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# Quaternary geochemical evolution of the salars of Uyuni and Coipasa, Central Altiplano, Bolivia

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#### ABSTRACT

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The central trough of the Bolivian Altiplano is occupied by two wide salt crusts: the salar of Uyuni, which is probably the largest salt pan in the world  $(10,000 \text{ km}^2)$  and the salar of Coipasa  $(2,500 \text{ km}^2)$ . Both crusts are essentially made of porous halite filled with an interstitial brine very rich in Li, K, Mg, B (up to 4.7 g/l Li, 4.3 g/l B, 30 g/l K and 75 g/l Mg). Lithium reserves are the highest known in the world, around  $9 \times 10^6$  tons. Potassium, magnesium and boron reserves in brines are also important (around  $194 \times 10^6$  tons K,  $8 \times 10^6$  tons B and  $211 \times 10^6$  tons Mg).

The crusts are the remnant of saline Lake Tauca (13,000–10,000 yr BP). Its salinity was estimated approximately at 80 g/l. Its paleochemistry was derived in two ways: (1) by dissolving the present amounts of all chemical components in the former lake volume, and (2) by simulating the evaporation of the major inflows to the basin. The resulting chemical compositions are quite different. The dissolution-derived one is 5 to 50 times less concentrated in Li, K, Mg, B than the evaporation-simulated ones. However all compositions present the same Na and Cl contents. This suggests either a removal of bittern salts or an enrichment of the former lake water in Na and Cl.

The most probable interpretation is that Lake Tauca redissolved a salt crust akin to that existing today. Several older lakes have been detected on the Altiplano. Nevertheless, such an explanation only pushes the problem back. It is likely that the anomaly was transferred from one lake to an other. Three hypotheses may be put forward: (1) bittern seepage through bottom sediments, (2) uptake of the missing components by minerals, and (3) leaching of ancient evaporites from the catchment area at the beginning of the lacustrine history of the basin. The excess halite could have been recycled from lake to lake. This latter process seems to be the most effective to explain the large excess of Na and Cl over the bittern solutes — Li, K, Mg and B. The occurrence of almost pure Na–Cl saline springs flowing out from a gypsum diapir in the northern Altiplano gives substantial support to this hypothesis.

### 1. Introduction

The Bolivian Altiplano is a 200,000 km<sup>2</sup> closed basin, at an altitude of 4000 m. It is enclosed between the Eastern and the Western Cordillera of the Andes (Fig. 1). The Eastern Cordillera is characterized by Paleozoic sediments (sandstones, shales) and granitic plutons (Ahlfeld, 1972). The Paleozoic formations also constitute the basement of the Altiplano. They are overlain with a thick fill of continental sediments of Cretaceous and Ter-

tiary age (sandstones, claystones, mudstones, shales and evaporites). Gypsum diapirs and gypsum-bearing fault gouges crop out in Cretaceous and Tertiary formations. During the Plio-Quaternary the western and the southern Altiplano were strongly affected by an intense volcanic activity. The Western Cordillera is mostly volcanic in origin. Volcanoes, lava flows and ignimbrites generally overlie the Tertiary formations. Volcanic rocks range from andesites to rhyodacites (Fernandez et al., 1973).

The topographic low of the central Altiplano

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Fig. 1. Geological map of the Bolivian Altiplano.

is filled with two wide salt crusts: the giant salar of Uyuni (10,000 km<sup>2</sup>, 3653 m), which is probably the largest salt flat in the world, and the salar of Coipasa (2500 km<sup>2</sup>, 3656 m). This paper first describes the sedimentology and brine chemistry of the salars of Uyuni and Coipasa and thereafter focuses on the main problems and hypotheses relative to their formation. Particular emphasis is laid on the origin of the components. A detailed study of present geochemical interactions between brines, salts and sediments will be developed elsewhere.

# 2. The salar of Uyuni

# 2.1. The salt crust

Field data were provided by 40 drill holes across the crust (locations in Fig. 2). The salt crust has a maximum thickness of 11 m. Isopachs are shown in Fig. 3. At the southeastern border the crust interfingers with fluviodeltaic sediments. The Uyuni crust is made of layered porous halite with little amount of fine-grained



Fig. 2. Location map. (a) Coipasa. CA, CB are drilled holes; C3 is a hand-drug hole; C1, C2, C4 and C5 are surface brine samples. (b) Uyuni. U and Y series are drilled holes. (c) Enlargement of a section of Uyuni to show ulexite deposit. R series are hand-dug holes.



Fig. 3. Isopachs of Uyuni salt crust (in m).

gypsum and filled with an interstitial brine. It is underlain by impermeable lacustrine sediments. The salar is completely flooded during the rainy season (January to March) and dry almost all over its surface the rest of the year. In the dry season the subsurface brine evaporates by capillary draw through the topmost centimetres of the crust, cementing it into a very compact and hard pavement, which drastically reduces the evaporation of brine. The brine table generally lies 10-20 cm below the surface. Only at the southeastern shore does the brine remain exposed all year, for a few centimetres above the crust, in small irregular pools. The porosity of the salt crust is almost completely saturated with brine. In the eastern area the crust shows deep, narrow pits.

The salt crust is composed of alternating layers around 10 cm thick of hard halite and crumbly crystal aggregates. Due to this texture, the average porosity of the whole crust is very difficult to estimate. Several determinations could only be made on hard samples, which led to rather low values: 20–30%. The porosity of the friable layers is likely to be significantly higher, around 40–50%. Therefore, we have assumed an average porosity of 30–40% for the whole crust. Busson and Perthuisot (1977) assumed similar values for recent halite deposits in Tunisia.

The mineralogical composition of the crust at drill hole UA is given in Table I. Gypsum and detritals make up 1–10% and 0–2% respectively, in weight of the solid phase. The remainder is exclusively halite. The chemical composition of halite crystals at drill point U2is given in Table II. Halite is of high purity grade, 98.5–99.8%. All other elements are only present as traces, probably in fluid inclusions. They will be taken into account in the mass balance calculations.

#### TABLE I

Mineralogical composition of Uyuni salt crust at location UA

Depth (cm)	Halite (wt%)	Gypsum (wt%)	Detrital (wt%)	
0	91.3	2.7	0.0	i
50	93.9	1.2	0.5	4
100	95.4	1.7	1.0	
150	85.2	11.6	1.5	
200	86.1	8.7	2.1	
250	86.6	5.9	1.9	* 1813.
300	93.0	3.5	1.5	ورج بهنا
345	95.9	1.2	1.3	
400	93.8	2.0	1.0	
450	97.6	1.3	0.5	
505	95.1	1.2	0.5	
550	94.9	1.9	0.5	
Average	92.4	3.6	1.0	

#### TABLE II

Chemical	composition	of halite at	location U2

Deptl (cm)	1NaCl (wt%)	Li (ppm)	K (ppm)	Ca (ppm)	Mg (ppm)	SO₄ (ppm)	B (ppm)
0	99.78	14.4	416	174	683	1,480	21.7
100	99.37	8.9	417	1,090	252	4,370	24.7
200	98.52	12.4	1,970	1,860	771	10,000	18.8
300	98.48	20.8	2,150	1,680	1,020	10,000	26.1
400	99.13	16.1	1,300	970	662	5,520	26.2
500	98.69	18.1	2,160	1,400	867	8,390	50.2
600	98.45	16.0	2,030	1,680	898	9,590	26.0
Ave-							
rage:	98.92	15.2	1,490	1,260	736	7,100	27.7

#### 2.2. Lacustrine sediments

The crust lies on impermeable and finely laminated lacustrine sediments made of detrital material, microcrystalline gypsum, calcite, organic matter and minor amounts of clay minerals (smectite and illite). Fossil Artemia faecal pellets are ubiquitous. They are made of calcite and gypsum and can be considered as a good criterion for recognizing lacustrine sediments. The measured porosity of lacustrine sediments average 50%. They are filled with interstitial brine.

# 2.3. Fluviodeltaic sediments

By far the largest permanent inflow to the salar is the Rio Grande which drains volcanic formations from the south. It has built up a 300 km<sup>2</sup> delta that intertongues with the salt crust (Fig. 4). Field data were provided by 26 handdug holes (location in Fig. 2). The delta is a complex system of clay layers containing silt and sand lenses. Clay minerals largely predominate; they are mainly smectite with some illite

and a little kaolinite. As a whole, deltaic sediments have a low porosity and permeability. Lacustrine sediments, similar to those found below the salt crust, underlie the fluviodeltaic formations. Generally, the water table lies close to the contact between lacustrine and deltaic sediments. Calcite, gypsum and ulexite (Na- $CaB_{5}O_{0} \cdot 8H_{2}O$ ) are precipitated in deltaic sediments by capillary draw. Here is the largest borate deposit in Bolivia (location in Fig. 2). The stratigraphic position of the borate lenses. within the deltaic sediments, indicates a postlacustrine age (Fig. 4). Ulexite has an average thickness of 0.1 m over a 120 km<sup>2</sup> area and a water content of 50%. Total boron reserves may then be roughly estimated to be around  $1.6 \times 10^6$  tons.

