests its use here. Although a small amount of Br is taken up in solid solution in precipitating halite, the fractionation strongly favors the residual solution (Braitsch and Hermann, 1963).

The relation of bromide to density for brines from Uyuni and Coipasa is given in Fig. 4. The sample points are most readily divided into two distinct groups: brines from the traverse across the central Salar de Uyuni, including brine collected at the margin of the Isla de los Pescadores in the middle of the salar, and those from the Rio Grande de Lipez delta area associated with the continuous halite crust of the main salar; and the majority of samples from the Rio Grande delta plus highly concentrated residual brines from the southeast Uyuni crustal edge and the Colchani salt works. The latter group

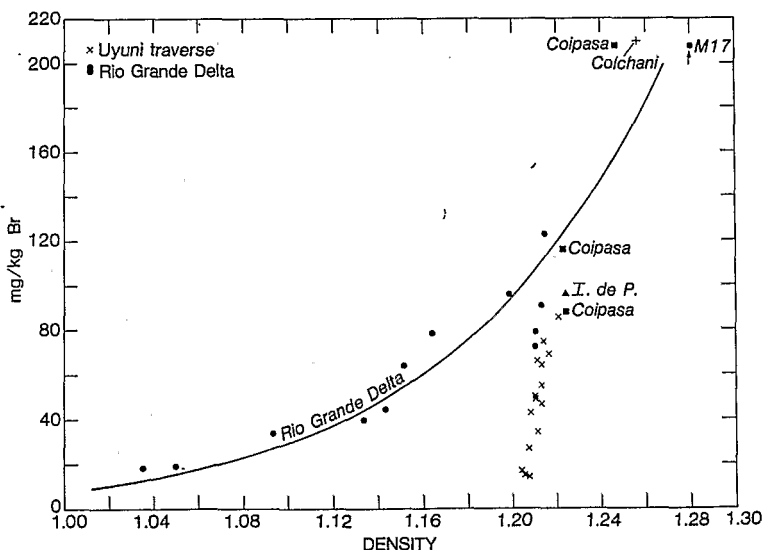


Fig. 4. Bromide concentrations of brines from Salar de Uyuni plotted against density. Location of samples is shown in Fig. 3 and analytical data are given in Table II.

can be fit to a power function with $r = 0.93$ (Table III), which suggests a single regular fractionation process accompanying continuous solution concentration. In contrast, the wide range of the bromide concentrations associated with the nearly constant chloride content and the narrow density range ($1.20\text{--}1.23\text{ g/cm}^3$) of the Uyuni crustal brines most probably reflects variable or cyclic surficial halite re-solution, resulting in progressive depletion of Br in associated fluids. The highest Br values from central Uyuni are associated with the brine pools described by Erickson et al. (1978), and may represent upwelling of denser residual brine from the lower crust along major fractures. The Salar de Coipasa brines fit the general relationships established for Uyuni. These relatively straightforward correlations appear to justify the use of bromide as a reference for delineation of processes affecting other solutes.

TABLE III

Regression parameters for interelement correlation — Brines of the Salar de Uyuni, Rio Grande de Lipez delta area, and Salar de Coipasa

Samples	Elements	Expression*	<i>a</i>	<i>b</i>	r^2 (correlation coeff.)
Central Uyuni					
+ Isla de Pescadores	Br, density	linear	1.20	0.0002	0.85
Rio Grande delta					
area + Colchani	Br, density	power	0.85	-0.076	0.93
Central Uyuni traverse	Na, Br	linear	313.0	-0.003	0.89
Central Uyuni traverse					
+ Colchani and SE Uyuni					
crust edge concentrate	Na, Br	linear	379.0	-0.0038	0.97
Central Uyuni +					
Isla de Pescadores	Mg, Br	linear	3.74	0.0070	0.87
All samples	Mg, Br	linear	12.0	0.0067	0.89
Central Uyuni traverse	K, Br	linear	6.15	0.0058	0.82
All samples	K, Br	linear	- 5.49	0.0095	0.83
Central Uyuni traverse	SO ₄ , Br	linear	5.92	0.0050	0.73
All samples	SO ₄ , Br	linear	5.97	0.0059	0.90
Uyuni traverse +					
Colchani + SE crust	Li, density	linear	1.20	$3.7 \cdot 10^{-5}$	0.97
Rio Grande delta					
+ Colchani + SE crust	Li, density	power	0.814	0.059	0.74
Uyuni traverse	Li, Br	linear	10.00	0.111	0.79
All Uyuni samples	Li, Br	linear	4.88	0.137	0.92
Uyuni traverse	B, Br	linear	8.03	0.199	0.83
Central Uyuni +					
Colchani + SE crust	B, Br	linear	-4.03	0.259	0.94
All samples	B, Br	linear	7.28	-0.195	0.82

