

## Geochemistry of Bolivian salars, Lipez, southern Altiplano: Origin of solutes and brine evolution

FRANÇOIS RISACHER<sup>1</sup> and BERTRAND FRITZ<sup>2</sup>

ORSTOM<sup>1</sup> and CNRS,<sup>2</sup> Centre de Géochimie de la Surface, 1, rue Blessig, 67084 Strasbourg cedex, France

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**Abstract**—The southern Bolivian Altiplano is a volcanic area which contains numerous undrained basins occupied by playas and saline lakes, locally named salars. Solute carried by springs and rivers into the salars originate mostly from the alteration of the volcanic rocks and the re-solution of ancient buried evaporites. Both weathering and hydrothermal alteration lead to Na-HCO<sub>3</sub> inflow waters of similar composition. High contents of lithium and boron are not specifically related to hydrothermal activity. Evaporite leaching leads to Na-Cl inflow waters of higher salinity. Atmospheric precipitation contributes only a small amount of Ca and SO<sub>4</sub>, and very little Na or Cl.

The calculated evaporative evolution of the inflow waters shows that about half of them should become highly alkaline brines and the other half should end as near-neutral brines. However, alkaline soda lakes are rare in this region. Most lake brines are of the Na-Cl and Na-Cl-(SO<sub>4</sub>) types. To understand this anomaly one characteristic sequence of evaporating waters was studied in detail. Precipitation of calcite and Mg-smectites accounts only partially for the reduction of alkalinity. A further loss of alkalinity is probably related to the oxidation of wind-blown native sulfur in peripheral ponds. Wind-blown sulfur is also deposited around the lakes, on the drainage basins. In the rainy season, ephemeral streams carry along sulfur particles in permanent pools of the preconcentration areas.

A hydrologic control of brine chemistry is suspected. Inflow waters, that should become alkaline, appear to evolve to neutral brines if they remain in contact with atmospheric dust and peripheral colluvium for a long time. On the contrary, inflow waters to soda lakes are generally close to the shore and have only minimal contact with atmospheric dust and peripheral sediments. Presently, all lakes are at relatively low levels, and inflow waters often drain an important area of the drainage basin before reaching the topographic low. In the past, lakes were at higher levels and less interaction occurred between inflow waters, atmospheric dust, and peripheral sediments. As a result, the chemistry of some lakes may have changed during the Quaternary.

### INTRODUCTION

#### Scope of the Study

THIS PAPER FOCUSES ON poorly understood processes related to saline lakes, or salars, of the southern Bolivian Altiplano. A morphologic classification system is described, and the origin of solutes in the inflow waters is discussed. Next, the actual chemical evolution of these inflow waters is compared with their theoretical evolution based on thermodynamic equilibria. The water chemistry of a specific sequence of evaporating waters is then scrutinized to determine which processes are responsible for a significant discrepancy which is apparent between the measured and the calculated evolution.

#### Methods

Temperature and pH of waters were determined in the field. All waters were filtered through a 0.45 micron membrane. Cations were determined by atomic absorption spectrometry with a Perkin-Elmer 430 spectrometer. Chloride, sulfate, and silica were determined colorimetrically with an automated Technicon Auto-Analyser II, according to the procedures described by SKOUGSTAD et al. (1979). Boron was complexed with azomethine H (BASSON et al., 1969) before determination by colorimetry. Alkalinity determinations were performed potentiometrically with a Mettler DL 40 RC potentiometer. Sulfur in solid samples was determined by using a combustion-infrared Leco SC-132 analyzer. The oxidation state of sulfur was determined according to the procedure described by JACKSON et al. (1987, p. G13). Other major and trace components in solid samples

were analyzed by using the inductively coupled plasma-atomic emission spectrometric technique, after fusion dissolution with lithium tetraborate.

#### Geographic and Geologic Setting

The Bolivian Altiplano is a wide, closed basin (200,000 km<sup>2</sup>) located between the Eastern and the Western Cordillera of the Andes (Fig. 1). During the Late Tertiary and the Quaternary, the southern Altiplano (Lipez) was affected by intense volcanic activity which filled the intervening region between the two Cordilleras. Volcanoes (which now reach up to 6000 m in elevation), related lava flows, and ignimbrites delineate a number of small, closed basins at high elevation (4100 to 4600 m, Fig. 2). Volcanic rocks range from andesite to rhyodacite (FERNANDEZ et al., 1973), locally containing deposits of native sulfur.

During the Quaternary, large lakes occupied the center of the Altiplano and the small intravolcanic basins of the south. SERVANT and FONTES (1978) described two major recent lacustrine phases: Minchin (30,000–25,000 years BP) and Tauca (12,000–10,000 years BP). Presently, the climate is arid, and all lakes are at low level or desiccated. The most recent pluvial lake left two extensive salt crusts in the central depression of the Altiplano: the salar of Uyuni (10,000 km<sup>2</sup>, probably the world's largest salt crust) and the salar of Coipasa (2500 km<sup>2</sup>). Their chemistry has been studied by RETTIG et al. (1980).

#### Climate

There is no meteorological station within the area. Fair estimates are obtained by extrapolating data from adjacent areas in Bolivia, Chile, and Argentina. In addition, some measurements were made



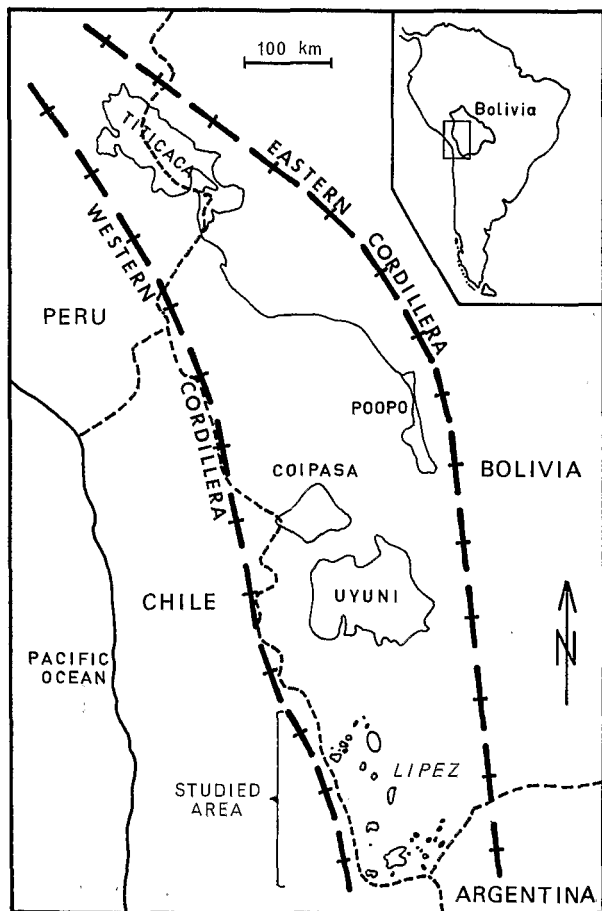


FIG. 1. Outline map of the Bolivian Altiplano.

during the field trip periods. Rainfall occurs in summer (December–February), and decreases southwards from 150 to 50 mm/a. The mean annual air temperature is estimated between 5 and 10°C, decreasing southwards and with altitude. Air temperature ranges from –30°C in winter (June–July) to 20–25°C in summer. Daily variations may reach 40°C. Remnants of ancient ice islands in several saline lakes indicate that the climate was much colder some centuries ago (HURLBERT and CHANG, 1984). Potential evaporation varies from 1000 to 1500 mm/a. Real evaporation may be much less than these values. Many lakes are frozen a large part of the year, which reduces their rate of evaporation. However, the lower freezing point of the brines increases the time of ice-free surface exposure. Owing to such aridity and low temperatures, soils and vegetation are sparse or completely lacking.

#### SALAR MORPHOLOGY

Bolivian salars can be classified morphologically into four types (Fig. 3):

1. *Saline lakes* consist of a permanent body of saline water lying on a low permeability substrate. They are relatively deep (some meters) and dry up only occasionally. On the Altiplano, salts mostly precipitate by freezing-out in winter, especially natron ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ), mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), and perhaps hydrohalite ( $\text{NaCl} \cdot 2\text{H}_2\text{O}$ ).
2. *Salt crusts* occupy the center of the basin and are generally highly porous. Their porosity is at least partially filled with

an interstitial brine. Obviously, such crusts are the result of the drying up of former saline lakes. Gypsum and halite are the dominant salts.

3. *Playas* occupy the central depression of a basin filled by lacustrine sediments. At a depth varying from meters to decimeters, an interstitial brine, often strongly reduced, saturates a confined aquifer. Commonly, a very shallow pool fed by shore springs may occupy a variable area of the surface. However, such a pool has no direct connection with the underlying brine and is often more dilute. Salts mainly precipitate within the sediment layers, where solutions are drawn by capillary forces. The interstitial brine undergoes evaporation and oxidation above the water table. Gypsum, mirabilite, and ulexite ( $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$ ) are commonly formed in this way. These salts may build up large irregular lenses. They generally do not show any vertical zonation.
4. *Exposed unconfined aquifers* occurs where the bottom of a basin is filled with coarse sediments, either gravel or sand. The water table stands at the topographic surface or just above, producing a very shallow lake of irregular shape. Lacustrine sediments are not abundant enough to fill the center of the basin. Salts precipitate by freezing-out and by direct evaporation.

Several salars are combinations of these four endmember types, especially the large ones. Their morphology changes laterally from one type to the other. They may also show seasonal changes, particularly during the rainy season. Table 1 gives the geographic features and the morphometric properties of each salar in the study area. It also indicates to which class (or classes) each salar belongs. Three freshwater lakes have been included (TUR, LAG, TOT), because they are in the same area. These lakes may display the first chemical evolutionary steps of the present saline lakes in this environment.

#### ORIGIN OF SOLUTES

##### Precipitation

The average composition of eight rainwater samples (collected over two years) is shown in Table 2, as is the estimated quantity of solute brought into the study area by rainwater and surficial inflows (springs, rivers, and underground discharges). Surficial inflows may be estimated through the hydrologic balance of a closed basin containing a permanent lake (HUTCHINSON, 1957; LANGBEIN, 1961):

$$V = S \times E$$

$S$ : lake surface area ( $\text{m}^2$ )

$E$ : net evaporation rate (evaporation minus precipitation: 1.15 m/a on average).

$V$ : annual volume of inflows ( $\text{m}^3/\text{a}$ ).

The volume of inflows is calculated for each lake. Then, this volume of water is multiplied by the average concentration of solutes of all inflow waters to the lake (Table 3). The amount of solute brought in each salar is then summed over all salars. The average annual volume of rainwater is estimated at  $721 \times 10^6 \text{ m}^3/\text{a}$  (total area:  $721 \times 10^7 \text{ m}^2$ ; average precipitation: 0.1 m/a).