### 2.4. Brine chemistry

#### 2.4.1. Major trends

Ericksen et al. (1978) and Rettig et al. (1980) published the first analyses of the topmost part of the brine. In this part we present 138 new analyses of brines at all depths within



Fig. 4. (a) Stratigraphy and (b) B-Li contents in brines of the southeastern fringe of the salar, at the mouth of the Rio Grande River. Arrow indicates the probable brine movement.

the halite crust. In addition, we also use 26 analyses of brines from the delta area of the Rio Grande (Table III).

In most of the salar, the brines are of the Na-Cl type with high boron and lithium contents (Ericksen et al., 1978). In southeastern Uyuni, the brines are more concentrated and belong to the Mg-Cl group. Their B and Li contents are among the highest in the world; up to 4.7 g/l Li and 4.3 g/l B. They originate from the alteration of the surrounding volcanic rocks (Risacher, 1984).

#### 2.4.2. The horizontal gradient

Figure 5 shows lithium iso-concentration curves of the brine, at various depths in the crust. The same pattern is also observed for boron, potassium, magnesium and sulfate. Owing to overall gypsum saturation, calcium concentration is inversely related to that of sulfate. The highest concentrations are found at the southeastern shore, close to the limit between the salt crust and the deltaic sediments. The variation in Li and B contents in the upper part of the brine across the southeastern area are shown in Fig. 4. The concentrations show sharp increases over a reduced area. The rest of the surficial brine shows a gentle northwards-decreasing gradient for Li and B concentrations.

# 2.4.3. The vertical gradient

Figure 6 presents lithium iso-concentration curves in vertical sections across the salt crust. In most of the salar the brine body is clearly stratified (see also brine analyses in Table III). Two layers can be distinguished: a homogeneous lower brine and an upper brine where all dissolved components show a gradient in concentration; Li, K, B, Mg and  $SO_4$  contents decrease upwards, while Ca and Cl contents exhibit the opposite trend. The stratification disappears in the eastern sector of the salar. Very locally, close to the shores, the general stratification may reverse (see brine analyses at locations UC, UD and UE in Table III). The brine table is permanently on a level with the crust surface, or even slightly above. Evaporation proceeds throughout the year and may reverse the concentration profile.

Brine stratification, with the lighter layer overlying the denser one, is very common (Sonnenfeld, 1984). They are generally interpreted as dilute inflows spreading upon concentrated brines. Each year rains and lateral inflows flood the salar, which gives rise to an ephemeral surface brine less concentrated in bittern solutes. Thereafter, this stratification vanishes as the brine recedes to its former level. The present stratification could be due to an older and dryer period during which the brine table dropped deeper within the crust. The present gradient in Li, K, Mg, SO<sub>4</sub> of the upper layer is due to the diffusion of the components from the lower layer within the upper one. The lack of stratification in the eastern area could be due to the achievement of diffusion. However, it is not clear why this is not the case in the whole salar. анар 19

# 2.5. Estimated bulk composition of Uyuni crust and brines

Since there is a large amount of available data, an attempt can be made to estimate the amount of chemical components present in the salar. Some reasonable hypotheses have to be made. We only have one vertical record of the mineralogical composition of the salt crust and one of the chemical composition of halite. Therefore in a first approximation we assume that these values are representative of the whole crust.

The total volume of the salar (salts and brines) is estimated from Fig. 3 at  $47 \times 10^9$  m<sup>3</sup>. Assuming an average porosity of 35%, the volumes of brine and salt amount to  $16.5 \times 10^9$  m<sup>3</sup> and  $30.5 \times 10^9$  m<sup>3</sup>, respectively. This latter value leads to a total crust mass of  $66 \times 10^9$  tons (halite+gypsum+detritals). Porosity is the less precise data (±5%). The derived error ranges on brine volume and salt mass are re-

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# TABLE III

# Brine analyses of Uyuni and Coipasa salars

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Sample	Depth (cm)	Density	Cl (g/l)	SO4 (g/l)	B (g/l)	Na (g/l)	K (g/l)	Li (g/l)	Ca (g/l)	Mg (g/l)
UA	15	1.211	190	9.55	0.302	107	9.38	0.412	0.545	7.78
UA	80	1.220	190	23.0	0.669	91.8	17.6	0.770	0.310	16.1
UA	200	1.226	191	22.4	0.655	90.3	17.3	0.812	0.316	16.6
UA	400	1.226	196	22.5	0.657	94.9	17.4	0.812	0.327	16.8
UA	600	1.228	192	24.4	0.668	91.4	17.6	0.826	0.315	17.3
UB	10	1 247	200	43.9	1.71	57.0	. 29.7	1.78	0.137	38.4
UR	100	1 242	210	32.8	2 02	36 1	19.4	2.56	0.149	51.0
UR	250	1 246	210	34 3	2.16	28.8	19.1	2.20	0.0501	55.4
UB	400	1.240	214	34.5	2.10	20.0	19.1	2.83	0.0501	55.9
	400 S	1.240	10/	30.7	1 23	68.3	20.1	1.46	0.0301	32.3
	100	1.227	100	25.6	0.843	88.6	10.0	0.888	0.255	10.2
	250	1.220	190	25.0	0.045	00.0	19.0	0.000	0.200	10.2
	400	1.222	192	20.2	0.871	80.0	10.0	0.000	0.209	10.2
	400	1.225	191 -	20.7	0.970	69.2	10.0	1.21	0.209	20.6
	100	1.224	197	30.8	1.24	00.2	20.7	1.51	0.200	30.0
	100	1.220	194	22.0	0.804	03.1	21.0	0.000	0.317	19.9
UD	250	1.222	193	25.3	0.864	87.0	20.3	0.819	0.293	19.2
UD	400	1.223	191	25.4	0.871	88.1	20.3	0.819	0.294	19.3
UE	5	1.226	195	27.7	0.987	/8.7	22.6	0.708	0.294	24.5
UE	100	1.224	190	29.4	0.871	92.0	19.3	0.708	0.269	17.6
UE	250	1.224	190	28.6	0.859	92.2	19.3	0.708	0.269	17.4
UE	400	1.221	189	28.1	0.860	92.0	19.3	0.708	0.269	17.3
UF	30	1.212	190	10.3	0.239	109	7.43	0.339	0.654	7.39
UF	110	1.211	190	10.7	0.232	108	7.51	0.339	0.618	7.63
UG	15	1.209	190	8.20	0.171	112	5.79	0.254	0.834	5.78
UG	95	1.211	191	9.14	0.199	110	6.18	0.266	0.738	6.39
UG	270	1.213	190	9.79	0.233	109	6.80	0.303	0.666	6.97
UH	10	1.212	191	8.96	0.236	109	7.19	0.315	0.750	6.93
UH	100	1.211	190	10.1	0.266	107	7.94	0.351	0.666	7.85
UH	300	1.219	189	18.7	0.372	100	10.3	0.463	0.437	11.5
UH	500	1.220	189	20.3	0.397	98.2	10.5	0.488	0.401	12.1
UH	700	1.223	190	20.7	0.405	99.4	10.8	0.489	0.391	12.1
UH	900	1.222	188	22.2	0.423	100	11.2	0.513	0.367	12.6
UI	15	1.212	190	9.37	0.226	109	7.12	0.303	0.714	6.66
UI	100	1.212	189	9.36	0.214	106	6.76	0.303	0.702	6.63
UI	1000	1.213	189	14.1	0.261	106	7.59	0.303	0.569	7.29
UJ	15	1.211	190	8.93	0.254	107	7.59	0.339	0.786	7.00
UJ	100	1.217	191	14.2	0.399	100	11.0	0.584	0.521	11.1
UJ	300	1.218	189	18.1	0.437	95.9	12.0	0.560	0.437	12.8
UJ	700	1.223	187	24.1	0.525	94.8	12.4	0.575	0.391	14.1
UK	10	1.215	191	11.0	0.288	103	8.88	0.413	0.622	8.82
UK	100	1.223	192	18.7	0.457	94.3	14.6	0.685	0.417	14.7
UK	200	1.228	190	25.1	0.453	93.8	14.4	0.688	0.319	15.6
UK	400	1.229	187	28.5	0.441	93.8	24.0	0.688	0.295	15.9
UL	20	1.218	194	16.0	0.452	87.6	19.5	0.805	0.401	17.5
UL	100	1.219	195	16.3	0.557	87.9	17.8	0.805	0.390	17.1
UL	250	1.216	190	18.1	0.590	82.8	17.4	0.840	0.340	18.9
UM	17	1.205	189	7.87	0.0669	109	7.16	0.277	0.638	6.42
UM	100	1.216	191	15.1	0.319	91.1	12.0	0.559	0.425	13.5
UM	400	1.222	187	26.0	0.461	92.5	13.9	0.672	0.269	16.3
UN	16	1 210	194	191	0.563	856	18.0	0.868	0.354	19.1
UN	100	1 220	103	19.3	0.505	85.0	19.4	0.916	0.354	19.4
UN	300	1 225	192	74.9	0.718	80.5	194	0 979	0 245	21.7
UO	000	1 208	191	2 <del>7</del> .0 11.6	0.710	103	10.8	0.271	0.533	10.5
<u>10</u>	100	1 220	190	20.0	0.230	80 7	16.6	0.784	0.342	17.8
ŬÕ	500	1 220	190	36.0	0.225	88.6	183	0.937	0.234	21.8
50	200	1.2.1	170	50.0	0.024	00.0	10.0	0.007	0.207	