*Linear: $y = a + bx$; power: $y = ax^b$.

Sodium

The most graphic illustration of the development of two distinct brine types at Salar de Uyuni is seen in the Br vs. Na relation concentration in solution (Fig. 5). Brines associated with the halite crust of the salar show a systematic increase in Br associated with a decrease in Na (and concomitant increases in Mg and K). Indeed, without much change in slope, this trend can be extended to include the most concentrated solutions analyzed from the area. However, samples from the Rio Grande delta which have not been in contact with the halite crust of the salar show a strong increase in Na with increasing bromide to the point of intersection with the trend of central Uyuni crustal brines and, apparently, saturation with respect to halite*, as indicated by a relatively constant chloride content (see Table I). The change in slope of Na increase at $\sim 5 \cdot 10^4$ mg/kg may be related to ulexite ($\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$) precipitation. At higher TDS concentrations, Na is replaced as the major cation by increasing amounts of K and particularly Mg, as mentioned earlier. Because of the predominance of chloride over Na at the onset of halite precipitation, further concentration forces a decrease in Na levels at nearly constant chloride content. This effect is enhanced by the proportionally greater increase in the activity coefficient of Na^+ over Cl^- on further concentration. These relations

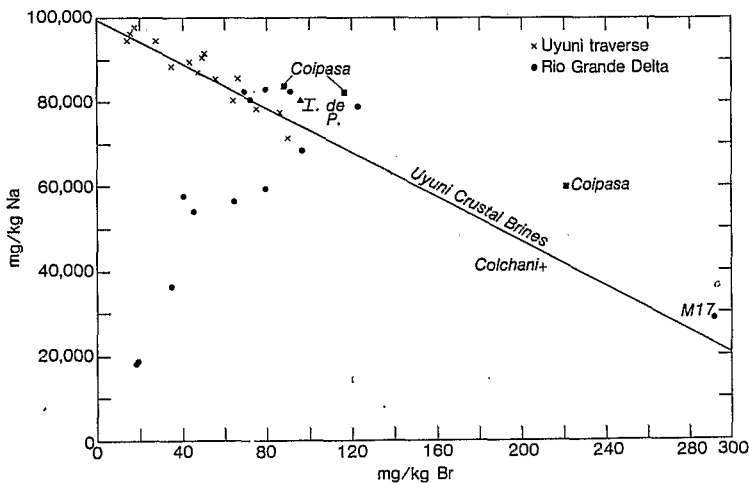


Fig. 5. Sodium concentrations of brines from Salar de Uyuni plotted against bromide content. Location of samples is shown in Fig. 3 and analytical data are given in Table II.

*Halite saturation indices — log of the ratio of the activity product to equilibrium constant at temperature of collection — are within 0.15 units or less of equilibrium, as calculated from the computer program WATEQF (Plummer et al., 1976), but Uyuni brine concentrations are beyond the theoretically prescribed application of the aqueous model.

further substantiate the subdivision of Uyuni brine compositions into primary and re-solution types, as suggested in the plot of bromide vs. density. On the other hand, the limited data on Coipasa brines indicates that they are proportionately higher in Na, especially at a higher concentration, and somewhat lower in chloride than those from Uyuni. As mentioned earlier, this may have resulted from a higher proportion of sodium salts in inflow to Coipasa since drainage separation of the salars.