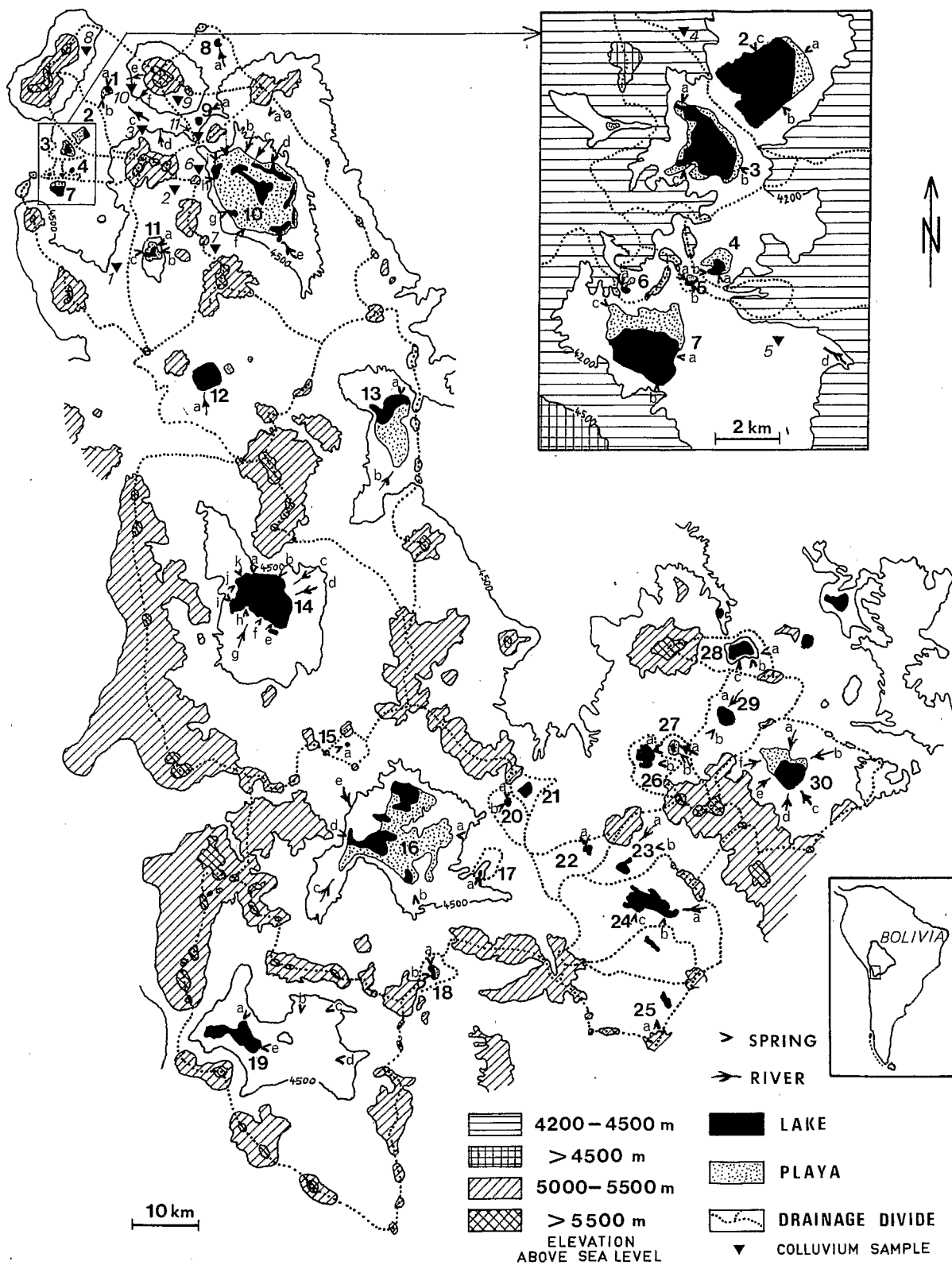


FIG. 2. Map of southern Altiplano showing location of salars, drainage basins, and inflow waters. Bold identification numbers relate to salar names in Table 1. Smaller numbers refer to sediment samples (Table 6).

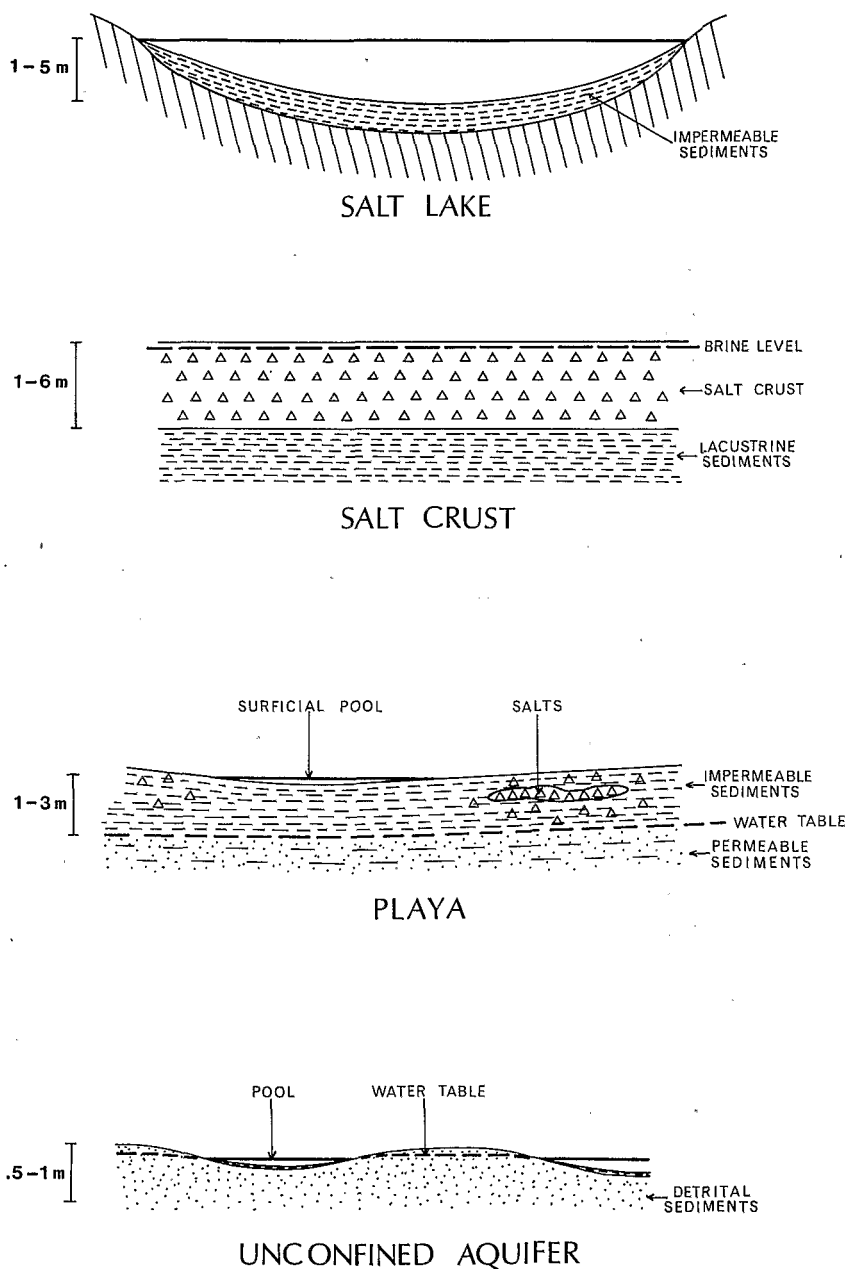


FIG. 3. Morphology of Altiplano salars.

Rainfall solute composition on the Altiplano does not seem to be influenced by seawater, which could be a major source for Na and Cl. Rather, the rainfall looks more closely related to water compositions of the inland Amazon Basin, characterized by high Ca + SO<sub>4</sub> and low Na + Cl (LIVINGSTONE, 1963, p. 37; STALLARD and EDMOND, 1981). This is in accord with an origin of the rains to the east (SERVANT and VILLARROEL, 1979). Rainfall solute contribution to surface inflows ranges from 1% for Na and Cl to about 10% for Ca and SO<sub>4</sub>.

#### Dissolution of Ancient Evaporites

Some spring waters are much more concentrated than would be expected if only meteoric or hydrothermal alteration

of volcanic rocks were involved (see HED b, CHI b, PAG g, VER e, COR c, in Table 3). For a comparison with thermal meteoric waters of deep circulation, see D. E. WHITE et al. (1963, p. 55). The average salinity of all spring waters of the study area is 820 mg/L, which is a rather high value. Figure 4 shows the sodium and chloride contents of all inflow waters. They are divided into two groups. When Cl content is low (<2 mM/L), Na concentration exceeds that of Cl and there is a considerable scatter in values. For all other waters (Cl > 2 mM/L), Na and Cl are nearly equivalent in concentration. This shift is probably due to the dissolution of sodium chloride from ancient evaporites. Therefore, about half of all inflow waters sampled are affected markedly by evaporite leaching.

Table 1. Geographic features, morphometric properties and chemical facies of Bolivian salars

NAME	CODE	MORPHOLOGY	ELEVATION meters	DRAINAGE		WATER SURFACE km <sup>2</sup>	MEAN DEPTH meters	BRINE CHEMISTRY	
				BASIN AREA km <sup>2</sup>	SALAR AREA km <sup>2</sup>				
1	Canapa	CAN	P	4140	227	1.5	0.4	0.2	Na-Cl-(SO <sub>4</sub> )
2	Hedionda	HED	P	4121	52	4.4	3.8	0.3	Na-(Mg)-Cl-(SO <sub>4</sub> )
3	Chiar Kota	CHI	P	4112	20	3.1	2.1	0.2	Na-Cl
4	Honda	HON	P	4110	38	0.5	0.3	0.3	Na-Cl-(SO <sub>4</sub> )
5	Pujio	PUJ	P	4110	5.3	0.1	0.07	0.15	Na-Cl-(SO <sub>4</sub> )
6	Balivian	BAL	P	4110	1.9	0.08	0.02	0.2	Na-Cl-(SO <sub>4</sub> )
7	Ramaditas	RAM	P-C	4117	277	4.0	2.4	0.25	Na-Cl
8	Turquiri	TUR	L	4270	74	0.4	0.4	0.5	n.c.
9	Chulluncani	CHU	P-A	4430	68	0.9	0.5	0.2	Na-Cl-(SO <sub>4</sub> )
10	Pastos Grandes	PAG	P	4440	655	125	12	0.1	Na-Cl
11	Cachi Laguna	CAL	A	4495	258	3.7	1.1	0.1	Na-Cl-CO <sub>3</sub> -(SO <sub>4</sub> )
12	Kara	KAR	L	4509	425	13	13	1	Na-Cl-(CO <sub>3</sub> )
13	Capina	CAP	P	4387	660	41	1.3	0.2	Na-Cl-(SO <sub>4</sub> ?)
14	Colorada	CLD	P-L	4278	875	52	50	0.2	Na-Cl
15	Lagunillas	LAG	L-A	4695	22	0.03	0.03	0.1	n.c.
16	Challviri	CHA	P	4394	1390	194	25	0.3	Na-Cl-(SO <sub>4</sub> )
17	Honda Sur	HND	P-A	4510	14	0.3	0.3	0.3	Na-Cl-(CO <sub>3</sub> )-(SO <sub>4</sub> )
18	Puripica	PUR	P	4730	21	1.5	0.7	0.2	Na-Cl-(SO <sub>4</sub> )
19	Laguna Verde	VER	L	4310	776	16	16	0.3	Na-Cl-(SO <sub>4</sub> )
20	Collpa	COL	L	4510	24	0.9	0.9	1.5	Na-Cl-CO <sub>3</sub>
21	Hedionda Sur	HDS	L	4530	27	2.9	2.9	0.75	Na-Cl-CO <sub>3</sub>
22	Totoral	TOT	L	4550	61	1.0	1.0	1	n.c.
23	Catalcito	CAT	L	4545	170	2.1	2.1	1	Na-Cl-(CO <sub>3</sub> )
24	Bush	BUS	L	4530	266	21	17	0.6	Na-Cl-(SO <sub>4</sub> )
25	Pelada	PEL	P-A	4590	141	1.9	1.9	0.65	Na-Cl-(SO <sub>4</sub> )-(CO <sub>3</sub> )
26	Loromayu	LOR	L	4650	64	8.0	7.2	0.5	Na-(Mg)-Cl
27	Luriques	LUR	P-L	4650	38	2.6	0.7	0.6	Na-(Ca)-Cl-(SO <sub>4</sub> )
28	Mama Kumu	MAM	P-L	4445	65	7.3	7.3	0.3	Na-Cl
29	Chojllas	CHL	L	4545	159	5.2	5.2	3	Na-Cl
30	Coruto	COR	P-L	4530	331	25	13	0.5	Na-(Ca)-Cl

P = playa ; C = salt crust ; L = lake ; A = unconfined aquifer.

Brines are classified according to EUGSTER and HARDIE (1978). A component shown in parentheses has a concentration ranging from 5 to 25 % (in mol %).

Above 25 %, components are shown without parentheses. n.c. = not classified (fresh water).

The most saline spring (HED b, 7.3 g/L) is close to the only known sedimentary outcrop in the entire area. It is composed of gypsiferous marl, probably of Tertiary age. Another source for evaporitic salts in inflow waters may be the reworking of Quaternary salars and associated brines buried below lava flows and ignimbrites.

D. E. WHITE et al. (1963) and A. F. WHITE et al. (1980) have reported typical compositions of waters from similar volcanic rocks of North America (andesite to rhyolite). The source of solutes in these waters is exclusively the alteration of volcanic rocks without involvement of evaporite dissolution or thermal fluids. Table 4 shows a comparison between concentrations of major elements in these characteristic waters and in the Bolivian dilute inflow waters not affected by evaporite dissolution (Cl < 2 mM/L). The striking similarity of both groups of waters strongly suggests that the alteration of volcanic rocks is also the main source of solutes in the dilute inflows to Bolivian salars. Subsequently, these waters are referred to as ALT waters, whereas those affected by evaporite leaching are referred to as EVA waters (Table 4).