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Sample	Depth (cm)	Density	Cl	$SO_4$	B (g/l)	Na $(\alpha/1)$	K	Li (g/l)	Ca	Mg
	(cm)		(5/1)	(6/1)	(5/1)	(5/1)	(5/1)	(6/1)	(5/1)	(5/1)
	1/	1.218	192	17.1	0.486	82.6	16.3	0.756	0.378	16.7
	500	1.220	193	21.0	0.002	10.2	19.4	0.930	0.303	20.0
	17	1.225	195	24.0 9.02	0.770	111	7.51	0.344	0.282	7 20
	100	1.204	190	10.9	0.141	104	9.46	0.313	0.577	9.40
	450	1.200	102	11.7	0.232	104	9.40	0.333	0.535	0.40
UQ	800	1.210	190	12.8	0.241	98.2	10.0	0.474	0.545	10.4
UR	15	1 205	190	8 09	0.202	112	5 47	0.424	0.507	5 69
UR	100	1 207	190	10.8	0.101	107	7.98	0.314	0.565	8.09
UR	450	1.207	188	11.2	0.134	106	8.33	0.338	0.577	8.31
UR	800	1.215	187	19.7	0.482	102	11.3	0.413	0.413	12.5
US	9	1.201	190	8.87	0.164	108	6.65	0.276	0.577	6.34
US	100	1.209	192	10.5	0.195	106	7,98	0.314	0.606	7.63
US	450	1.216	187	21.6	0.494	99.4	12.0	0.389	0.401	11.2
US	800	1.224	186	30.3	0.785	101	14.0	0.465	0.294	13.5
UT	15	1.209	190	10.1	0.198	109	7.47	0.278	0.642	6.83
UT	100	1.203	189	10.2	0.197	107	7.35	0.277	0.626	6.97
UT	450	1.208	190	10.2	0.195	106	7.23	0.266	0.630	6.90
UT	800	1.210	189	13.0	0.244	106	8.80	0.327	0.533	8.31
UU	20	1.206	188	12.3	0.273	106	6.65	0.350	0.565	10.3
UU	350	1.211	191	11.8	0.275	103	7.59	0.291	0.533	8.97
UU	700	1.214	188	19.2	0.328	107	9.58	0.316	0.388	10.8
UV	10	1.208	191	10.1	0.235	110	6.45	0.242	0.630	8.14
UV	100	1.208	190	10.6	0.244	110	6.49	0.242	0.618	8.02
UV	500	1.208	191	10.7	0.226	108	6.37	0.242	0.618	8.02
UW	22	1.226	200	18.8	1.08	69.9	22.8	1.03	0.380	27.7
UW	100	1.228	196	14.2	0.878	86.3	16.2	0.784	0.453	20.9
UX	90	1.226	195	22.6	1.06	72.0	17.7	1.13	0.294	28.9
UX	300	1.228	195	23.0	1.05	72.0	17.9	1.18	0.307	28.9
UY	16	1.208	191	8.69	0.238	111	6.33	0.254	0.726	7.19
UY	100	1.213	190	11.1	0.315	105	8.13	0.340	0.581	9.55
UY	300	1.220	189	22.2	0.650	97.8	12.6	0.500	0.354	14.5
UY	600	1.216	188	24.8	0.712	96.4	13.1	0.511	0.316	15.3
UZ	12	1.211	191	9.89	0.303	101	9.19	0.484	0.557	8.89
UZ	100	1.218	191	16.3	0.557	95.7	12.4	0.536	0.413	15.1
UZ	450	1.222	192	19.3	0.608	92.9	13.4	0.599	0.354	17.1
UZ	800	1.220	190	19.5	0.665	91.1	13.3	0.598	0.342	17.0
UI	12	1.215	196	17.0	0.578	92.0	15.8	0.701	0.425	16.6
UI	400	1.226	197	29.5	0.987	86.5	19.2	0.895	0.264	21.3
Ul	800	1.228	193	31.7	1.04	83.7	19.5	0.930	0.247	21.6
U2	13	1.212	195	15.9	0.480	92.9	14.3	0.640	0.433	14.5
U2	100	1.219	196	23.0	0.618	92.0	16.6	0.750	0.331	17.3
U2	200	1.221	193	25.2	0.700	88.3	17.4	0.791	0.307	17.7
U2	300	1.222	190	27.4	0.766	86.5	17.9	0.826	0.284	18.7
U2	400	1.226	187	33.1	0.976	85.6	18.6	0.909	0.234	20.4
U2	500	1.228	189	34.1	1.01	85.6	18.6	0.916	0.223	20.5
U2	600	1.228	187	34.1	1.02	85.6	18.4	0.895	0.223	20.7
YA	17	1.207	192	10.1	0.360	102	12.3	0.435	0.577	9.53
YA	100	1.210	191	13.7	0.483	95.9	13.6	0.557	0.449	12.2
YB	11	1.202	190	5.83	0.155	111	4.69	0.144	0.758	<u>,</u> 4.37
YB	100	1.208	190	10.2	0.299	103	8.91	0.338	0.581	8.65
YB	500	1.213	189	19.8	0.488	93.2	12.9	0.534	0.364	14.1
YC	12	1.202	191	5.07	0.103	112	3.86	0.120	0.662	3.84
YC	100	1.204	189	8.54	0.219	107	6.45	0.229	0.638	6.66
YD	9	1.203	191	7.47	0.216	107	6.45	0.229	0.758	6.03