Magnesium

Mg appears to offer a good correlation with bromide over the entire concentration range of all salar brines examined (Fig. 6). The regression line derived for Mg vs. Br contents of brines from the central Uyuni salt crust has a nearly identical slope to that obtained for Mg vs. Br in all samples analyzed. However, significant departure from a simple evaporative concentration reference line indicates a continuous loss of Mg from solution as total solutes increase. Specifically, the Mg loss seems to have been greater in the lower Rio Grande delta than at central Uyuni, and still greater at Coipasa. Without further information on associated mineralogy or ion balances, one can only speculate whether this may be due to uptake by carbonate or silicate (Jones and Van Denburgh, 1966; Garrels and MacKenzie, 1967; Hardie and Eugster, 1970; Eugster and Hardie, 1978; Eugster and Jones, 1979).

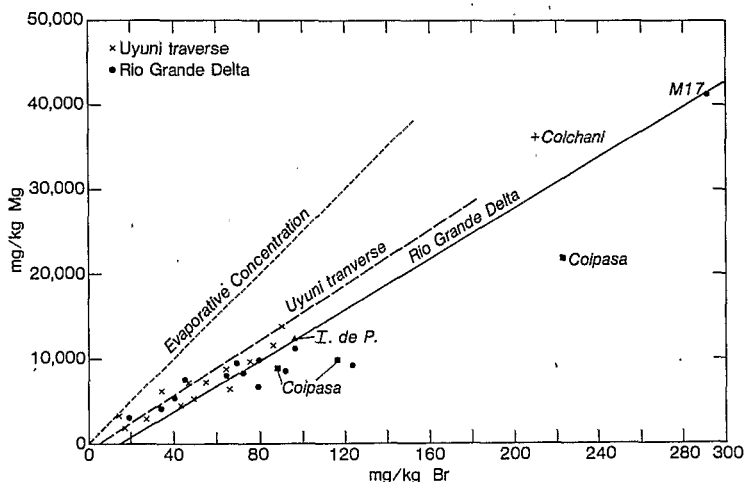


Fig. 6. Magnesium concentrations of brines from Salar de Uyuni plotted against bromide content. Location of samples is shown in Fig. 3 and analytical data are given in Table II.

Potassium

K shows a relation to bromide similar to that for Mg overall, with some subtle but significant differences (Fig. 7). For the brines of the central Uyuni

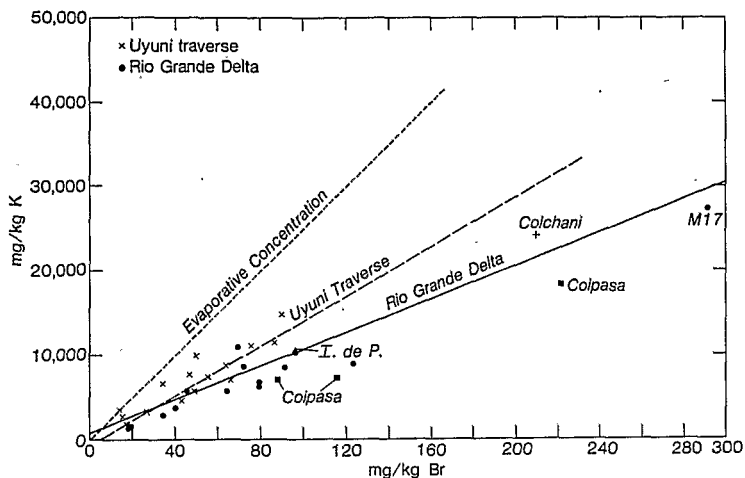


Fig. 7. Potassium concentrations of brines from Salar de Uyuni plotted against bromide content. Location of samples is shown in Fig. 3 and analytical data are given in Table II.

salt crust, the slope of the K vs. Br regression is close to that for Mg vs. Br, but the departure from the slope of simple evaporative concentration is greater. The relative loss of K from solution is even more pronounced when all samples are taken into account, and the deviation from the central Uyuni trend is apparent, especially for the Coipasa samples. In fact, the Rio Grande delta—Coipasa data for both Mg and K vs. Br describe trends that could be examples of Eugster and Jones' (1979) type-IIa curve for the dominant ion of a binary precipitate, or the type-IV curve of sorption or exchange, or combinations. The distinct differences seen in the highest total solute concentration brines from the Colchani salt works, Coipasa, or the SE Uyuni salt crust edge area suggest that more than one process is involved. Indeed, sylvite has been identified in the salt crusts at Uyuni (F. Risacher, unpublished data, 1978), indicating that simple salt precipitation is operative in addition to the commonly presumed uptake by clays.