An outstanding feature of almost all waters of the southern Altiplano is their very high contents of lithium and boron (ERICKSEN et al., 1978). Some brines have Li and B concentrations among the highest in the world (RISACHER, 1984). The origin of these elements is suggested to be the leaching of volcanic rocks by the correlations of Li to Na and B to Cl of ALT waters (Fig. 5).

The influence of evaporite redissolution on the content of all major solutes is illustrated in Table 4. The average con-

centration of components in EVA waters is a good indicator of the contribution of older evaporites in the supply of each of these solutes. Except for silica and bicarbonate, all other constituents are readily released from ancient salts and trapped brines. The reworked evaporites belong to the neutral facies (see below), Na-K-Ca-Mg-Cl-SO<sub>4</sub>. There is no indication of sodium carbonate leaching.

#### Meteoric versus Hydrothermal Alteration

In the southern Altiplano the boundary between cold and thermal springs is around 10°C (2°C above the mean annual air temperature; HEATH, 1983, p. 70). Inflow waters have been divided into four classes: river water, cold springs (below 10°C), moderately hot springs (from 10 to 15°C), and hot springs (above 15°C). Based on this classification, around 60% of all springs are thermal.

Table 2. Rainfall contribution to the dissolved load of inflow waters in Bolivian salars.

	Amount carried annually by inflows (10 <sup>6</sup> moles)	Average concentration in rainwater (mM/l)	Amount carried annually by rainwaters (10 <sup>6</sup> moles)	Percentage of rain contribution
Cl	1200	0.020	14	1.2
SO <sub>4</sub>	180	0.023	17	8.6
Na	1300	0.022	16	1.2
K	100	0.0076	5.5	5.2
Ca	140	0.027	19	11.9
Mg	76	0.007	5	6.2

Table 3. Chemical analyses of inflow waters and central brines of Bolivian salars  
(Temperature in °C; density in g/cm<sup>3</sup>; alk in meq/l; others in mM/l).

	Temp.	Density	pH	alk	Cl	SO <sub>4</sub>	B	Si	Na	K	Li	Ca	Mg
CAN a	7.5	1	6.50	1.70	7.63	1.30	0.102	1.05	6.30	0.522	0.187	1.50	0.741
b	12.2	1	7.18	1.39	5.69	0.94	0.09	1.14	4.61	0.412	0.144	1.08	0.675
c	(5)	1	7.23	0.53	0.106	0.375	0.032	0.783	0.544	0.072	0.007	0.224	0.148
d	8.5	1	3.80	0.064	0.045	0.570	0.020	0.052	0.072	0.107	0.01	0.268	0.122
e	7	1	6.20	0.104	0.024	0.111	0.026	0.285	0.214	0.046	0.01	0.038	0.020
f	5.5	1	4.33	0.003	0.084	0.214	0.030	0.131	0.183	0.102	0.004	0.069	0.033
UB 5	5	1.114	7.79	13.4	2110	356	58.2	0.71	2460	162	54.7	14.3	43.2
HED a	9	1	6.68	0.929	2.23	0.823	0.139	1.02	3.04	0.23	0.069	0.449	0.362
b	10	1.006	7.28	3.65	106	4.74	1.94	2.05	91.3	5.12	2.16	7.48	4.69
c	13	1	7.00	1.0	2.96	0.802	0.129	1.22	3.50	0.256	0.061	0.449	0.354
UB 15	15	1.170	6.69	25.0	3360	370	101	0.487	3360	224	101	9.65	272
CHI a	13.5	1	7.31	0.812	1.49	0.781	0.088	1.07	2.17	0.164	0.071	0.424	0.305
b	9.5	1.003	6.72	3.58	53.2	7.81	1.43	1.38	54.4	3.33	1.34	3.49	3.09
c	15	1.001	7.50	1.83	27.3	1.11	0.57	1.50	21.7	1.54	0.591	2.79	1.23
UB 8	8	1.164	7.38	12.9	4000	113	72.4	0.608	3440	216	102	28.2	190
HON a	12	1	7.63	2.18	7.18	0.781	0.166	1.53	6.16	0.547	0.123	1.30	0.634
b	14	1	7.60	1.39	3.10	0.391	0.102	1.08	3.06	0.256	0.048	0.748	0.305
UB 6	6	1.124	7.94	5.52	465	46.9	10.2	1.22	435	40.4	10.7	20.2	7.20
FUJ a	9	1	7.52	2.89	6.65	1.09	0.268	1.12	8.26	0.368	0.084	1.37	0.354
b	1	1	6.77	1.76	5.80	0.552	0.180	0.983	6.52	0.358	0.073	0.698	0.255
UB 10	10	1.044	7.62	21.2	735	120	29.1	1.30	860	40.9	9.65	15.5	18.5
BAL a	14	1	7.18	0.943	8.45	1.71	0.194	1.17	8.48	0.599	0.065	1.63	0.465
UB 10	10	1.079	7.10	12.4	1730	106	30.5	0.983	1655	106	11.2	31.2	65.8
RAM a	8.5	1.001	8.28	1.14	7.32	6.46	0.166	1.0	5.68	0.568	0.049	7.36	1.15
b	25	1	8.00	0.791	5.58	1.83	0.148	1.20	6.13	0.379	0.033	1.75	0.206
c	15	1.001	8.55	1.62	13.4	2.43	0.268	0.8	17.4	1.41	0.092	0.748	0.126
d	(8)	1	7.09	0.325	0.108	0.208	0.032	0.65	0.203	0.072	0.0014	0.177	0.102
UB 11	11	1.045	7.08	5.44	995	45.8	14.3	0.883	860	52.7	4.03	47.6	31.3
TUR a	(12)	1	7.86	0.58	0.21	0.145	0.056	0.91	0.50	0.097	0.005	0.172	0.079
SL 12	12	1	8.31	3.05	1.53	0.69	0.378	0.625	3.38	0.59	0.039	0.526	4.428
CHU a	(5)	1	8.10	0.359	0.127	0.135	0.042	0.617	0.435	0.072	0.001	0.044	0.066
SL 5	5	1.087	8.80	35.0	1240	277	86.7	0.783	1310	327	3.24	18.2	78.2
PAG a	9	1	8.60	0.236	0.081	0.102	0.016	0.58	0.15	0.067	0.0004	0.099	0.058
b	(0)	1	8.91	0.80	0.293	0.099	0.04	0.487	0.709	0.0652	0.014	0.17	0.115
c	(10)	1	8.92	1.36	4.23	0.052	0.10	0.8	3.70	0.322	0.17	0.312	0.305
d	(1)	1	7.12	0.76	0.158	0.057	0.03	0.772	0.287	0.0417	n.d.	0.224	0.132
e	(8.5)	1	8.00	0.61	0.11	0.125	0.029	0.487	0.287	0.042	n.d.	0.17	0.123
f	10	1	6.95	3.30	2.54	1.09	0.092	1.33	3.48	0.422	0.073	1.27	0.831
g	9.5	1.002	6.50	2.95	43.1	1.32	0.749	1.62	40.4	3.22	1.59	1.17	0.551
h	32	1.001	6.60	1.63	15.4	0.74	0.27	1.28	14.8	0.995	0.626	0.491	0.36
i	15	1	7.00	0.788	4.03	0.283	0.088	0.895	4.24	0.258	0.163	0.207	0.147
j	13	1	7.82	0.61	1.67	0.075	0.03	0.32	2.03	0.11	0.075	0.082	0.066
SL 5	5	1.211	7.20	22.9	5460	25.6	87.3	1.12	4480	363	236	77.3	143
CAL a	18	1	9.82	2.35	0.375	0.364	0.138	1.5	1.63	0.194	0.028	0.536	0.246
b	5	1	9.15	2.46	1.38	0.677	0.134	1.17	2.87	0.435	0.065	0.499	0.535
c	12	1	7.53	2.08	0.104	0.12	0.03	1.6	1.67	0.286	0.043	0.157	0.111
SL 25	25	1.238	10.05	2500	1610	373	231	7.2	4000	910	122	0.15	0.12
KAR a	(1)	1	8.50	4.88	0.211	0.146	0.046	1.37	2.61	0.46	0.027	0.324	0.534
SL 5	5	1.007	9.40	37.2	116	2.17	7.86	1.13	134	7.16	5.19	0.09	2.74
CAP a	1	1	7.88	0.52	0.056	0.055	0.052	0.633	0.183	0.076	0.014	0.11	0.081
b	(2)	1	8.28	2.05	0.749	0.215	0.118	0.938	1.61	0.266	0.029	0.459	0.267
SL 6	6	1.020	8.60	12.4	487	NA	25.8	1.22	370	37.3	27.8	20.0	10.7
CLD a	22	1	7.62	1.17	2.18	0.343	0.079	1.24	3.15	0.271	0.04	0.173	0.153
b	29	1.001	7.88	0.92	13.3	1.81	0.464	1.39	15.4	0.806	0.223	0.259	0.198
c	(8)	1	7.98	0.763	0.37	0.268	0.048	0.75	0.59	0.121	0.003	0.307	0.187
d	(11)	1	7.85	0.703	0.085	0.201	0.018	0.705	0.478	0.032	0.007	0.146	0.189
e	2	1	8.18	2.55	2.10	0.661	0.093	0.85	3.30	0.343	0.046	0.683	0.369
f	26	1.001	7.40	3.26	12.2	2.10	0.429	1.47	13.9	0.957	0.195	1.01	1.05

Table 3. (Continued)