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<u> </u>	Denth	Densites		<u> </u>			V	τ;		Ma
Sample	Deptn (cm)	Density	(a/l)	$SU_4$	В (a/l)	$(\alpha/1)$	κ (α/1)	(a/l)	$(\alpha/1)$	$(\sigma/1)$
	(en)		(g/1)	(g/1)	(g/1)	(8/1)	(g/1)	(g/1)	(8/1)	(5/1)
YD	100	1.209	192	14.4	0.427	94.8	12.5	0.496	0.421	12.2
YD	. 450	1.217	191	20.2	0.615	90.2	14.5	0.621	0.341	15.5
YD	800	1.218	192	22.7	0.692	90.2	15.4	0.670	0.329	16.5
YE	8	1.205	192	6.30	0.204	110	5.75	0.193	0.662	5.30
YE	100	1.213	192	15.2	0.438	95.9	12.6	0.509	0.400	12.4
YE	450	1.247	195	28.1	0.790	91.5	16.1	0.673	0.274	17.2
YE	800	1.226	191	27.4	0.791	89.5	15.8	0.661	0.269	16.9
YF	23	1.202	192	4.69	0.0880	113	3.09	0.0722	1.03	2.96
YF	200	1.203	190	6.24	0.143	109	4.65	0.144	0.854	4.50
YG	15	1.211	191	12.0	0.301	100	10.6	0.521	0.473	11.0
YG	100	1.201	191	6.02	0.164	112	5.16	0.228	0.806	4.52
YH	1	1.260	207	44.4	2.03	37.3	26.8	2.46	0.100	51.0
YH	100	1.246	212	29,2	1.95	34.0	19.9	2.59	0.137	53.2
YH	250	1.245	213	29.5	2.04	32.4	19.9	2.59	0.0870	53.9
YI	8	1.207	192	9.03	0.273	105	8.80	0.362	0.517	8.41
YI	100	1.208	192	9.59	0.305	101	9.31	0.399	0.533	9.33
YI	450	1.209	191	10.1	0.321	100	9.93	0.411	0.509	9.84
YI	800	1.210	191	11.5	0.351	95.4	11.0	0.484	0.437	11.0
YJ	17	1.204	193	8.11	0.271	110	8.64	0.301	0.698	6.66
YJ	100	1.211	194	12.8	0.428	94.1	12.7	0.545	0.461	11.8
YJ	400	1.222	189	27.2	0.620	88.8	16.1	0.743	0.257	16.9
YK	1	1.204	191	10.4	0.277	105	8.21	0.325	0.710	7.78
YK	100	1.207	192	11.7	0.320	101	10.2	0.410	0.529	9.87
YK	400	1.216	190	24.0	0.522	93.6	13.9	0.584	0.304	15.1
YK	700	1.220	189	27.0	0.576	97.5	15.3	0.634	0.281	16.4
YL	22	1.201	192	6.25	0.141	112	4.93	0.156	0.794	4.37
YL	100	1.209	193	12.8	0.324	102	9.58	0.375	0.485	9.38
YL	400	1.209	191	14.8	0.360	100	10.5	0.423	0.421	10.4
RA	130	1.005	3.38	0.600	0.0210	1.55	0.0802	0.0100	0.429	0.197
RB	180	1.019	12.5	2.40	0.0316	6.65	0.300	0.0265	1.20	0.566
RC	120	1.050	40.1	5.70	0.116	19.6	1.80	0.149	0.846	3.40
RD	160	1.093	79.5	5.12	0.250	39.8	3.20	0.217	1.95	4.67
RE	100	1.143	129	3.60	0.481	61.6	6.14	0.575	2.67	8.65
RF	90	1.151	135	5.70	0.837	65.1	7.31	0.631	1.66	9.43
RG	30	1.164	147	7.65	0.546	69.2	7.90	0.674	1.25	11.4
RH	10	1.210	190	11.1	0.368	97.5	10.5	0.538	0.565	10.2
RI	15	1.198	171	15.6	0.507	81.9	12.4	0.736	0.457	13.5
RJ	10	1.215	190	12.8	0.626	95.7	11.0	0.633	0.390	11.4
RK	90	1.151	137	5.10	1.02	62.6	7.82	0.701	1.93	10.5
RL	110	1.112	96.6	4.83	0.971	45.5	5.00	0.417	2.53	6.44
RM	100	1.092	80.2	5.10	0.318	37.0	4.50	0.347	2.13	5.78
RN	75	1.149	132	5.00	0.491	79.1	4.50	0.359	2.02	3.89
RO	80	1.139	122	7.20	0.965	62.6	5.40	0.483	1.59	6.73
RP	50	1.099	82.0	5.99	0.137	45.5	2.80	0.182	1.96	2.33
RQ	70	1.126	110	9.70	0.507	62.6	4.50	0.272	1.32	5.27
RR	60	1.163	145	7.25	0.419	88.1	4.50	0.239	1.24	4.13
RS	15	1.273	231	31.4	3.70	12.5	17.6	4.23	0.0525	69.0
RT	15	1.272	229	29.5	3.52	14.0	17.6	4.03	0.0601	68.8
RU	1	1.243	198	30.9	1.42	66.2	26.4	1.60	0.238	27.2
RV	20	1.216	189	13.9	0.507	101	11.7	0.563	0.413	13.4
RW	10	1.224	191	19.8	0.623	97.5	15.7	0.763	0.338	15.1
RX	10	1.269	223	32.0	3.45	21.3	19.1	3.55	0.0698	61.0
RY	95	1.160	138	6.10	0.766	63.0	6.84	0.763	1.84	11.7
RZ	1	1.279	253	26.5	4.33	10.7	15.1	4.72	0.102	75.3
CA	0	1.235	185	28.1	0.723	105	9.23	0.237	0.315	10.9

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Sample	Depth (cm)	Density	Cl (g/l)	SO <sub>4</sub> (g/l)	B (g/l)	Na (g/l)	K (g/l)	Li (g/l)	Ca (g/l)	Mg (g/l)
CA	150	1.244	172	54.0	0.870	104	10.0	0.275	0.194	14.1
CA	250	1.264	132	104	0.644	111	8.33	0.212	0.164	10.5
CB	0	1.233	187	29.3	0.690	108	9.19	0.237	0.301	10.7
CB	150	1.264	168	80.1	1.35	94.7	14.3	0.416	0.102	23.0
ĈĨ	0	1.213	189	14.7	0.601	104	7.12	0.198	0.541	10.2
C2	Ō	1.218	188	17.6	0.952	99.1	11.6	0.333	0.521	15.1
Č3	Ō	1.221	179	25.9	0.614	109	7.31	0.205	0.319	10.1
C4	Ō	1.217	187	18.0	0.640	107	8.56	0.230	0.509	10.8
C5	Õ	1.211	186	13.9	0.428	111	5.98	0.154	0.738	6.80
RIO	•	1.001	0.875	0.300	0.010	0.515	0.027	0.0036	0.161	0.045
LAUCA		1.001	0.331	0.229	0.0043	0.260	0.0324	0.0008	0.0529	0.0445
TITIC		1.000	0.255	0.233	0.0013	0.174	0.015	0.00034	0.0632	0.033

Origin of analyses. U and Y series: Lithium Corporation of America, Bessemer City, NC, USA; RA to RJ=US Geological Survey (Rettig et al., 1980: 8 series); RK to RZ=INRA, Soil Laboratory, Versailles, France; C series, RIO and LAUCA=Centre de Géochimie de la Surface, Strasbourg, France; TITIC=Carmouze et al., 1978, except Li and B.



Fig. 5. Lithium iso-concentration curves of the Uyuni intercrustal brine (in g/l).



Fig. 6. Lithium vertical profiles of the Uyuni intercrustal brine (in g/l).

#### TABLE IV

Total amounts of chemical components at Uyuni and gross estimates of Rio Grande inputs for the last 10,000 years In million tons,

	Brines		Salts		Total	Rio Cara da
	Whole salar (m <sup>.</sup> ton)	Southern fringe (m ton)	Halite+ gypsum (m ton)	Traces in halite (m ton)	(m ton)	inputs (m ton)
Li	9	0.5		0.9	10	1
ĸ	194	5		91	285	10
Mg	211	10		45	256	16
B	8	0.4		1.7	10	4
Ca	8	0.04	550	77	635	60
SO₄	278	7	1,300	430	2,000	100
Na	1600	12	24,800		26,400	200 <sup>°</sup>
Cl	3100	48	38,200		41,300	300

The total is obtained by summing columns 2, 4 and 5. Amounts in the southern fringe are also included in the whole salar.

spectively  $\pm 15\%$  and 8%. The 15 cm thick superficial dry salt can be neglected in the determination of the brine volume. The related

imprecision is around 2%, well within the range of uncertainty linked to porosity ( $\pm 15\%$ ). Estimated amounts of each component in the brine and in the salt are given in Table IV. Error range for brine components is also around  $\pm 15\%$ . All salts, in crust and brine, amount to  $72 \times 10^9$  tons of which the most part is sodium chloride ( $68 \times 10^9$  tons):  $63 \times 10^9$  tons in halite and  $5 \times 10^9$  tons in brines. The southeastern fringe, within the 1000 mg/l average lithium iso-concentration curve, has been differentiated. This sector has a surface of  $276 \text{ km}^2$ . The volume of the related portion of salar is  $690 \times 10^6 \text{ m}^3$ ;  $450 \times 10^6 \text{ m}^3$  of salt and  $240 \times 10^6$ m<sup>3</sup> brine.

Lithium reserves in brines, about  $9 \times 10^6$ tons, are the most striking point. The known reserves of all occidental countries in 1978 only amounted to  $4.1 \times 10^6$  tons (U.S. Geological Survey, 1978). Potassium reserves, about  $194 \times 10^6$  tons, are almost twice as high as the reserves of the United States ( $100 \times 10^6$  tons; Searls, 1983).

### 3. The salar of Coipasa

### 3.1. Salts and sediments

Available data for the salar of Coipasa are scanty: two drill holes and one hand-dug hole. At central Coipasa the crust is 2.5 m thick and is underlain by lacustrine sediments. The crust consists of an upper layer (0-2 m at CA) of porous halite, similar to that of Uyuni, and of a lower layer (2-2.5 m at CA) made of crumbly aggregates of mirabilite crystals. Lacustrine sediments are similar to those of Uyuni: detritals, gypsum, calcite, *Artemia* faecal pellets, organic matter and clay minerals. They are impermeable and contain an interstitial brine.