Sulfate

The plot of SO_4 vs. Br shows the most clear-cut separation of the central Uyuni salt crust brines from the fluids of the Rio Grande de Lipez delta area (Fig. 8). Although the trend of sulfate increase with increasing bromide (and total solute concentration) for both data sets falls below the slope for straightforward evaporative concentration, the Rio Grande delta brines appear progressively more depleted in SO_4 than the central Uyuni crustal brines. This also appears to be the case for the most concentrated brines from Colchani, Coipasa and the SE Uyuni crustal edge (e.g., M-17, Fig. 3), though not as markedly. Both data sets appear to offer an example of Eugster and Jones'

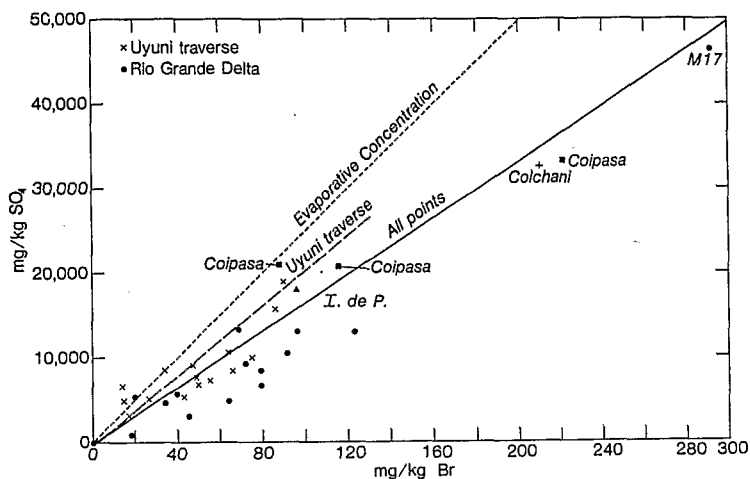


Fig. 8. Sulfate concentrations of brines from Salar de Uyuni plotted against bromide content. Location of samples is shown in Fig. 3 and analytical data are given in Table II.

(1979) type-III curve for a continuous concentration independent process. Bacterial reduction is the most obvious mechanism to provide progressive depletion of sulfate, following gypsum precipitation. Sulfur species reduced in the fine muds of the Rio Grande delta area or beneath the central halite deposits are probably re-oxidized to some extent at the surface, especially in the course of crustal re-solution by oxidized surficial runoff waters, resulting in less net depletion in the central Uyuni crustal brines than in the principal delta area. In the most concentrated brines, sulfate proportions increase as a consequence of the limit on chloride increase imposed by halite precipitation, and, to a much lesser extent, because of the decreased solubility of CaSO_4 with increased total salinity.

Lithium and boron

The elements of perhaps the greatest current economic interest, the minor solutes Li and B, which have been particularly associated by Risacher and Miranda (1977) with the volcanic terrane south of Uyuni, also provide insights to processes affecting the geochemical evolution of the salar brines. With respect to density, the Li values show definite similarity to the relationship developed for bromide, whereby brines with densities between 1.20 and 1.23 g/cm^3 associated with the continuous salt crust are apparently lower in Li than other samples with either higher or lower densities (Fig. 9). The brines from the Salar de Coipasa have particularly low Li contents, suggesting lack of source. Although not as satisfactory a correlation as obtained for Br, a power equation with $r = 0.78$ can be fit to Li vs. density values for the more