	Temp.	Density	pH	alk	Cl	SO <sub>4</sub>	B	Si	Na	K	Li	Ca	Mg
g (9)	1	8.48	3.40	0.069	0.61	0.019	1.41	1.33	0.269	0.007	0.731	0.807	
h 17	1.001	7.80	2.45	10.4	1.45	0.403	1.15	12.7	0.923	0.173	0.459	0.551	
i 23	1	7.88	0.83	10.8	1.38	0.347	1.21	12.2	0.683	0.173	0.282	0.335	
j 2	1.001	7.90	2.05	12.5	2.24	0.403	1.20	15.5	0.821	0.209	0.638	0.65	
k 18	1	7.40	0.70	5.85	1.1	0.235	1.18	7.55	0.404	0.101	0.179	0.18	
SL 6	1.081	8.40	31.5	1830	67.1	56.6	1.63	1770	109	28.2	6.48	37.6	
LAG a 12	1	8.38	0.55	0.078	0.138	0.021	0.605	0.338	0.051	0.0005	0.175	0.096	
SL 8	1	9.80	1.07	0.611	1.63	0.277	1.24	2.08	0.852	0.001	0.94	0.108	
CHA a 14.5	1	7.69	0.45	0.232	0.205	0.031	0.572	0.492	0.07	0.01	0.148	0.121	
b 30	1.001	7.92	1.43	12.0	1.29	0.775	1.3	11.6	1.21	0.496	1.04	0.407	
c (1)	1	8.08	1.73	0.71	1.13	0.087	1.09	2.67	0.173	0.035	0.519	0.302	
d 36	1	8.40	0.795	0.12	1.72	0.031	1.16	2.57	0.116	0.007	0.686	0.091	
e (10)	1	7.75	0.31	0.06	0.149	0.013	0.883	0.276	0.099	0.0007	0.107	0.053	
SL 3	1.015	8.34	4.32	330	24.9	9.18	1.39	313	9.72	9.87	10.9	10.1	
HND a 10.8	1	7.95	0.722	1.01	0.44	0.086	0.98	1.33	0.081	0.023	0.571	0.065	
SL 5.5	1.109	9.50	468	1420	242	59.0	2.37	2160	66.5	28.8	0.095	0.05	
PUR a 5	1	8.72	0.833	0.515	0.424	0.158	0.805	1.12	0.36	0.032	0.249	0.095	
b 23	1	8.12	1.25	10.4	1.08	0.551	1.13	10.0	1.08	0.403	0.706	0.322	
SL 4	1.024	8.52	7.80	430	48.5	22.0	0.735	415	44.0	15.7	11.6	11.3	
VER a 15	1.002	8.28	1.86	14.3	5.97	1.05	1.73	20.8	1.57	0.382	2.01	0.794	
b 30.5	1.001	6.28	1.09	15.4	2.60	0.883	2.0	13.6	1.45	0.634	2.21	0.938	
c 15	1	7.30	0.395	0.083	0.235	0.023	1.10	0.390	0.046	0.003	0.193	0.07	
d 20	1	7.28	0.788	2.52	0.254	0.128	1.08	2.22	0.098	0.059	0.464	0.179	
e 7	1.002	8.40	2.68	24.3	2.31	1.55	0.825	25.2	0.91	0.764	1.22	1.48	
SL 5	1.046	8.48	18.9	873	102	54.1	0.942	870	35.0	23.2	19.3	47.7	
COL a 2	1	7.67	0.530	0.183	0.021	0.037	0.574	0.291	0.077	n.d.	0.114	0.086	
b 4.5	1	7.53	0.775	0.237	0.117	0.046	0.493	0.761	0.072	n.d.	0.102	0.074	
SL 5	1.037	10.81	562	188	4.93	9.07	2.50	744	32.2	0.086	0.175	0.132	
HDS SL 5	1.028	10.60	362	189	17.3	10.5	3.16	548	43.0	0.072	0.409	0.263	
TOT a 13.4	1	8.65	0.597	0.121	0.083	0.018	0.62	0.509	0.035	0.006	0.16	0.013	
SL 2.8	1	10.30	3.40	0.524	0.465	0.118	1.64	3.93	0.012	0.037	0.439	0.027	
CAT a (5.5)	1	7.80	1.19	1.98	0.173	0.091	0.875	2.14	0.154	0.084	0.439	0.125	
b 15.1	1	8.20	0.75	0.146	0.138	0.033	0.75	0.60	0.034	0.007	0.264	0.006	
SL 4	1.007	9.10	14.2	136	7.50	4.90	1.56	144	8.06	4.47	1.43	0.35	
BUS a (3.8)	1	7.95	1.36	0.476	0.099	0.066	0.815	0.974	0.075	0.026	0.414	0.071	
b 13.9	1	8.10	0.665	3.61	0.372	0.145	0.735	3.66	0.136	0.091	0.384	0.087	
c 13.4	1	8.45	0.95	3.15	0.574	0.212	0.64	4.43	0.056	0.095	0.240	0.028	
SL 8.8	1.052	8.30	14.4	966	109	44.9	1.07	1100	25.4	25.4	15.1	6.71	
FEL a 9.2	1	8.35	0.358	0.088	0.109	0.021	0.68	0.271	0.073	0.0014	0.131	0.03	
SL 6.2	1.015	9.10	16.0	161	54.8	28.2	0.655	229	28.9	2.77	6.76	3.25	
LOR a 5.8	1	7.85	2.81	2.41	0.473	0.099	1.31	3.45	0.368	0.108	1.0	0.16	
b 6.8	1	8.05	2.40	1.02	0.221	0.05	1.07	2.30	0.363	0.056	0.511	0.101	
SL 11.2	1.235	7.80	126	5040	272	240	0.105	3620	946	444	3.79	360	
LUR a (4)	1	7.80	1.85	0.101	0.466	0.026	0.975	0.778	0.317	0.004	0.601	0.260	
b (4)	1	7.90	2.40	0.904	0.207	0.074	1.11	1.70	0.317	0.053	0.711	0.136	
SL 0.7	1.026	8.85	7.22	501	38.4	12.4	0.525	422	51.9	20.7	39.4	6.91	
MAM a 14.5	1	9.40	0.580	0.307	0.083	0.022	0.455	0.522	0.041	0.004	0.202	0.043	
b 2.3	1	7.50	1.01	2.75	0.146	0.097	0.515	2.93	0.107	0.036	0.299	0.105	
c 10	1	7.50	0.610	2.06	0.155	0.076	0.62	2.35	0.096	0.027	0.141	0.062	
UB 6.3	1.086	7.35	1.95	2170	9.20	18.9	0.475	1720	69.1	23.8	100	85.2	
CHL a (0.2)	1	8.30	0.676	0.151	0.078	0.027	0.535	0.349	0.055	0.004	0.208	0.077	
b 8.6	1	8.40	0.474	1.71	0.125	0.102	0.50	1.94	0.067	0.095	0.104	0.032	
SL 5	1.013	7.60	4.88	304	4.25	9.48	1.35	238	10.4	9.37	18.5	7.70	
COR a (9.3)	1	7.50	0.560	0.167	0.104	0.026	0.41	0.308	0.044	0.003	0.202	0.09	
b (0.7)	1	6.05	0.449	0.212	0.101	0.024	0.47	0.336	0.048	0.004	0.185	0.057	
c (1.9)	1.002	7.25	2.64	33.5	1.19	1.16	1.19	22.4	2.09	1.2	5.31	1.04	
d (4.4)	1	7.40	1.83	4.31	0.128	0.296	1.42	4.83	0.409	0.242	0.419	0.051	
e (12.3)	1	8.90	2.22	1.26	0.29	0.091	1.39	2.33	0.32	0.082	0.566	0.182	
f (8.3)	1	8.35	0.51	0.087	0.118	0.02	0.795	0.255	0.098	0.0014	0.168	0.067	
SL 2.5	1.083	7.75	10.6	2040	22.5	37.1	1.08	1570	70.1	48.7	136	65.0	

UB = underground brines ; SL = surface lake ; NA = not analysed; n.d. = not detected.  
 Temperatures (°C) of river waters shown in parentheses. Samples not listed as UB, SL  
 or with ( ) are spring waters.

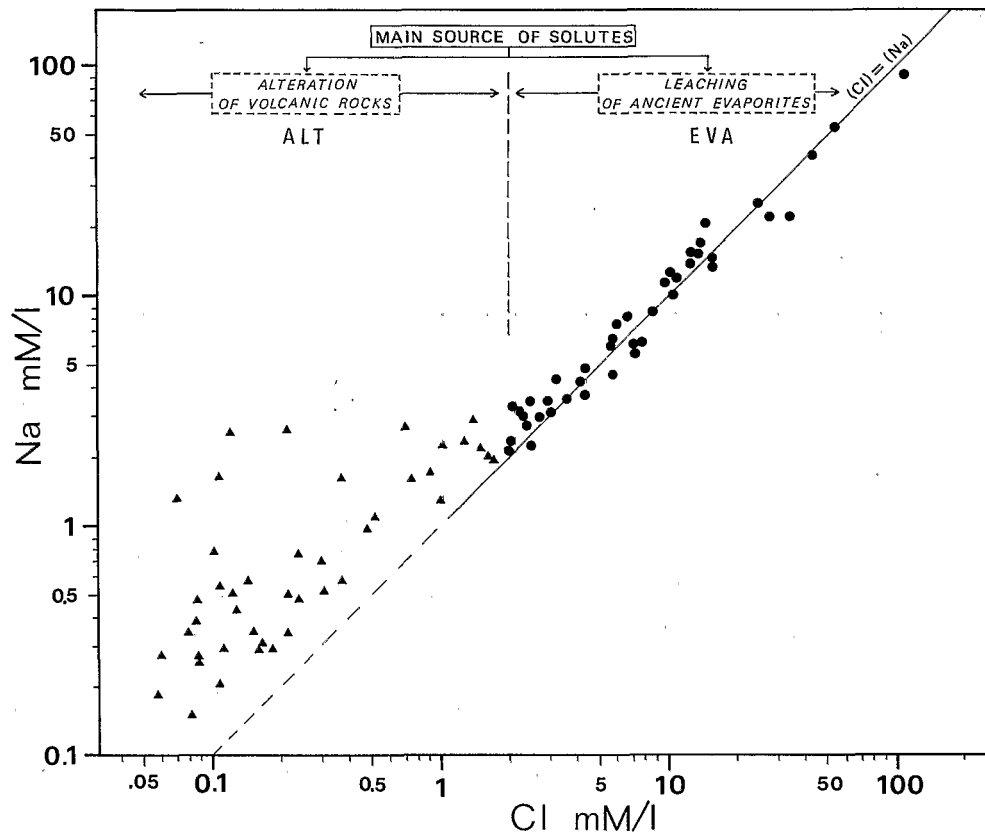


FIG. 4. Sodium versus chloride concentration for inflow waters in Bolivian salars.

Most of the river waters of the southern Altiplano (20 out of 24) belong to the ALT water group. Almost all of the rivers dry up during the dry season. This suggests that rivers are fed mainly by atmospheric precipitation. Each year rainwater partially recharges ground water systems, which in turn discharge in topographic depressions. Such waters do not undergo deep circulation, which would put them in contact with ancient evaporites. They owe their composition almost exclusively to the weathering of volcanic rocks.

The compositions of all inflow waters are represented in trilinear diagrams in Fig. 6. There is no clear evolution in composition with increasing temperature. However, the data exhibit a shift from sodium bicarbonate to sodium chloride waters for inflow that has been subjected to evaporite leaching.

With regard to lithium and boron, RISACHER (1984) has shown that these elements are not preferentially enriched in thermal springs (Fig. 7). Both meteoric and hydrothermal alteration of volcanic rocks lead to the same contents of Li and B relative to salinity in spring waters. Nevertheless, geothermal waters are generally enriched in Li and B (CHOWDHURY et al., 1974; WHITE et al., 1976; BERTHOLD and BAKER, 1976; SMITH, 1976). These authors assume a selective leaching of Li from rocks at high temperatures, typically around 400°C. The much lower temperatures of thermal spring waters could be due to the mixing of hydrothermal fluids with cold waters (see FRITZ, 1981, p. 55). If this is the case, the Li and B content of all inflow waters would reflect some hydrothermal activity in the water cycle. However, such

an hypothesis is at odds with the high contents of Li and B relative to salinity in the ephemeral streams (see Fig. 7). These waters apparently do not undergo deep circulation, and their contact with hydrothermal waters must be minimal. Lithium and boron in streams are from meteoric alteration. Therefore, the source of lithium and boron in ALT inflow waters is likely to be the leaching, either meteoric or hydrothermal, of volcanic rocks.

## BRINE EVOLUTION

### Theory

Waters entering a closed basin under an arid climate will undergo evaporative concentration leading to the precipitation of a sequence of minerals, each removing ions selectively from the solution and thus altering its composition. The chemistry of the final brine is then fundamentally dependent on the initial composition of inflow water and on the sequence and quantity of minerals which precipitate in the successive stages of the evolution of the water. The very first steps of the early evolution, and the most important ones, may be worked out in a simple way, as has been done by GARRELS and MACKENZIE (1967), HARDIE and EUGSTER (1970), EUGSTER and HARDIE (1978), and EUGSTER and JONES (1979).

The concept of alkalinity must be considered carefully in these solutions. Its usual formulation is (STUMM and MORGAN, 1970, pp. 129-131)

$$\begin{aligned} (\text{alk}) = & 2(\text{CO}_3) + (\text{HCO}_3) + (\text{OH}) \\ & + (\text{silicates}) + (\text{borates}) - (\text{H}) \quad (1) \end{aligned}$$

where parentheses denote total molality. This formulation corresponds



Table 4. Comparison between Bolivian inflow waters with North-American waters from similar volcanic environments (in mM/l, except alk in meg/l).

	Average compositions of waters from andesite to rhyolite rocks of North America		Average composition of inflow waters in Bolivian salars	
	WHITE et al. (1963) Table 1, analyses 1-5 Table 3, analyses 1-2	WHITE et al. (1980) Table 1 Table 2 (36 analyses)	Average of all analyses (62)	by alteration of volcanic rocks (ALT) by leaching of ancient evaporites (EVA)
Cl	0.14	0.75	0.24	12.7
SO <sub>4</sub>	0.06	0.43	0.15	1.52
Na	0.71	1.73	1.33	12.5
K	0.054	0.176	0.12	0.86
Ca	0.24	0.265	0.24	1.33
Mg	0.10	0.104	0.09	0.62
Si	0.68	0.97	0.84	1.17
alk	1.17	1.14	1.30	1.70
pH	7.3	7.8	7.5	7.5
			0.38	0.41
			0.21	0.27
			1.02	1.02
			0.14	0.14
			0.29	0.29
			0.15	0.15
			0.83	0.83
			1.10	1.10
			8.1	8.1

to the effectively titrated function but is difficult to handle because all terms are interdependent. Another expression of alkalinity may be derived by substituting Eq. (1) into the electrical neutrality equation (AL-DROUBI et al., 1980):

$$(\text{alk}) = (\text{Na}) + (\text{K}) + (\text{Li}) + 2(\text{Ca}) + 2(\text{Mg}) - (\text{Cl}) - 2(\text{SO}_4) \quad (2)$$

Thus, alkalinity is also the difference between the sum (in milliequivalents) of all cations of strong bases and the sum of all anions of strong acids. In this paper, these species will be referred to collectively as "strong (acid/base) ions." Anions of weak acids (carbonates, silicates, borates) will be named "weak (acid) anions." Of course, alkalinity is not determined by means of Eq. (2), because of the large error yielded from difference equations. Anyhow, water analyses must be of good quality and electrically well balanced. The waters considered here are dilute inflow waters, not brines. Dilute waters do not need high dilution procedures, and so analytical errors are small.