### 3.2. Brines

Seasonal flooding and drying is also observed at Coipasa. Nevertheless the drying is only partial. The northern area is permanently filled with a shallow lake fed by the Lauca River, which is the major permanent inflow to the salar. In the dry season the crust at southern Coipasa is filled to the brim. Some years the salar does not even dry up. Ericksen et al. (1978) and Rettig et al. (1980) have already published three analyses of surface brines. Five others are given in Table III. In addition four analyses of brines from drill hole CA and CB are also presented (location in Fig. 2). All brines belong to the Na-Cl-SO<sub>4</sub> group. Surface concentrations do not show any clear gradient. On the contrary, just like Uyuni brine, Coipasa interstitial brine is stratified. There is an upper layer less concentrated in Li, K, Mg, B, SO<sub>4</sub> and a lower layer with higher contents of these solutes.

# 3.3 Estimated bulk composition of Coipasa crust and brine

Owing to the reduced number of analyses, amounts of components are only tentatively given as orders of magnitude (Table V). The least imprecise data is the total amount of halite (about  $3 \times 10^9$  tons) which has to be compared with the  $63 \times 10^9$  tons of halite at Uyuni. Of all the halite deposited in the central depression of the Altiplano, about 95% is stored in the salar of Uyuni and only 5% in the salar of Coipasa. The total amount of mirabilite was very speculatively estimated to be

#### TABLE V

Total amounts of chemical components at Coipasa and gross estimates of Lauca River inputs for the last 10,000 years

	Brine (m ton)	Crust (m ton)	Lauca inputs in 10,000 yr	
Li	0.2		0.7	
K	7		27	
Mg	13		37	
В	0.7		4	
Ca	0.2		44	
$SO_4$	30	100	190	
Na	70	1200	220	
Cl	120	1700	330	

 $300 \times 10^6$  tons, which corresponds to a 20 cm thick layer of 40% porosity over 2,000 km<sup>2</sup>.

# 4. Former lakes

In the past large saline lakes successively filled the Altiplano (Ahlfeld, 1972; Servant and Fontes, 1978; Lavenu et al., 1984). Five lacustrine phases have been detected. The last two, Lake Minchin (30,000-20,000 yr BP) and Lake Tauca (13,000-10,000 yr BP) were more precisely studied owing to rather numerous and well-preserved outcrops. Striking algal encrustments all around the basin clearly show at least two major shorelines at 3,700 and 3,748 m. Unfortunately they are not dated and therefore cannot be linked to a lacustrine phase. When Lake Tauca receded and dried up, it deposited the salt crusts of Uyuni and Coipasa. Outlines of Lake Tauca are shown in Fig. 7. Its level fluctuated between 3,700 and 3,720 m. It was subdivided into three lakes connected by narrow straits: Lakes Poopo (5700 km<sup>2</sup>), Coipasa (7900 km<sup>2</sup>) and Uyuni (17,300 km<sup>2</sup>). Its



Fig. 7. Outline map of Paleolake Tauca (after Servant and Fontes, 1978).

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maximum depth was 75 m, at Uyuni. Three major inflows were feeding the lake. Lake Titicaca, at 3815 m, was discharging into Lake Poopo, as it still does today. Lake Coipasa was mainly fed by the Lauca River and Lake Uyuni by the Rio Grande.

# 5. Recent contributions to the salars of Uyuni and Coipasa

Since Lake Tauca dried up 10,000 years ago, both salars have been receiving dissolved and solid material carried in by their respective main inflows: the Rio Grande into Uyuni and the Lauca River into Coipasa. Streamflow characteristics of both rivers are almost unknown. Lauca River discharge has been recorded for 4 years 40 km north of its mouth into Coipasa. No major tributary joins the Lauca River downstream of the gaging station. Annual discharge is about  $140 \times 10^6$  m<sup>3</sup> (Servicio Nacional de Meteorología e Hidrología de Bolivia, 1985, unpublished data). Rio Grande discharge 20 km south of its delta, has been very roughly estimated from episodic measurements during field trips, at  $60 \pm 30 \times 10^6$  m<sup>3</sup>/yr (width = 30-70 m; mean depth = 0.15 - 0.20 m; surface water velocity=0.3 m/s; correction factor=0.7, to account for the flat cross-section).

The problem arises in extending such poorly determined values over a long period of time. At present, Rio Grande discharge is not high enough to allow a permanent lake to establish at southern Uyuni. However, several permanent pools at the boundary between the salt crust and the delta plain suggest that a slight increase of the mean Rio Grande discharge would result in a permanent lake at the mouth of the river, exactly as Lauca River does at northern Coipasa. If this occurred during the last 10,000 years, then thin lacustrine layers should be interbedded within the deltaic sediments, which has not been observed. This suggests that the Rio Grande discharge was not significantly higher during the last 10,000 years

than it is today. In contrast, the river discharge could well have been lower at some periods. The climate was not uniform during the Holocene. Soubies (1979) has described a dry period in the Amazon Basin from 6000-3000 yr BP. Servant et al. (1981a) documented a severe drought in the nearby Bolivian Amazon Basin during the time intervals 7000-5000 and 3400-1400 BP. Wirrmann and Oliveira Almeida (1987) detected a very dry period in the northern Altiplano from 7700 to 3650 yr BP. This 4000 year drought is very likely to have affected the whole Altiplano. Therefore we considered only 6000 yr (10,000 minus 4000) to calculate a very rough estimate of the recent contribution to both salars for the last 10,000 yr.

This implies that the catchment area of the Lauca River and the Rio Grande did not change during the Holocene. In such a short timespan on the geological time scale, only glaciation or volcanism could have significantly modified the morphology of the basins. The last glaciation in the Central Andes occurred at the end of the Pleistocene (Mercer and Palacios, 1977; Servant et al., 1981b). Volcanic activity on the Altiplano began in the Miocene, increased during the Pliocene and died away during the Holocene (Fernandez et al., 1973). Most volcanoes show eroded features associated with moraines, indicating that major volcanic activity was pre-glacial. This indicates that all major volcanic structures are anterior to the Holocene.

Analyses of Rio Grande and Lauca water are given in Table III (Rio and Lauca). Very rough estimates of the recent dissolved contributions to both salars over the last 10,000 yr are tentatively given in Tables IV and V. Although we are dealing with very broad orders of magnitude, some interesting results can be pointed out.

The total quantity of halite brought into the salar of Uyuni since the desiccation of the lake  $(0.5 \times 10^9 \text{ tons})$  amounts to less than 1% of the total salt mass of the salar  $(63 \times 10^9 \text{ tons})$ .

Therefore the salar of Uyuni is definitely not the result of an annual cyclic sedimentation process. The crust is the remnant of a former large saline lake. As for Coipasa, the last 10,000 yr of halite input  $(0.65 \times 10^9 \text{ tons})$  accounts for 20% of the total halite now present in the salar  $(3 \times 10^9 \text{ tons})$ .

The amounts of Li, K and Mg contributed to the salar of Uyuni over the last 10,000 yr are about twice their present reserves in the sharp anomaly in concentration at southeast Uyuni. This suggests that the high concentrations in Li, K, Mg in this area are due to the last 10,000 yr of contribution from the Rio Grande. The remaining part of the Rio Grande input must have been lost within the lacustrine and deltaic sediments before reaching the salt crust. As for B, the sum of the present reserves in brine in the southeastern area  $(0.4 \times 10^6 \text{ tons})$  and of those in the ulexite deposit  $(1.6 \times 10^6 \text{ tons})$ may be compared to the amount brought in by the Rio Grande  $(4 \times 10^6 \text{ tons})$ .

One may wonder at the presence of the most concentrated brines close to the mouth of the Rio Grande, which would be expected to dilute the brines. In the dry season the river infiltrates some 20 km south of the concentrated brine area and feeds a confined aquifer (see Fig. 4). The water then moves towards the salt crust and concentrates by evaporation through the delta plain. Evaporation of the brine at the surface of the halite crust may induce an "evaporative pumping" process (Hsu and Siegenthaler, 1969). In the rainy season, the Rio Grande floods the southeastern area and dilutes the brine. The rest of the salar is essentially flooded by direct rainfall. Then the water evaporates rapidly and only the dissolved components added by the river remain. This very restricted area can be considered, with regard to K, Li, Mg, B, as a playa lake.

An outcome of this is that brine seepage through bottom sediments in the southeast of Uyuni is reduced. This is probably not the case for the salar of Coipasa. As shown in Table V, the amounts of Li, K, Mg and B contributed to the salar by the Lauca River over the last 10,000 yr are about four times higher than the present reserves in the salar. Even allowing for the very broad orders of magnitude used here, such a difference is likely to be significant and means that these elements are not conserved in the interstitial brine. They probably move downwards with the brine and/or diffuse within bottom sediments.