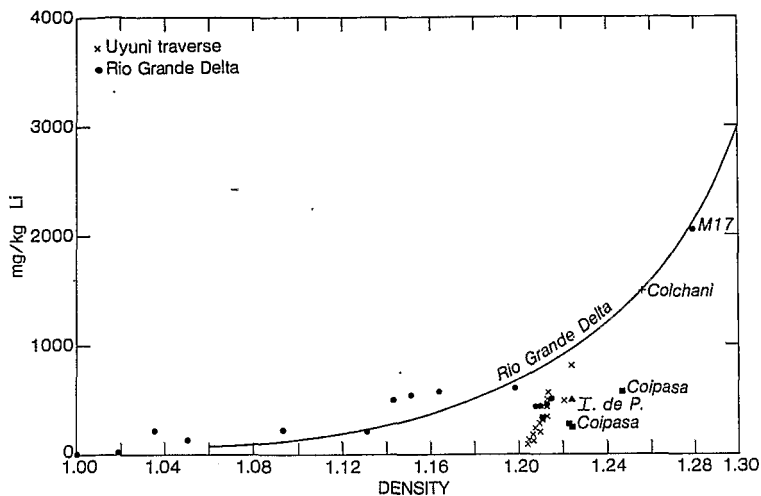


Fig.9. Lithium concentrations of brines from Salar de Uyuni plotted against density. Location of samples is shown in Fig. 3 and analytical data in Table II.

dilute (density $< 1.20 \text{ g/cm}^3$) samples from the Rio Grande delta plus the bitterns of Colchani and the SE Uyuni crustal edge. With the exception of the sample from one of the central brine pools described by Ericksen et al. (1978), crustal brines of the Salar de Uyuni contain half or less the Li predicted by the power equation. In contrast, the most highly concentrated non-crustal brines of the Rio Grande delta contain even more Li than indicated by the equation (Risacher, 1978).

The Li vs. Br content relation (Fig.10) suggests a tenuous explanation for the previous results. The Li vs. Br regression slope for the central Uyuni crustal brines is nearly parallel to the evaporative concentration trend, indicating that Li is basically conserved in these fluids. At the same time, a few less concentrated samples from the Rio Grande delta contain unusually high amounts. An apparent limit to Li enrichment is reached at about 600 mg/kg in the presence of mud and/or thin crust. This limit is probably related to uptake by smectite clays. Some such mechanism has apparently been very effective at Coipasa; the low slope prescribed by its three points cannot be related to lack of source alone. Similar, though less pronounced, effects have been noted previously for both Mg and K.

From the B vs. Br content relation (Fig.11) it is apparent that, as with Li, a few less concentrated brines from the Rio Grande delta fit a relation close to that for simple evaporative concentration. However, the data from the majority of brines from the Salars de Uyuni and Coipasa, including the most concentrated fluids, suggest a long-term depletion of B from solution. The ulexite deposits in the Rio Grande delta area and disseminated crystals in the muds elsewhere readily account for precipitation of B from the brines (Risacher, 1978).

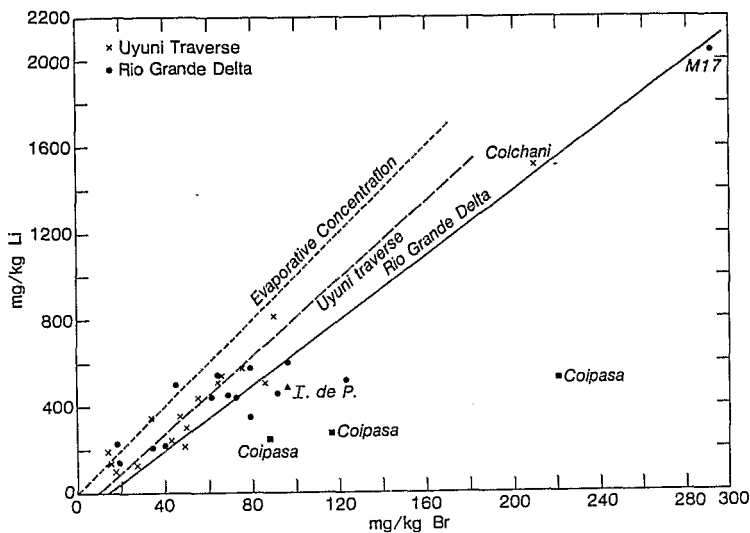


Fig. 10. Lithium concentrations of brines from Salar de Uyuni plotted against bromide content. Location of samples is shown in Fig. 3 and analytical data in Table II.