Expression (2) shows that alkalinity is not altered by precipitation or dissolution of any mineral made up of both strong-acid cations and strong-base anions (e.g., NaCl, CaSO<sub>4</sub>·2H<sub>2</sub>O). Alkalinity is modified only by precipitation or dissolution of a weak-anion-bearing mineral (e.g., CaCO<sub>3</sub>, Mg-silicates). Sulfate reduction lowers the term (SO<sub>4</sub>) in Eq. (2) and increases alkalinity. Conversely, the oxidation of sulfide or sulfur increases (SO<sub>4</sub>) and decreases alkalinity.

### The First Critical Steps

Calcite is commonly one of the first minerals to precipitate from an evaporating water. The related evolution of alkalinity (alk) may be inferred from the initial ratio (alk)/2 (Ca). The so-called residual alkalinity may be expressed from Eqn. (2) (for a detailed analysis of this concept, see AL-DROUBI et al., 1980):

$$(\text{alk}) - 2(\text{Ca}) = (\text{Na}) + (\text{K}) + (\text{Li}) + 2(\text{Mg}) - (\text{Cl}) - 2(\text{SO}_4) \quad (3)$$

If (alk) is greater than 2(Ca) in the initial inflow water, then the right-hand side of Eqn. (3) will be always positive and will increase regularly during evaporation as long as only calcite precipitates. On the other hand, (alk) is directly related to (CO<sub>3</sub>) in Eqn. (1) and inversely related to (Ca), because the ion activity product  $a\text{Ca}^{++} \cdot a\text{CO}_3^{--}$  in the solution must remain constant as the concentration of the water increases. Both (Ca) and (CO<sub>3</sub>) (or alk) cannot increase simultaneously as the water evaporates. If one of these solutes increases, then the other one must decrease. Even if the precipitation of calcite removes (Ca) and (CO<sub>3</sub>) from the solution, the overall effect during evaporative concentration (if (alk) > 2(Ca)) is an increase of (alk) and a decrease of (Ca). In that case, the solution becomes carbonate-rich and calcium-poor (alkaline facies; pH above 10). If (alk) is lower than 2(Ca) in the initial inflow water, the exact opposite path is followed. The evaporating water becomes enriched in calcium and depleted in carbonates (neutral facies; pH below 9).

Therefore, as already emphasized by HARDIE and EUGSTER (1970), the fundamental dichotomy in natural brine chemistry, neutral versus alkaline brines, is controlled by the initial water composition and the early precipitation of calcite. Figure 8 shows the distribution of all inflow waters of Bolivian salars in a diagram of (alk) versus 2(Ca). Waters are differentiated according to their main source of solutes: volcanic rock weathering (ALT inflows) or evaporite leaching (EVA inflows). The diagram shows that almost all ALT inflow wa-

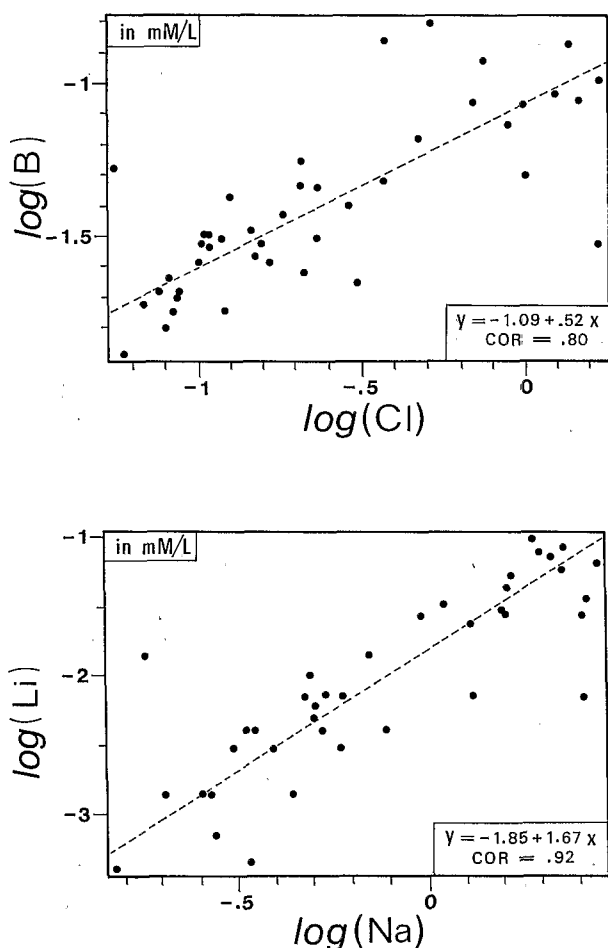


FIG. 5. Boron versus chloride and lithium versus sodium concentration for dilute (ALT) inflow waters in Bolivian salars (COR = correlation coefficient).

ters and about half of EVA inflow waters should become carbonate-rich brines. The lower proportion of EVA inflow waters predicted to become alkaline is probably due to the higher amount of Ca relative to  $\text{HCO}_3^-$  in ancient evaporites. However, as shown in Fig. 9 and Tables 1 and 3, only 6 salars out of 30 are actually alkaline with brine pH above 9. All others are of the Na-Cl and Na-Cl-( $\text{SO}_4$ ) types with brine pH below 9. Several of them are fed largely, or even exclusively, by inflow waters that should end up as carbonate-rich brines. Two out of three of the freshwater lakes (TUR and TOT) show a clear incipient alkaline evolution. Trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ), a typical mineral of alkaline soda lakes, has been found in efflorescent crusts around several springs feeding neutral salars (CHU a, PAG c, PAG e, CLD a, CLD d, CLD h). Trona disappears completely downstream. Only salts of the neutral facies are found in the salars themselves. All these observations suggest that carbonate-rich salars should be more common on the Altiplano. The usual explanation to this anomaly is the precipitation of Mg-silicates (HARDIE and EUGSTER, 1970).

Authigenic Mg-silicates are commonly formed in closed-basin environments (HARDIE, 1968; HUERTAS et al., 1970; HARDIE and EUGSTER, 1970; TARDY et al., 1974; GAC et al.,

1977; CARMOUZE et al., 1977; SINGER, 1981). Updated information may be found in studies by JONES (1986) and GUVEN (1988) for Mg-smectites and by JONES and GALAN (1988) for chain clays. Authigenic smectites, probably of the stevensite group, crystallize at the expense of diatom frustules in several Bolivian salars (BADAUT and RISACHER, 1983). The effect of coprecipitation of calcite and Mg-silicates on the evolution of an evaporating water can be considered as follows:

$$\begin{aligned} (\text{alk}) - 2(\text{Ca}) - 2(\text{Mg}) \\ = (\text{Na}) + (\text{K}) + (\text{Li}) - (\text{Cl}) - 2(\text{SO}_4). \quad (4) \end{aligned}$$

If (alk) is greater than  $2(\text{Ca}) + 2(\text{Mg})$  in the initial inflow water, then the right-hand term will remain positive and regularly increasing during evaporative concentration, as long as only calcite and Mg-silicates precipitate. The water will become alkaline. On the other hand, if (alk) is lower than  $2(\text{Ca}) + 2(\text{Mg})$ , then the water will evolve into a neutral brine. Magnesium-silicate formation is thus another critical step in water evolution. If (alk) -  $2(\text{Ca})$  is positive, and (alk) -  $2(\text{Ca}) - 2(\text{Mg})$  negative, then the precipitation of Mg-silicates will reverse the initial evolution of the water from an alkaline to a neutral facies. A good illustration is described by HARDIE and EUGSTER (1970). Figure 10 presents the distribution of the representative points of all inflow waters in a plot of (alk) versus  $2(\text{Ca}) + 2(\text{Mg})$ . Solid circles and triangles with an arrow are inflow waters that effectively become alkaline. Those without an arrow are waters that should become alkaline but that actually evolve into neutral brines. Therefore, Mg-silicate authigenesis alone does not appear to explain the reverse evolution of many inflow waters.

The removal of Mg by Mg-calcite or dolomite has an effect on alkalinity similar to that caused by the removal of Mg by Mg-silicates. Actually, the fundamental ratio (alk)/ $2(\text{Ca}) + 2(\text{Mg})$  is not dependent on the nature of the weak-acid anion associated to Ca and Mg during evaporative concentration. Emphasis has been put on calcite and Mg-silicates because of their common occurrence in such environments.

Therefore, a peculiar process must be accounted for to explain the reverse evolution of many inflow waters and the subsequent scarcity of Na- $\text{CO}_3$  salars in the Bolivian Altiplano. To determine the nature of this process, we have looked for a sequence of evaporating waters that presents a clear anomaly in its evolutionary path.

#### BRINE EVOLUTION AT THE EASTERN SHORE OF LAGUNA COLORADA

##### Geological and Geochemical Setting

Laguna Colorada (CLD) is fed by numerous springs and rivers. At the eastern shore several rivers feed an unconfined aquifer in volcanic gravels (Fig. 11). The water table is very close to the topographic surface and sometimes slightly above, giving rise to small, shallow pools of 1 to 10 meters in diameter where waters undergo evaporative concentration. Six dilute to saline waters were sampled in these pools. The lake brine was also collected. Results of chemical analyses are given in Table 5. The lake brine is of the Na-Cl type. The most dilute of these waters is referred to as the inflow water. Calcite and Mg-smectites, of the same kind as those described by BADAUT and RISACHER (1983), were found in these pools. Aragonite is precipitating in the lake. Around the pools, efflorescent salts are principally made up of mirabilite (which dehydrates into pulverulent thenardite,

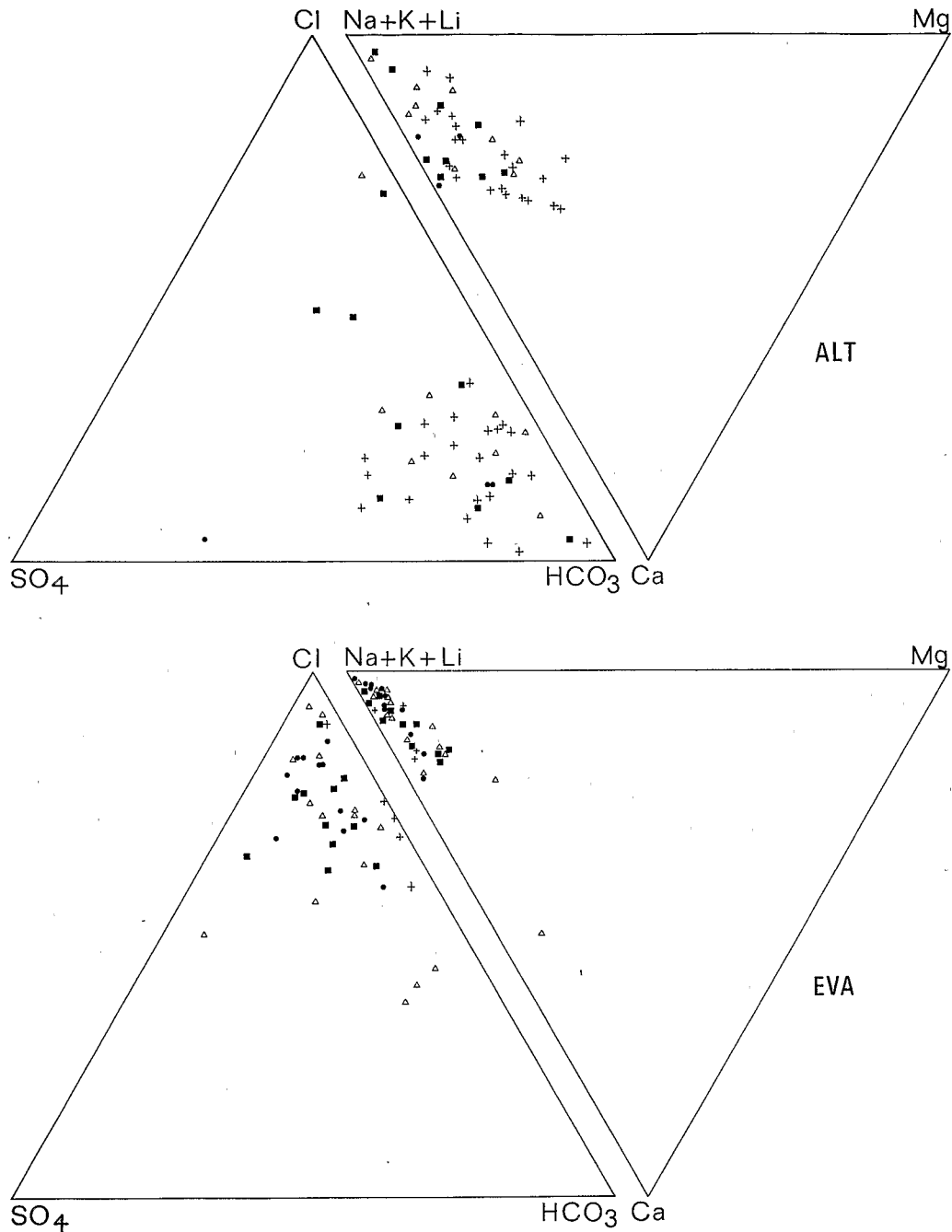


FIG. 6. Composition of inflow waters in Bolivian salars. Crosses = rivers; open triangles = springs,  $T < 10^{\circ}\text{C}$ ; solid squares = springs,  $10 < T < 15^{\circ}\text{C}$ ; solid circles = springs,  $T > 15^{\circ}\text{C}$ .