### 6. Paleosalinity of Lake Tauca

#### 6.1. Biological markers

Several indicators may help to bracket the average salinity of the former Lake Tauca. Servant-Vildary (1978) made a preliminary study of diatoms from lacustrine outcrops, which led to a salinity of about 40 g/l for both Lakes Uyuni and Coipasa. However all outcrops are located in ancient ravines at the outmost fringe of the lake. In such places the lake water was probably more dilute owing to possible mixing with fresh inflows. Diatoms-are probably not representative of the central lake flora. Therefore we may consider the value of 40 g/l as a lower limit. Artemia faecal pellets are common in central sediments at both Uyuni and Coipasa. They exhibit the same morphology and size as those presently deposited in Lake Poopo and other small saline lakes at concentrations ranging from 50 to 100 g/l. Biological markers from deep saline lakes must be used with caution. Such lakes are generally stratified. Most of the biota lives in the upper oxygenated layer. The lower and denser brines are almost always anoxic. If this were the case for Lake Tauca, then its actual mean salinity would be slightly higher than those given by biological markers. A different approach without such drawbacks, the salt balance, will now be used to estimate the paleosalinity of the former lake.

# 6.2. Salt balance

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The dissolution of the total salt mass of Uyuni and Coipasa salars in the former lake

volume only leads to a lower limiting value. All lakes whose drying up has been precisely monitored have lost a significant amount of their solute load while they receded. Devils Lake (USA) lost 65% of its salt tonnage as it shrank from 1899 to 1948 (Swenson and Colby, 1955). Some 45% of the solute load of Lake Erye (Australia) was removed during the 1950-51 recessive phase (Bonython, 1955). Owen Lake (USA) dried up sixty years ago and lost about 50% of its initial salt content (Alderman, 1985). Precipitating salts on the lake bed are not sufficient to explain all the loss. Wind deflation, seepage and diffusion of dissolved salts into bottom sediments generally account for much of the depletion (Langbein, 1961; Jones and Van Denburgh, 1966; Alderman, 1985; Spencer et al., 1985). However, the loss is reduced in the case of a deep saline lake such as Tauca. The seepage rate through bottom sediments has to be extremely low, or else the lake would never have become saline. On the other hand, most of the salts have been deposited on the lake bed within the thick brine body, which has protected them from the wind.

The subdivision of Lake Tauca into three lakes leads to some complications. The threshold between Poopo and Coipasa basins is at 3,700 m. Consequently, when Lake Poopo receded, it was no longer connected superficially with Coipasa and Uyuni Lakes. Therefore we will not take account of it in the calculations. though some leakage into Coipasa basin may have occurred. In contrast, the sill between Uyuni and Coipasa basins is at 3,657 m, just one metre above the Coipasa salt crust and 4 m above Uyuni's. The lakes were connected until the very last stages of desiccation. When the water level was at 3,710 m, the volume of Uyuni and Coipasa Lakes was 850 and 350 km<sup>3</sup>, respectively. The present salt tonnage is  $72 \times 10^9$  tons at Uyuni and  $3 \times 10^9$  tons at Coipasa. By dividing these values by their respective former lake volumes, we obtain a salinity of 85 g/l for Uyuni Lake and 9 g/l for Coipasa Lake. The latter value is unrealistic. It is in

contradiction with the biological markers which indicate that both lakes had similar salinities. The most likely explanation is that most of the dissolved salts of Coipasa Lake passed into Uyuni basin as the lakes dried up. Coipasa basin is topographically higher than that of Uyuni and the sill between them is only 1 m above Coipasa's present crust. If all the dissolved salts in Coipasa Lake were deposited in Coipasa basin, then the surface of the salt crust would be at 3-4 metres above the sill, which is impossible. Therefore, the total amount of salt now present in Uyuni and Coipasa ( $75 \times 10^9$  tons) must be divided by the volume of the two former lakes (1200 km<sup>3</sup>). This leads to a mean salinity for both Uyuni and Coipasa Lakes of some 60 g/l. Assuming a reasonably low salt loss of about 30% during desiccation, we obtain a paleosalinity for Lake Tauca of between 60 and 90 g/l.

These values are in good agreement with those obtained by the biological markers and therefore suggest that the mean paleosalinity of Lake Tauca, in both Uyuni and Coipasa Lakes, was likely to be around 80 g/l. As for Lake Tauca-Poopo, we have no indication of its paleosalinity. The lack of halite in the Poopo basin could be due to a rather high seepage rate in this basin (Carmouze et al., 1978).

# 7. Paleochemistry of Lake Tauca

Theoretically, the chemistry of the former Lake Tauca may be deduced in two ways: (1) by dissolving in the lake volume the amounts of all components (including trace elements) of the salts and brines present to day in the salars and (2) by simulating the evaporation of the present major inflows to the salars. Spencer et al. (1985) used a similar approach in their study of the paleochemistry of Great Salt Lake. They compared the total amount of components now present in the basin with the total estimated input.

Strictly, we are only concerned with Lakes Coipasa and Uyuni. Salts formerly present in Paleolake Poopo do not seem to have passed into Coipasa and Uyuni basins when the lakes dried up. However, when all lakes were connected, dissolved salts could have passed from Poopo to Coipasa. Lake Poopo was mostly fed by the overflow of Lake Titicaca. Therefore we have also taken into account the possible influence of Lake Titicaca water in the paleochemistry derived by evaporation.

# 7.1. Paleochemistry derived by dissolution

The total amounts of components to be dissolved in the volume of Lake Tauca should be corrected for post-Tauca inputs. However, at Uyuni, such inputs make up only 1–10% of the total amount of components, which is within the range of uncertainty of these amounts  $(\pm 15\%)$ . As for Coipasa, most of the recent contributions seem to have been removed in bottom sediments.However, since the amounts of salts and solutes at Coipasa are low in comparison with those at Uyuni, large uncertainties about recent contributions will not seriously affect the paleochemistry derived by dissolution. The paleochemistry thereby obtained (with corrections) is given in Table VI.

#### TABLE VI

Paleochemistry of Lake Tauca

### 7.2. Paleochemistry derived by evaporation

The main assumption to be made is that there has been no change in the geology of the catchment area over the last 10,000 yr. The chemistry of subsurface waters, springs and rivers is not likely to have changed. Absolute concentrations may have varied in the same way they vary today, according to the seasons, but relative concentrations probably did not change. The evaporation of Titicaca, Lauca and Rio Grande waters was simulated using the program of Risacher and Fritz (1984). In all cases, the calculation was ended when the total salinity reached 80 g/l. The chemical composition of the brines are given in Table VI. The calculated sequence of minerals is: calcite, Mgsilicate, gypsum.

# 7.3. Minor differences

The difference in salinity between the evaporation-simulated and the dissolution-derived brines reflects the above-mentioned loss of salts when the lake receded. The simulation was stopped at a higher concentration (80 g/l total dissolved salts, TDS) than that obtained by

	Brine derived by	v evaporation		Brine	Possible	Tarcamaya
	Rio Grande Uyuni (g/l)	Lauca Coipasa (g/l)	Titicaca Poopo (g/l)	derived by dissolution (g/l)	composition of Lake Tauca brine (g/l)	saline spring B (g/l)
Li	0.18	0.073	0.042	0.009	0.01	0.0025
K	1.33	2.96	1.83	0.24	0.29	0.0508
Mg	2.02	2.23	3.86	0.22	0.27	0.282
В	0.51	0.40	0.16	0.008	0.01	0.0079
Ca	1.04	0.23	0.366	0.53	1.7	2.19
SO₄	5.83	20.7	22.0	1.8	4.4	3.98
Na	25.1	23.3	21.4	23.2	28.4	26.2
Cl	44.0	30.1	30.4	36.7	44.9	43.7
TDS	80	80	80	62.7	80	76.4

Columns 2, 3, 4 are brine compositions obtained by simulating the evaporation of the main inflow waters. Column 5 is the composition obtained by dissolving all components in salts and brines now present in Uyuni and Coipasa salars. Concentrations of column 6 are those of column 5 multiplied by 1.22 to obtain a total salinity of 80 g/l, except for Ca and SO<sub>4</sub> whose contents were increased so as to reach saturation with respect to gypsum.

dissolving the salt crust (62 g/l). The dissolution-derived concentration should be multiplied by a factor of 1.22 to obtain a total salinity of 80 g/l in order to account for probable salt loss during desiccation. Such an adjustment will be made only at the end of the discussion when other refinements have been made.

The evaporation of the inflow waters leads to distinct brine types. According to the classification of Eugster and Hardie (1978), Titicaca and Lauca simulated brine belongs to the Na-Cl-SO<sub>4</sub> group, whereas that of Rio Grande is of the Na-Cl group. This difference is emphasized by the conspicuous occurrence of mirabilite in Coipasa crust and its almost complete absence in that of Uyuni. This suggests that the brine of Lake Tauca-Coipasa was somewhat more concentrated in sulfate than that of Lake Tauca-Uyuni.