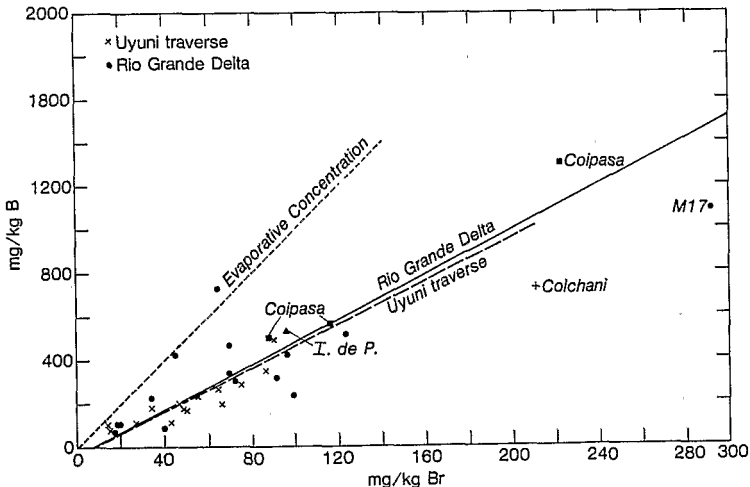


Fig. 11. Boron concentrations of brines from Salar de Uyuni plotted against bromide content. Location of samples is shown in Fig. 3 and analytical data in Table II.

As compared with the other solutes referenced to conservative Br, the Li and, to a lesser extent, B contents of the Salar de Uyuni brines appear to be less affected by the more complex processes and potential mechanisms of loss from solution than the major solutes. The common association of the two elements has suggested use of borate deposits as a prospecting tool for Li-rich

solutions. Consequently, Li and B concentrations of dilute water from Lake Titicaca and streams tributary to the Salar De Uyuni from the south were plotted against TDS (Fig. 12). The results indicate that drainages such as the Rio Grande de Lipez established in relatively fresh volcanic (rhyolitic) terrain carry Li and B together in direct and relatively high proportion to total solutes, whereas other streams may contain much B without correspondingly high levels of Li. A contrast may also be seen in the relations of the two elements to bromide for the brines. Li levels at Coipasa are notably lower than at Uyuni, whereas B contents are similar for a given Br content.

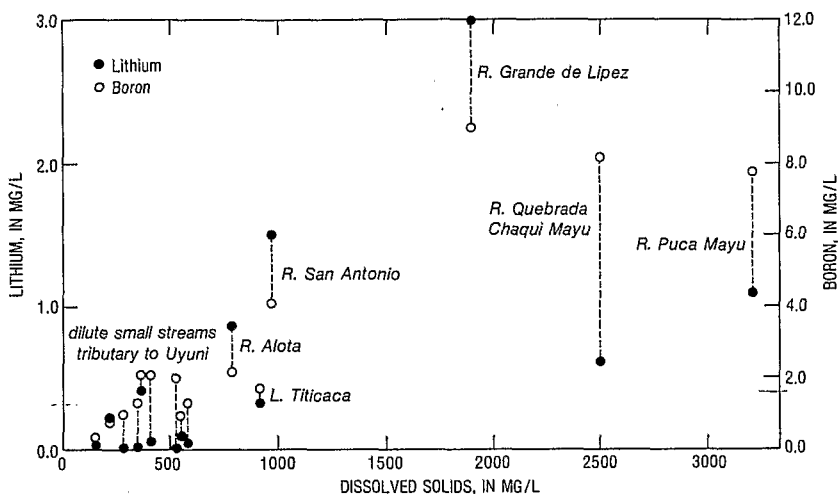


Fig. 12. Lithium and boron concentrations plotted against dissolved solids for Uyuni inflow. The Rio Grande de Lipez is the largest inflow stream; its tributaries include the Rio San Antonio and Rio Alota. The Rio Quebrada Chaqui Mayu, and Rio Puca Mayu flow directly into Uyuni from the west and east of the Rio Grande, respectively. Lake Titicaca is shown for comparison.