$\text{Na}_2\text{SO}_4$ ) and halite. Mirabilite precipitates also by freezing-out in the lake. Aphantite has been found in minor quantity in efflorescences derived from the most dilute waters. Trona has been detected only far up-river in efflorescences on one river bank. The representative point of the inflow water (named CLD) in Figs. 8 and 10 is clearly in the alkaline evolution area. Plots of saturation index for each mineral are shown in Fig. 12.

The evaporation of the inflow water has been simulated with the program of RISACHER and FRITZ (1984). This code is based on an ion-association model and an extended Debye-Hückel equation for activity coefficients. It accurately handles solutions at ionic strength up to 1 ( $\sim 50$  g/L TDS). At higher concentration, its accuracy de-

creases, especially for minor minerals. This is of little concern to our modeling inasmuch as the crucial shift in the water evolution occurs at low concentration (0.5–1 g/L), which corresponds to ionic strengths below 0.02. Moreover, this code takes into account the temperature dependence of almost all constants, and includes silica and Mg-silicate in its mineral data bank. The final calculated brine (TDS = 120 g/L) is of the Na-Cl type, but with higher pH (9.4) and higher alkalinity (49 meq/L) than those of the lake brine (8.4 and 31.5, respectively). The calculated final brine is in equilibrium with calcite, Mg-silicate, hydromagnesite, mirabilite, and borax, the latter a typical mineral of highly alkaline environments. Hydromagnesite and borax do not precipitate from the actual concentrated CLD brines.

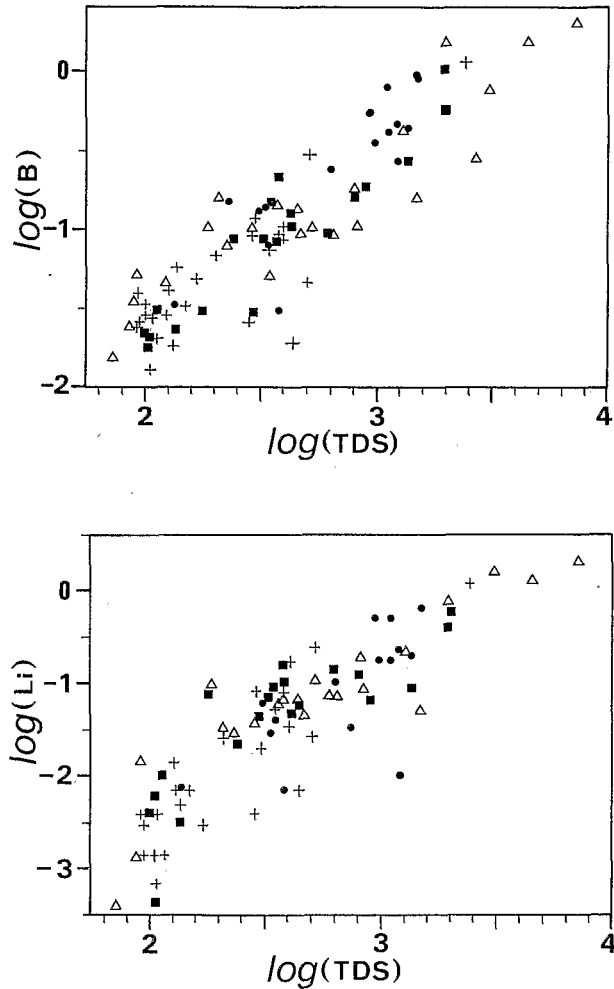


FIG. 7. Lithium and boron concentrations (in mM/l) versus Total Dissolved Solids (in mg/L) for all inflow waters in Bolivian salars. Modified from RISACHER (1984). Symbols as in Fig. 6.

#### Behavior of Components

To understand the shift in CLD water chemistry, the concentration evolution of each component has been investigated. Chloride, one of the most conservative solutes, was chosen as a tracer, which is valid as long as there is no precipitation of Cl-bearing minerals, such as halite. Efflorescent salts complicate the solute behavior somewhat. Deflation (wind transport) removes an unknown proportion of these salts. Rainfalls redissolve the most soluble remaining salts and recycle them to the groundwater. Chloride is leached the most rapidly (DREVER and SMITH, 1978) and can thus be considered as the best conservative solute over a long-term period.

Figure 13 shows the relative variation of all components in CLD waters with respect to chloride. The calculated evaporation path is drawn for each solute. The theoretical sequences of precipitating minerals are indicated along these paths. Such ratio plots are very sensitive tests of the behavior of solutes (EUGSTER and JONES, 1979). Almost all solutes of CLD waters show a decrease in  $M/Cl$  ratio with increasing

Cl concentration, which indicates a loss relative to Cl. Only lithium behaves as a conservative solute. This confirms chloride as the best choice for a major-element tracer.

Sodium and sulfate behave in a quite similar way. They are likely to be removed by mirabilite in efflorescent crusts. However, all the waters sampled except the lake brine are undersaturated with respect to mirabilite, which occurs in efflorescences known to be derived from these same waters. This is emphasized in Fig. 13 by the observed non-conservative evaporation path of Na and  $SO_4$  as compared to their calculated conservative path up to the theoretical precipitation of borax and mirabilite. At low salinity, the loss of Na and  $SO_4$  is important. As the salinity of the water increases, the rate of removal decreases, and both Na and  $SO_4$  behave almost conservatively up to the precipitation of mirabilite (by freezing-out) in the lake brine. Only at this point do the theoretical and the actual evaporation path show the same trend. One possible explanation of the shape of the actual evaporation path is that the relative amounts of Na and  $SO_4$  removed by mirabilite in efflorescent salts are high with regard to their content in rather dilute waters, and then becomes increasingly small and unnoticeable as the salinity of the water increases. SMITH and DREVER (1976) discussed the control on groundwater chemistry by precipitation of salts during capillary draw. They concluded that such salts can effectively control groundwater chemistry in some settings, even though the groundwater is undersaturated with respect to these salts. However, the precise mechanism is not clear.

Sulfate depletion at CLD cannot be related to the reduction of sulfate to sulfide. In such a case alkalinity would increase and the evaporating water would tend to evolve to an alkaline brine (WHITTIG and JANITZKY, 1963; MAGLIONE, 1976, pp. 125-126; HAWKINS, 1985).

Calcium is removed by formation of calcite and aragonite

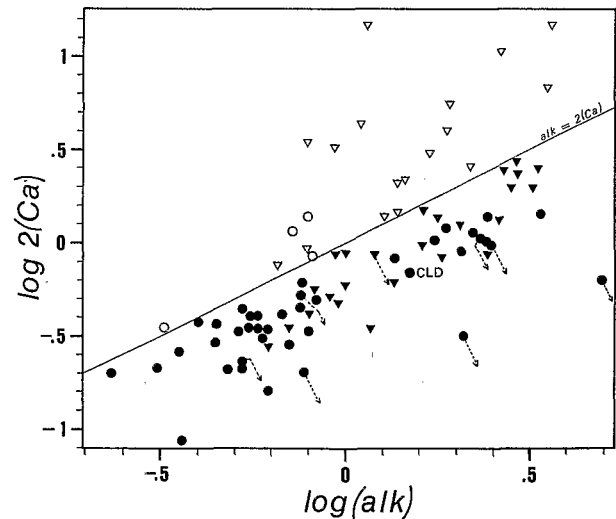


FIG. 8. Calcium concentration ( $\times 2$ ) versus alkalinity for inflow waters in Bolivian salars. Calcium in mM/L and alk in meq/L. Circles = ALT inflow waters; triangles = EVA inflow waters. Open symbols are waters which should become calcium-rich and carbonate-poor by calcite precipitation and evaporation. Solid symbols are waters which should evolve conversely and become alkaline. Arrows indicate those waters which actually become carbonate-rich.

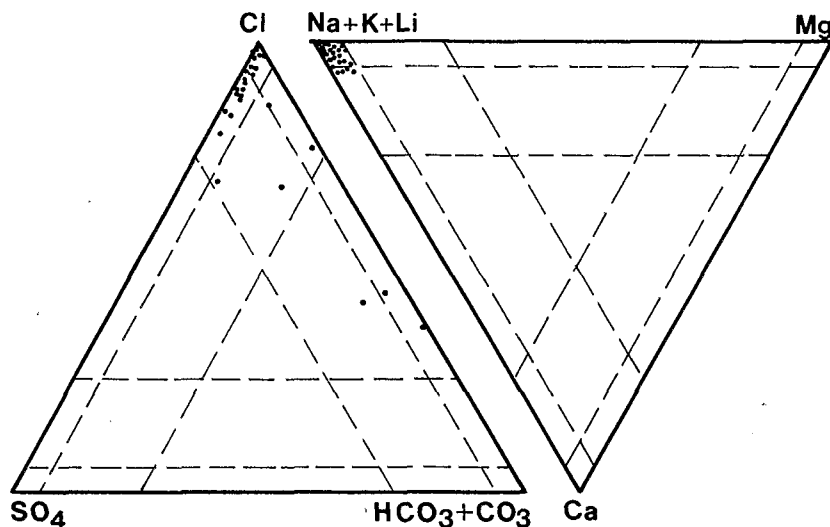


FIG. 9. Brine compositions (in mol%) of Bolivian salars. Field boundaries are at 5 and 25%, according to the classification of EUGSTER and HARDIE (1978). For more details, see Table 1.

in the pools. The calculated loss of calcium is also related to the precipitation of calcite. It is higher than the real loss. The calculated evaporating water evolves theoretically into an alkaline-rich brine very low in calcium. In contrast, the real evaporating water, because of its lower alkalinity, has a higher calcium content. Gypsum does not seem to interfere inasmuch as all waters are markedly undersaturated with respect to gypsum (Fig. 12). Moreover, this mineral has not been detected by XRD. Magnesium is taken up by magnesium-silicates associated with diatom frustules. There is a good agreement between the calculated and the actual evaporation path, up to the theoretical precipitation of hydromagnesite. Silica is removed by diatoms and Mg-smectites. The calcu-

lated loss of silica is controlled by the formation of Mg-silicates. It is higher than the measured loss. The behavior of silica in CLD waters seems to be controlled by an amorphous silica phase (Fig. 12). Boron shows an erratic behavior, which might be related to adsorption on detrital illite (HARDER, 1959; ADAMS et al., 1965), to substitution for Si in silica precipitates, or to the uptake by organisms (see JONES et al., 1977, p. 68). The loss of alkalinity is the main problem. Calcite, aragonite, and Mg-silicates use up only a fraction of the alkalinity, so there remains an unexplained additional deficit.

A semi-quantitative approach to mass balance during evaporative concentration at CLD was attempted. The ab-

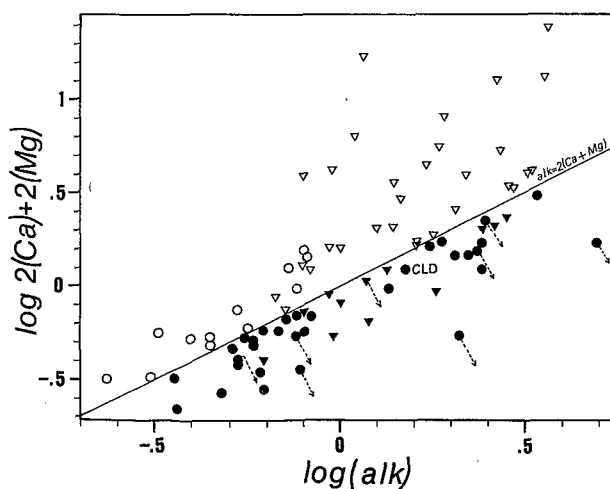


FIG. 10. Calcium ( $\times 2$ ) plus magnesium ( $\times 2$ ) concentration versus alkalinity for inflow waters in Bolivian salars. Calcium and magnesium in mM/L, alk in meq/L. Circles = ALT inflow waters; triangles = EVA inflow waters. Open symbols are waters which should become calcium-rich and carbonate-poor. Solid symbols are waters which should evolve conversely and become alkaline. Arrows indicate those waters which actually become carbonate-rich.