# 7.4. Major difference

The striking point is the large difference between the concentrations of minor components obtained by dissolving the salt crust and those obtained by simulating the evaporation of the major inflows. Contents of Li, K, Mg, B,  $SO_4$  are 5–50 times lower in the dissolutionderived brine than in the evaporated-derived ones. On the contrary, Na, Cl and Ca concentrations are similar. Fig. 8 emphasizes the anomalous composition of the dissolutionderived brine in relation to other waters and brines of the Altiplano. The evaporationderived compositions, on the contrary, fit the general trends of all other Altiplano brines perfectly.

A very likely explanation is that Lake Tauca dissolved a salt crust similar to that existing today. If a new lake was to flood the Altiplano again, it would first dissolve some of the present halite crust and would be relatively depleted in Li, K, Mg, B,  $SO_4$  and enriched in Na and Cl with respect to the input water. Therefore the actual Lake Tauca contents in Li, K, Mg, B, SO<sub>4</sub> are probably more akin to the dissolution-derived ones than to the evaporationsimulated ones. However, this explanation only pushes the problem further back in time. Why would the former Lake Minchin have had such an anomalous composition? The actual process, whatever it is, is a long-term one, inasmuch as the present anomaly has probably been transferred from lake to lake. Three hypotheses are discussed below.

# 7.4.1. Brine seepage, or diffusion of solutes, at Uyuni

For a constant seepage or diffusion rate the absolute loss of bittern solutes (Li, K, Mg, B) in vertical sections of the brine, is the same whatever the thickness of the section. This is not true for their relative loss (in percent of the total amount); concentrations would decrease more rapidly where the crust is thinner. Theoretically, if the interstitial brine had a uniform composition just after the deposition of the crust and if the seepage rate were constant throughout the salar, then the isopachs of the crust and the isoconcentration curves of Li, K, Mg, B would show the same trends. Even if we are not dealing with such an ideal case, some correlation should appear. However, there is no obvious relation between isopachs in Fig. 3 and Li iso-concentration curves in Fig. 5. The thickest part of the crust (and brine) is related to the lowest concentrations in the brine. If seepage or diffusion of bittern solutes occurs at Uyuni, then their importance is probably small in regard to other processes affecting the brine.

# 7.4.2. Uptake of the vanished components by minerals

Some magnesium, potassium and lithium may have been exchanged by smectites and some boron adsorbed by illite (Harder, 1959). However, clay minerals are almost completely lacking in the salt crust and they make up a minor fraction of the lacustrine sediments. They



Fig. 8. Paleochemistry of Lake Tauca brine. Crosses = composition of present-day lake brines; dots = dilute waters of the Altiplano. Open symbols among the dots are the main inflow waters; inverted triangle = Rio Grande; star = Lauca; square = Titicaca. Solid symbols of the same shape, among the crosses, are the brines obtained by evaporation of these inflow waters, large dot = Tauca dissolution-derived brine; triangle = Tarcamaya saline spring waters.

are only detected by XRD after separation procedures. Furthermore, lacustrine sediments are filled with an interstitial brine whose dissolved components are much more readily available. Such a process may only account for a small fraction of the missing Mg, K, Li, B.

Sulfate may have precipitated as gypsum. Gypsum in lacustrine sediments beneath the crust is finely laminated, which is indicative of a primary origin (Hardie et al., 1985) and therefore of the fact that Lake Tauca was saturated with respect to gypsum. However, the dissolution-derived brine (Table VI) is markedly undersaturated with respect to this mineral, which suggests that some SO<sub>4</sub> and Ca, formerly present in the lake water, were not found in the salt crust. Some gypsum may have precipitated before the deposition of the halite crust when the lake began to recede. This amount of early gypsum was not taken into account in the total salt masses, but may be estimated by increasing the concentrations of SO<sub>4</sub> and Ca of the dissolution-derived brine in equimolar amounts up to saturation with respect to gypsum. The calculation is based on an ion interaction model using Pitzer's equations (Harvie and Weare, 1980). The added amounts of SO<sub>4</sub> and Ca correspond to the gypsum precipitated before the deposition of halite. The mean concentrations of the lake water (Uyuni and Coipasa) thus obtained are: 4.4 g/ 1 SO<sub>4</sub> and 1.7 g/l Ca. The mass of early precipitated gypsum is about  $4 \times 10^9$  tons.

# 7.4.3. Leaching of older evaporites from the catchment area

This hypothesis differs from the former ones, as it states that the peculiar composition of Lake Tauca water is not the outcome of the removal of Li, K, Mg, B, but of an enrichment in Na and Cl. Halite outcrops in the drainage basin are not known. However, there are some indications of past halite occurrences. In some layers of Cretaceous formations, east of Uyuni, crystal casts of halite are commonly observed.



Fig. 9. Location map of Tarcamaya gypsum diapir and related saline springs.

In the northern Altiplano, within the drainage basin of Paleolake Tauca, groundwaters from a Tertiary gypsum diapir (Tarcamaya, location in Fig. 9) are concentrated enough in Na and Cl to be worked in evaporating pans to produce common salt. The saline springs flow into the Tarcamaya River, which is a small tributary feeding Poopo Lake. Analyses of the spring waters are given in Table VII. They are almost pure NaCl brines with very few bittern solutes. The representative compositions of these brines are shown in Fig. 8. Their relative contents of Mg, Li, B and, to a lesser extent, K are very similar to those of the dissolutionderived brine of Paleolake Tauca.

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Analyses of Tarcamaya saline spring waters

Spring	Density	Cl (g/l)	SO <sub>4</sub> (g/l)	B - (g/l)	Na (g/l)	K (g/l)	Li (g/l)	Ca (g/l)	Mg (g/l)	TDS (g/l)
Ā	1.035	27.2	2.69	0.0131	15.9	0.0579	0.0053	1.76	0.408	48.0
В	1.054	43.7	3.98	0.0079	26.2	0.0508	0.0025	2.19	0.282	76.4
С	1.078	66.7	4.32	0.0059	40.9	0.0669	0.0012	2.23	0.186	114
D	1.142	131	5.14	0.0013	81.4	0.0512	0.0016	1.99	0.235	220
E	1.196	185	4.73	0.0138	119	0.0606	0.0017	1.57	0.223	311

TDS=total dissolved salts.

It is likely that dilute groundwaters are dissolving halite rocks inside the Tarcamava gypsum diapir. It is possible that several, or even most, of the numerous gypsum diapirs in the Altiplano were in the past associated with halite rocks. Their leaching could have contributed large quantities of halite to the oldest lakes, giving rise to a strong excess of Na and Cl in brines in the early history of the basin. Thereafter, halite could have been recycled from lake to lake up to the present. Recycling of older salt deposits has frequently been reported (Bradbury, 1971; Eaton et al., 1972; Krinsley, 1972; Antsiferov, 1979; Lindsey et al., 1981). A review of such occurrences can be found in Sonnenfeld (1984, p. 146). In nearby northern Chile, the large salar of Atacama, a thick halite body, is surrounded by Tertiary sediments containing well exposed halite beds (Dingman, 1962; Moraga et al., 1974; Stoertz and Ericksen, 1974; Chong, 1984). The area is extremely arid, which has prevented the dissolution of the exposed salt.

# 8. Conclusion

The evaporation of the present major inflows does not reflect the former composition of Paleolake Tauca. This lake owed its composition to the dissolution of a pre-existent crust very similar to the present one. A possible composition of the lake water is given in Table VI. The concentration of all components, except SO<sub>4</sub> and Ca, are those of the dissolution-derived brine, multiplied by a factor of 1.22 in order to account for a probable loss of salts during desiccation and to obtain a paleosalinity of 80 g/l. Contents in SO<sub>4</sub> and Ca were increased in equal molar amounts so as to reach saturation with respect to gypsum. Analysis of Tarcamaya saline spring B, flowing out from a gypsum (and halite?) diapir is given in Table VI, together with the likely composition of Lake Tauca brine. Except for the Li and K contents, both brines are strikingly similar.

The key process to account for the strong enrichment in Na and Cl in relation to the other components in the salar of Uyunie is likely to be the leaching of ancient evaporites from the catchment area at an early stage of the basin evolution in Pleistocene times. Once all halite was leached, each ancient lake inherited its peculiar chemistry by redissolving the salt crust deposited by its predecessor. The salar of Uyuni is the final stage of a very long lacustrine history. Lake Tauca dissolved and deposited again a former salt crust of quite similar composition.

A problem arises as to the main origin of the bittern solutes: Li, K, Mg, B. Their relative content in Lake Tauca brine and in Tarcamaya saline springs are similar. On the other hand, the amount of bittern solutes brought into the salar of Uyuni by the Rio Grande for the last 10,000 years is very small in relation to their total amount in Lake Tauca. There is no need to consider major inputs from the Rio Grande, even for large time spans, to account for the present amount of Li, K, Mg, B in Uyuni basin. Their high concentration at the mouth of the Rio Grande is only a minor geochemical anomaly, but of major economical interest.