Strontium

Sr concentrations in the central Uyuni crustal brines appear to bear no relation to total solute content or any other specific constituent, ranging from 3.6 to 22 mg/kg for densities between 1.20 and 1.23 g/cm³. This scatter may be the result of variability in the recrystallization of sulfate or carbonate minerals bearing Sr in solid solution. The Sr contents of brines from the Rio Grande delta, however, show a very interesting trend with increasing density (Fig. 13). Sr content increases to a maximum of 37 mg/kg at a density of 1.143 g/cm³. At higher densities the Sr concentration decreases abruptly in what appears to be a logarithmic manner to minimum of 0.5 mg/kg at a density of 1.279 g/cm³ in the SE Uyuni crustal concentrate. This abrupt decrease suggests the precipitation of a Sr-bearing mineral; from current thermodynamic data, the most likely phase seems to be celestite.

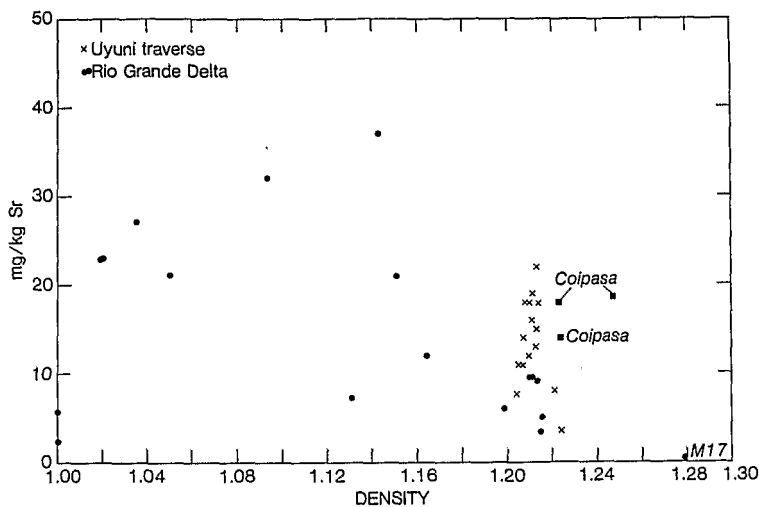


Fig. 13. Strontium concentrations of brines from Salar de Uyuni plotted against density. Location of samples is shown in Fig. 3 and analytical data in Table II.

SUMMARY

Examination of recent hydrochemical data from the Bolivian Altiplano has outlined the compositional trends and principal processes leading to the present chemistry of brines in the largest playa in the world, the Salar de Uyuni. These trends have been delineated with respect to total solute concentration in the succession of remnants of two very large lakes, connected by overflow, which occupied much of the floor of the Altiplano during the Pleistocene. They have illustrated the effects of evaporative concentration, the widespread precipitation of calcite, gypsum and halite and the development of a residual K—Mg—Cl—(SO₄) brine in a continental environment. Although the basic trends were already established in the geochemical evolution of the present hydrologic system between Lakes Titicaca and Poopo, the greatest constituent percentage change has been shown to be between southwest Lake Poopo and the surficial brines of the Salar de Coipasa.

Composition trends have also been worked out for brines from *within* the area of the Salar de Uyuni and compared with Coipasa, utilizing the conservation of bromide in the fluid phase during evaporative concentration. This has permitted the differentiation of truly residual from re-solution brines, particularly from the relation of Br with Na. Similarly, reference to Br has indicated the sorptive or precipitate loss of K, Mg and Li, especially at Coipasa, and the reductive loss of sulfate. It has also demonstrated the relative conservatism of these elements in solution in contact with salt crust rather than fine sediment. At the same time, B appears to be influenced by a similar precipita-

tion process at both places. Precipitate control on Sr concentration is suggested in one part of the Uyuni system.

The Bolivian Altiplano has presented a unique opportunity to look at the geochemical evolution of closed-basin waters. Though the precipitation of calcite, gypsum and halite, and resulting trends might have been predicted, the Altiplano area has provided insights into the importance of related processes in a major hydrologic system.

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