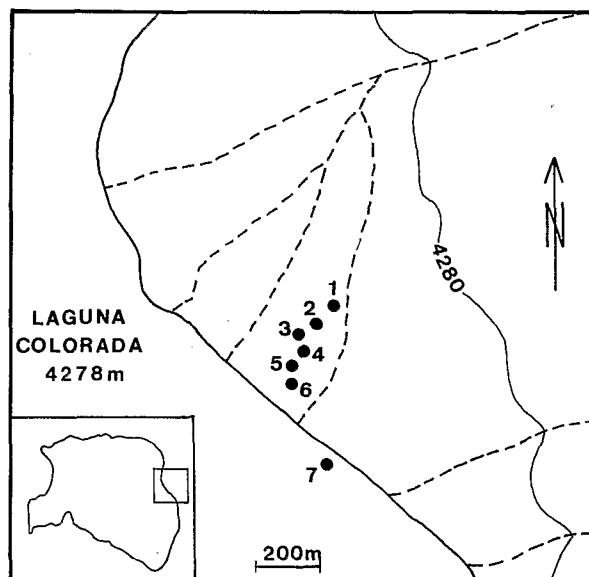


FIG. 11. Index map of Laguna Colorada. Numbers refer to analyses given in Table 5.

Table 5. Chemical analyses of CLD waters (Temperature in °C; density in g/cm<sup>3</sup>; alk in meq/l; TDS in mg/l; others in mM/l). Sampling locations are shown in Fig. 11.

	Temp.	Density	pH	alk	Cl	SO <sub>4</sub>	B	Si	Na	K	Li	Ca	Mg	TDS
1	6	1	8.76	1.49	6.59	0.99	0.500	1.01	8.48	0.583	0.110	0.344	0.272	752
2	4.5	1.001	8.78	1.88	15.8	1.70	0.709	0.983	18.4	1.19	0.223	0.484	0.560	1410
3	5	1.002	8.88	3.42	43.9	3.79	1.06	1.36	47.8	2.32	0.663	1.52	1.53	3520
4	5	1.006	8.92	3.69	106	8.59	3.57	1.04	113	6.27	1.63	1.60	1.98	7880
5	5	1.017	9.10	13.3	335	26.8	19.4	1.27	350	21.4	5.26	2.99	5.88	24760
6	10	1.040	8.52	12.9	831	62.3	24.3	1.16	865	54.0	12.5	2.57	15.7	59180
7	6	1.081	8.40	31.5	1830	67.1	56.6	1.63	1770	109	28.2	6.48	37.6	120400

solute loss,  $\Delta E$ , of any component can be calculated as a function of chloride as follows:

$$\Delta E = V_o E_o - VE \quad (5)$$

where  $V_o$  and  $V$  are, respectively, the volume of inflow water and the remaining volume of water after evaporation.  $E_o$  and  $E$  are, respectively, the concentration of solute  $E$  in the inflow water and in the evaporated water.

If Cl is conserved, then

$$V_o Cl_o = V Cl \quad (\Delta Cl = 0). \quad (6)$$

By combining Eqns. (5) and (6) and eliminating  $V$ , we obtain

$$\Delta E = V_o Cl_o [E_o / Cl_o - E / Cl]. \quad (7)$$

Figure 14 presents the cumulative deficits of the main components as a function of chloride calculated by means of Eqn. (7). Such a diagram is only a crude attempt to compare semi-quantitative estimates of the loss of each component. This representation first confirms that calcite and Mg-silicates (Ca + Mg deficits) are not sufficient to account for the total loss of alkalinity. Another anomaly can be observed. If Na and K are removed exclusively as sulfate minerals, then their deficit should equal that of sulfate. However, as shown in Fig. 14, there is a large excess loss of alkali cations relative

to sulfate loss. Two possible processes can be contemplated: (1) the loss of alkali cations used up with weak anion-bearing minerals or adsorbed on active surfaces, and (2) the oxidation of sulfide or sulfur into sulfate. Both processes would lead to a significant reduction of alkalinity.

### The Removal of Alkali Cations

The removal of alkali cations in neutral facies salts does not preclude some other depletion process for these cations. Except for the very local up-river occurrence of trona, no alkali carbonates have been detected in salts associated with brackish waters and brines. Boron depletion is much too low and erratic to be associated with the loss of alkali cations. Therefore, alkali cations should be associated with silicates. Several mechanisms are possible.

*Incorporation in Mg-smectites.* In Bolivian salars, authigenic smectites belong to the stevensite-saponite group. Such minerals also include some alkali cations. WEAVER and POLLARD (1975, pp. 78–80) report contents as high as 2.2% Na<sub>2</sub>O and 0.43% K<sub>2</sub>O in stevensite-hectorite samples. In one Bolivian sample, BADAUT et al. (1979) report as much as 0.9% K<sub>2</sub>O. If we relate all the Mg deficit to the authigenesis of Mg-smectites, then the associated deficits of Na and K would amount, respectively, to about 0.3 and 1% of their real deficits. Even dealing with gross estimates, these values suggest some other process for the removal of alkali cations.

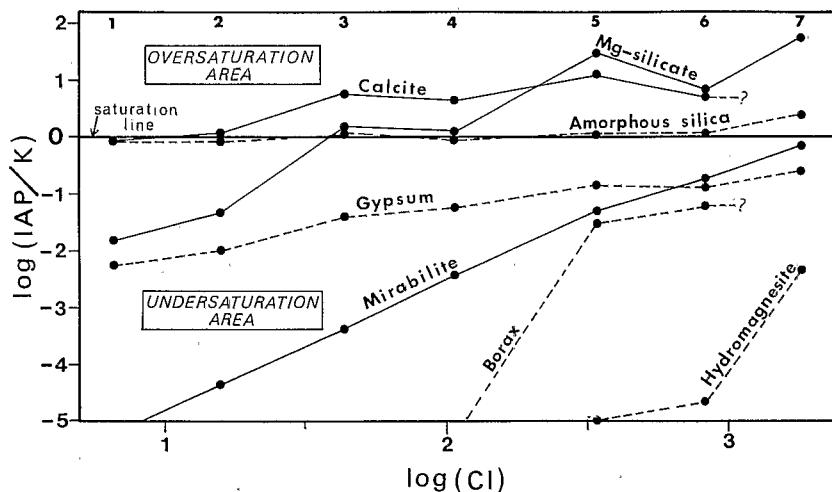


FIG. 12. Plots of saturation index for minerals of interest in the evaporating waters at CLD. IAP = Ionic Activity Product;  $K$  = solubility product. Chloride concentration in mM/L. Upper numbers refer to sample numbers in Table 5.

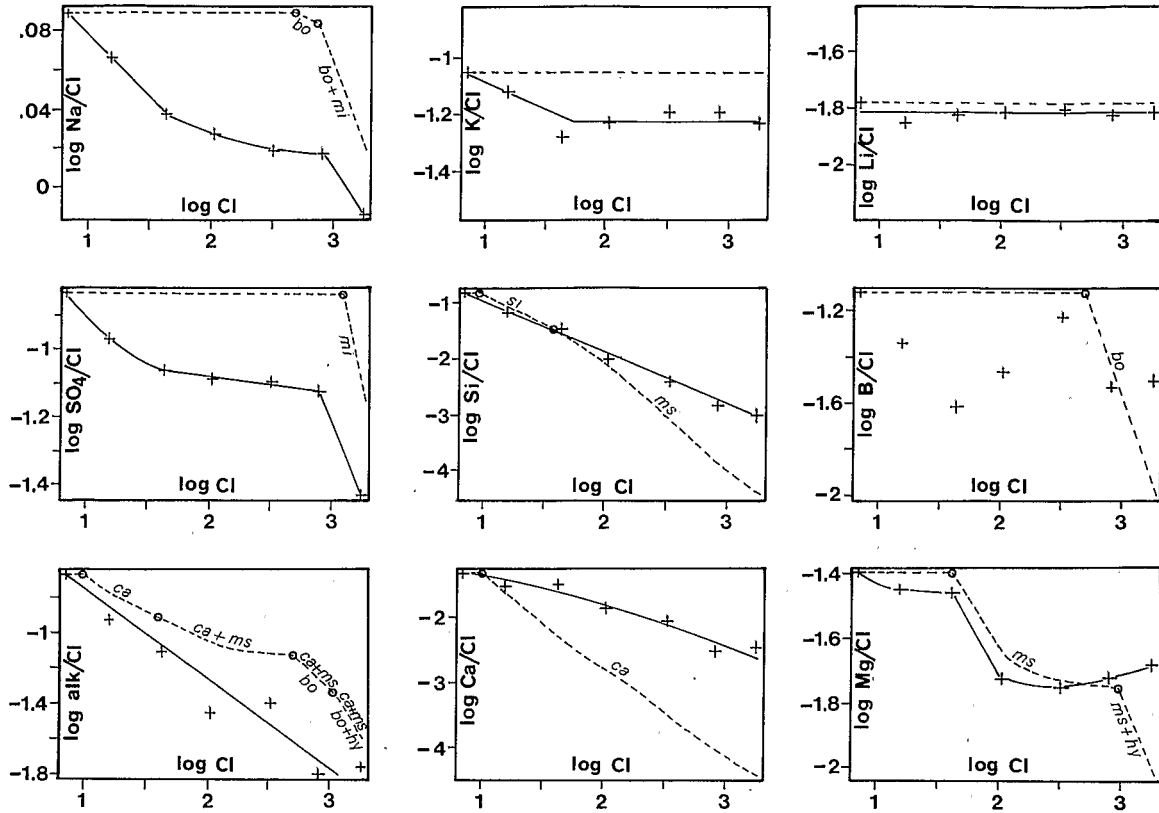


FIG. 13. Evolution of components in a sequence of evaporating waters at CLD. All concentrations are in mM/L, except alk which is in meq/L. Solid curves show the observed evolution of the solutes. Dashed curves show the calculated evaporative concentration. Open circles on the dashed curves indicate the appearance of minerals. The sequence of minerals is pointed along the curves: si = amorphous silica; ca = calcite; ms = Mg-silicate; bo = borax; mi = mirabilite; hy = hydromagnesite.

The formation of zeolites would explain both the qualitative and the quantitative features of CLD water evolution. Volcanic glass is undergoing alteration in brackish and saline waters of rather high pH (8.4–9.1) and high silica content. These are two main conditions for zeolite formation (HAY,

1977; SURDAM, 1977). However, XRD and SEM examinations of volcanic material of the gravel aquifer did not show the least trace of zeolites. This does not prove the lack of zeolites at CLD but suggests that such minerals are probably not responsible for the strong depletion of alkali cations.

*Other processes.* The removal of K is often related to adsorption on active silica surfaces (EUGSTER and JONES, 1979). However, such a process is not commonly reported for Na, which is the major alkali cation at CLD. Experimental data are difficult to extend to natural environments. The best way is to compare CLD with other similar basins. Lake Magadi (JONES et al., 1977) and Lake Natron (GUEDDARI, 1984; FRITZ et al., 1987) are soda lakes in volcanic areas. Springs flow into peripheral lagoons which act as preconcentration basins in the same way as surface pools do at CLD. In both cases, Na is perfectly conserved. THOMAS et al. (1989) even report an enrichment of Na in a closed basin in Nevada where Ca and Mg in the water are exchanged for Na adsorbed on clays. This is not the case for closed basin lakes of the Ethiopian Rift (VON DAMM and EDMOND, 1984). The authors assume a removal of Na by Na-montmorillonite or Na-feldspar. None of these mineral has been detected at CLD. YURETICH and CERLING (1983) report a substantial loss of Na in waters from Lake Turkana by ion exchange processes involving detrital smectites. At CLD, illite is the main detrital mineral. However, it only constitutes a small fraction of the

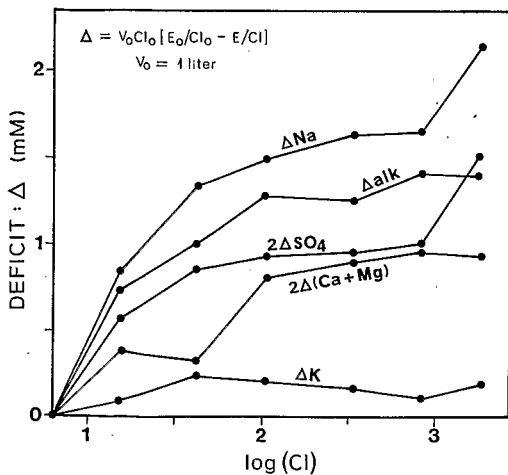


FIG. 14. Cumulative deficits (in mM) of cations, sulfate, and alkalinity as a function of chloride (in mM/L). Deficits are related to one liter of CLD inflow water.