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#### References

- Ahlfeld, F.E., 1972. Geología de Bolivia. Los Amigos del Libro, La Paz, Bolivia, 190 pp.
- Alderman, S.S., 1985. Geology of the Owens Lake evaporite deposit. In: B.C. Schreiber and H.L. Harner (Editors), Int. Symp. on Salt, 6th, The Salt Inst., Vol. 1, pp. 75-83.
- Antsiferov, A.S., 1979. Genesis of Jurassic basins in the Sayan region. Dokl. Akad. Nauk SSSR, 244(2): 421– 424. English translation in Dokl., Am. Geol. Inst., 244: 76–78.
- Bonython, C.W., 1955. Lake Eyre, South Australia; The great flooding of 1949–50. Cited in Langbein (1961): Salinity and Hydrology of closed lakes. US Geol. Surv. Prof. Pap., 412, 20 pp.
- Bradbury, J.P., 1971. Limnology of Zuni Salt Lake, New Mexico. Geol. Soc. Am. Bull., 82: 379–398.
- Busson, G. and Perthuisot, J.P., 1977. Intérêt de la Sebkha El Mehla (Sud-Tunisien) pour l'interprétation des séries évaporitiques anciennes. Sediment. Geol., 15 (2): 139-164.
- Carmouze, J.P., Arze, C. and Quintanilla, J., 1978. Circulacíon de materia (agua-sales disueltas) a través del sistema fluvio-lacustre del Altiplano: La regulación hídrica e hydroquímica de los lagos Titicaca y Poopo. Cah. ORSTOM, Sér. Géologie, Vol. 10 (1): 49-68.

Chong, G., 1984. Die Salare in Nordchile - Geologie,

Struktur und Geochemie. Geotektonische Forsch., 67: 1–146.

- Dingman, R.J., 1962. Tertiary salt domes near San Pedro de Atacama, Chile. U.S. Geol. Surv. Prof. Pap. 450-D: 92–94.
- Eaton, G.P., Peterson, D.L. and Schumann, H.H., 1972. Geophysical, geohydrological, and geochemical reconnaissance of the Luke Salt Body, Central Arizona. U.S. Geol. Surv. Prof. Pap. 753, 28 pp.
- Ericksen, G.E., Vine, J.D. and Ballon, R., 1978. Chemical composition and distribution of lithium-rich brines in salar de Uyuni and nearby salars in Southwestern Bolivia. Energy, 3: 355–363.
- Eugster, H.P. and Hardie, L.A., 1978. Saline Lakes. In: A. Lerman (Editor), Lakes, Chemistry, Geology, Physics. Springer, Berlin, pp. 237–293.
- Fernandez, A., Hörmann, P.K., Kussmaul, S., Meave, J., Pichler, H. and Subieta, T., 1973. First petrologic data on young volcanic rocks of SW-Bolivia. Tschermaks Mineral Petrogr. Mitt., 19: 149–172.
- Harder, H., 1959. Beitrag zur Geochemie des Bors: II. Bor in Sedimenten. Nachr. Akad. Wiss. Göttingen: II. Math. Phys. Kl., 6: 123–183. English translation in: C.T. Walker (Editor), 1975. Geochemistry of Boron. Benchmark Papers in Geology. Academic Press, New York, pp. 83–104.
- Hardie, L.A., Lowenstein, T.K. and Spencer, R.J., 1985. The problem of distinguishing between primary and secondary features in evaporites. In: B.C. Schreiber and H.L. Harner (Editors), Int. Symp. on Salt, 6th, The Salt Institute, Alexandria, Va., Vol. 1, pp. 11–39.
- Harvie, C.E. and Weare, J.H., 1980. The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O system from zero to high concentration at 25°C. Geochim. Cosmochim. Acta, 44: 981-997.
- Hsu, K.J. and Siegenthaler, C., 1969. Preliminary experiments on hydrodynamic movement induced by evaporation and their bearing on the dolomite problem. Sedimentology, 12: 11–25.
- Jones, B.F. and Van Denburgh, A.S., 1966. Geochemical influences on the chemical character of closed lakes. Int. Ass. Sci. Hydrol. Publ., 7: 435-446.
- Krinsley, D.B., 1972. Dynamic processes in the morphogenesis of salt crusts within the Great Kavir, northcentral Iran. In: J.E. Gill (Editor), Proc. Int. Geological Congr., 24th, (Montreal), Sect. 12 (Quaternary Geology), pp. 167-174.
- Langbein, N.B., 1961. Salinity and hydrology of closed lakes. U.S. Geol. Surv. Prof. Pap., 412, 20 pp.
- Lavenu, A., Fornari, M. and Sebrier, M., 1984. Existence de deux nouveaux épisodes lacustres quaternaires dans l'Altiplano peruvo-bolivien. Cah. ORSTOM, Sér. Géol., 14 (1): 103–114.
- Lindsey, D.A., Glanzman, R.K., Naeser, R.K., Naeser, C.W. and Nichols, D.J., 1981. Upper Oligocene evap-

orites in basin fill of Sevier Desert Region, western Utah. Bull. Am. Assoc. Petrol. Geol., 65 (2): 251–260.

- Mercer, J.H. and Palacios, O., 1977. Radiocarbon dating of the last glaciation in Peru. Geology, 5: 600-604.
- Moraga, A., Chong, G., Fortt, M.A. and Henriquez, H., 1974. Estudio Geológico del salar de Atacama, provincia de Antofagasta. Bol. Inst. Invest. Geol., Chile, 29: 1-56.
- Rettig, S.L., Jones, B.F. and Risacher, F., 1980. Geochemical evolution of brines in the salar of Uyuni, Bolivia. Chem. Geol., 30: 57-79.
- Risacher, F., 1984. Origine des concentrations extrêmes en bore et en lithium dans les saumures de l'Altiplano bolivien. C.R. Acad. Sci., Paris, Sér. 2, 299: 701–706.
- Risacher, F. and Fritz, B., 1984. Simulation de l'évaporation sur micro-ordinateur. Sci. Geol., Bull., 37 (3): 239–251.
- Searls, J.P., 1983. Potash. Mineral Commodity Profiles. Bur. Mines, US Dept. Inter., 10 pp.
- Servant, M. and Fontes, J.Ch., 1978. Les lacs quaternaires des hauts plateaux des Andes boliviennes. Premières interprétations paléoclimatiques. Cah. OR-STOM, Sér. Géol., 10, (1): 9–23.
- Servant, M., Fontes, J.Ch., Rieu, M. and Saliège, J.F., 1981a. Phases climatiques arides holocènes dans le sudouest de l'Amazonie (Bolivie). C.R. Acad. Sci. Paris, Sér. 2, 292: 1295-1297.
- Servant, M., Fontes, J.Ch., Argollo, J. and Saliège, J.F.,

1981b. Variations du régime et de la nature des précipitations au cours des 15 derniers millénaires dans les Andes de Bolivie. C.R. Acad. Sci. Paris, Sér. 2, 292: 1209-1212.

- Servant-Vildary, S., 1978. Les diatomées des dépôts lacustres quaternaires de l'Altiplano bolivien. Cah. OR-STOM, Sér. Géol., 10 (1): 25-35.
- Sonnenfeld, P., 1984. Brines and Evaporites. Academic Press, New York, 613 pp.
- Soubies, F., 1979. Existence d'une phase sèche en Amazonie brésilienne datée par la présence de charbons dans les sols (6000-3000 ans B.P.). Cah. ORSTOM, Sér. Géol., 11 (1): 133-148.
- Spencer, R.J., Eugster, H.P. and Jones, B.F., 1985. Geochemistry of Great Salt Lake, Utah. II: Pleistocene– Holocene evolution. Geochim. Cosmochim. Acta, 49: 739–747.
- Stoertz, G.E. and Ericksen, G.E., 1974. Geology of salars in northern Chile. U.S. Geol. Surv. Prof. Pap. 811, 65 pp.
- Swenson, H.A. and Colby, B.R., 1955. Chemical quality of surface waters in Devils Lake basin, North Dakota. U.S. Geol. Surv. Water-Supply Pap. 1295, 82 pp.
- U.S. Geological Survey, 1978. Lithium, Nature's lightest metal. U.S.G.S., Inf-75-27,15 pp.
- Wirrmann, D. and Olivera Almeida, L.F., 1987. Low Holocene level (7700 to 3650 years ago) of Lake Titicaca (Bolivia). Palaeogeogr. Palaeoclimatol. Palaeoecol., 59: 315–323.

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