Table 6. Elemental sulfur content (in ppm) and main components of colluvium sediments (in weight percent). Sampling locations in Fig. 2.

	S (ppm)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	CaO	Fe <sub>2</sub> O <sub>3</sub>	Mn <sub>3</sub> O <sub>4</sub>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>
1 T	175	68.8	16.3	3.28	2.87	1.15	4.0	3.5	0.050	0.43	0.16
F	587	61.7	16.0	2.98	2.39	2.60	4.3	7.1	0.114	0.83	0.20
R	100	71.2	14.9	3.26	2.94	0.63	3.6	2.3	0.037	0.35	0.11
2 T	339	64.2	16.0	3.04	2.83	2.55	4.1	6.1	0.118	0.70	0.19
F	795	61.0	17.5	2.76	2.20	2.61	4.0	7.5	0.130	0.97	0.20
R	136	64.4	14.6	3.02	2.83	2.56	4.0	5.9	0.113	0.74	0.17
3 T	1240	67.1	16.2	3.02	2.34	1.69	3.3	4.6	0.071	0.66	0.21
F	752	62.2	17.1	2.70	2.44	2.21	3.7	6.7	0.133	0.90	0.21
R	108	68.4	15.5	3.08	3.11	1.74	3.5	4.3	0.062	0.65	0.17
4 T	408	56.7	17.6	3.40	1.66	3.77	5.7	8.1	0.143	0.84	0.22
F	419	61.4	16.7	2.70	1.94	2.54	3.9	8.2	0.154	1.13	0.22
R	136	58.5	17.0	3.71	1.58	3.92	6.2	7.9	0.117	0.83	0.19
5 T	378	61.6	16.9	3.08	2.44	2.88	4.5	6.2	0.109	0.78	0.22
F	403	63.1	17.8	2.77	2.02	2.32	4.1	6.5	0.125	0.86	0.22
R	160	63.9	16.2	3.31	2.53	2.94	4.8	5.2	0.085	0.70	0.20
6 T	295	63.6	16.7	2.92	2.89	2.34	3.9	5.7	0.115	0.67	0.21
F	616	63.5	17.7	2.56	2.38	2.02	2.9	6.3	0.106	0.82	0.24
R	135	64.5	16.0	3.08	2.83	2.60	4.4	6.0	0.108	0.69	0.19
7 T	257	65.9	16.7	3.24	3.06	1.56	3.8	4.6	0.081	0.60	0.18
F	593	63.2	17.7	2.75	2.28	2.51	3.7	7.6	0.118	0.94	0.24
R	126	67.3	15.9	3.35	3.25	1.34	3.7	3.9	0.060	0.54	0.15
8 T	685	63.9	16.2	3.46	2.67	2.22	4.1	5.5	0.092	0.84	0.21
F	992	65.4	16.3	2.55	2.23	1.90	3.1	6.2	0.115	0.83	0.26
R	355	64.8	15.6	3.66	2.74	2.29	4.2	5.3	0.077	0.79	0.20
9 T	7580	66.8	17.5	2.68	3.49	1.28	2.7	5.3	0.094	0.79	0.26
F	6050	62.8	19.2	2.42	2.42	1.62	3.0	7.3	0.174	0.96	0.29
R	8640	68.1	15.3	2.72	3.66	1.25	2.4	4.3	0.059	0.74	0.21
10T	7920	67.0	15.6	2.48	3.25	1.32	2.4	4.9	0.045	0.83	0.25
F	6250	63.8	17.6	2.06	2.69	1.57	2.4	8.2	0.043	0.85	0.29
R	6070	69.7	14.6	2.58	3.40	1.20	2.5	4.3	0.050	0.85	0.22
11T	701	65.6	16.2	2.98	3.13	1.83	3.3	5.9	0.081	0.77	0.15
F	602	63.9	16.7	2.88	2.64	2.01	3.6	6.5	0.120	0.94	0.20
R	302	67.3	15.1	3.18	3.61	1.58	3.0	4.6	0.065	0.70	0.19

T: total sediment; F: fraction size below 63  $\mu$ ; R: cleaned rock particles.

whole sediment. It is only detectable by XRD after separation procedures. Moreover, its exchange capacity is low (about 25 meq/100 g) and potassium is the major interlayer cation (WEAVER and POLLARD, 1975).

Therefore, alkali cations are probably not removed significantly as silicate phases and thus are probably not responsible for the excess deficit of alkalinity. Their removal must be almost completely related to the formation of neutral-facies salts, especially sulfates, precipitating in efflorescent crusts.

#### The Oxidation of Sulfide and/or Sulfur into Sulfate

One possible explanation for the data in Fig. 14 is the existence of an excess sulfate source. In this model, additional sulfur (or sulfide) is brought in the waters of the gravel aquifer where it is oxidized into sulfate and rapidly removed as sulfate minerals. The overall effect as shown in Fig. 14 is an apparent slight depletion of sulfate. If all alkali cations are removed as sulfate, the amount of oxidized sulfate would be the difference between the total loss of alkali cations and the apparent loss of sulfate. Such oxidation leads to an acidification of the water and therefore to a reduction of alkalinity. This process has been described in the Lake Chad basin by CHEVERRY (1974) and EUGSTER and MAGLIONE (1979).

#### ORIGIN OF ADDITIONAL SULFUR

The question arises as to the origin of the possible additional sulfur or sulfide. The anomalously low alkalinities are

observed in the whole study area. Anomalous salars do not seem to be associated with peculiar rocks in their drainage basin, nor to sulfide-containing ore deposits. The possibility of detrital or bedrock sulfides from an eroded fossil hydrothermal system cannot be discounted (ALPERS and BARNES, 1986; ALPERS and WHITTEMORE, 1990). However, it is difficult to generalize such a mechanism to the whole study area.

A possibility is that significant native sulfur may occur in wind-blown sediments, which could account for its wide distribution. Eleven colluvium samples from the northern part of the study area were investigated (location in Fig. 2). Each sample was divided into three subsamples: (1) a part of the total sample (*T*), (2) the silt and clay-size fraction (below 63  $\mu$ ), to which most of the wind-blown particles belong (*F*), and (3) the volcanic rock fragments carefully cleaned by ultrasound to remove all attached particles (*R*). Elemental sulfur as well as major and minor elements were determined in each subsample (Table 6). No sulfides nor sulfates were detected.

In most samples, sulfur is clearly enriched in the silt and clay fraction of the total sediment. Samples 9 and 10, of high sulfur content, were collected close to native sulfur deposits, where volcanic rocks are already enriched in sulfur. Major and minor element contents are not significantly different in each set of three subsamples. This strongly suggests a surficial enrichment of elemental sulfur eroded from the exposed sul-

Table 7. Chemical analyses of leachates of colluvium sediments (in mM/L, except alk in meq/L). The identification number following L is the same as in Table 6. Leached fractions: T: total sediment; F: fraction size below 63  $\mu$ ; R: cleaned rock particles.

	pH	alk	Cl	SO <sub>4</sub>	Si	Na	K	Ca	Mg
L1 T	5.48	0.016	0.078	0.192	0.224	0.105	0.097	0.105	0.051
F	6.16	0.050	0.048	0.191	0.036	0.051	0.077	0.123	0.056
R	6.87	0.079	0.023	0.005	0.236	0.057	0.035	0.012	0.005
L2 T	5.84	0.188	0.140	0.078	0.254	0.162	0.064	0.096	0.025
F	5.89	0.088	0.084	0.034	0.042	0.067	0.051	0.048	0.014
R	7.13	0.150	0.022	0.014	0.234	0.126	0.047	0.016	0.009
L3 T	6.86	0.181	0.560	0.138	0.447	0.137	0.482	0.200	0.042
F	6.07	0.055	0.112	0.030	0.089	0.068	0.088	0.038	0.009
R	6.88	0.094	0.022	0.024	0.249	0.070	0.034	0.026	0.011
L4 T	7.12	0.284	0.188	0.240	0.510	0.200	0.133	0.301	0.065
F	6.16	0.069	0.054	0.035	0.099	0.053	0.064	0.037	0.009
R	7.17	0.163	0.012	0.007	0.215	0.043	0.020	0.045	0.030
L5 T	7.37	0.969	0.145	0.133	0.516	0.201	0.240	0.414	0.094
F	6.60	0.062	0.135	0.023	0.139	0.050	0.089	0.037	0.009
R	7.13	0.156	0.013	0.006	0.194	0.052	0.028	0.041	0.019
L6 T	5.41	0.016	0.113	0.163	0.212	0.120	0.047	0.144	0.028
F	6.44	0.038	0.088	0.079	0.036	0.075	0.053	0.066	0.013
R	6.78	0.063	0.012	0.049	0.198	0.095	0.036	0.019	0.014
L7 T	5.69	0.166	0.070	0.055	0.204	0.101	0.050	0.079	0.013
F	6.41	0.056	0.030	0.027	0.039	0.038	0.030	0.029	0.007
R	6.95	0.088	0.011	0.008	0.204	0.058	0.035	0.014	0.006
L8 T	7.14	0.353	0.104	0.086	0.212	0.088	0.139	0.184	0.028
F	6.31	0.143	0.089	0.043	0.042	0.042	0.107	0.080	0.015
R	6.86	0.097	0.026	0.032	0.271	0.116	0.047	0.017	0.008
L9 T	7.43	1.09	0.171	0.248	0.486	0.231	0.470	0.445	0.155
F	6.50	0.148	0.075	0.049	0.137	0.055	0.154	0.056	0.019
R	6.40	0.025	0.019	0.071	0.162	0.055	0.043	0.035	0.015
L10 T	3.76	-0.253	0.157	4.92	0.787	1.51	0.275	3.34	0.492
F	3.91	-0.180	0.013	2.78	0.083	0.267	0.260	2.19	0.218
R	4.84	-0.031	0.039	0.224	0.288	0.082	0.034	0.137	0.034
L11 T	6.70	0.209	0.132	0.113	0.442	0.212	0.092	0.120	0.045
F	6.41	0.056	0.063	0.013	0.071	0.042	0.058	0.020	0.008
R	7.20	0.169	0.020	0.021	0.275	0.159	0.044	0.013	0.005



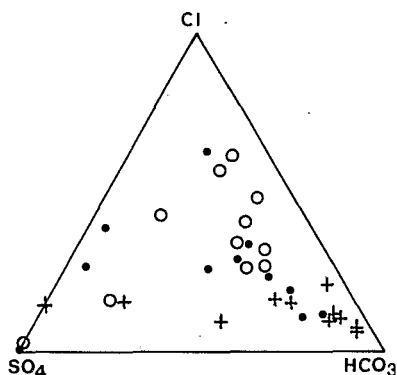


FIG. 15. Anion proportions in leachates of three fractions of eleven colluvium samples. Open circles = total samples (*T*); solid circles = fraction-size  $< 63 \mu$  (*F*); crosses = clean rock fragments (*R*).

fur deposits and blown away by the wind. These deposits occur most commonly near the summits of the volcanoes, where they undergo active wind erosion. Fumaroles may also contribute to the supply of sulfur in the atmosphere.

Wind-blown sulfur is not only deposited on the dry land but also on every body of water: rivers, pools, and lakes. Moreover, in the rainy season, surface runoff may carry along suspended sulfur particles into permanent pools of the pre-concentration areas. Additional sulfur has no major effect on the chemistry of concentrated waters, because of the already high sulfate content of these waters. In contrast, sulfur addition in dilute waters may have an important outcome in the evolution of these waters.

To check this point, each subsample was leached with deionized water. The total sample (*T*) and the cleaned rock fragments (*R*) were leached for two hours and the silt-clay fraction for ten minutes. Then, the leachates were analyzed for major components (Table 7). Anion proportions are plotted on a trilinear diagram (Fig. 15). Waters that have leached volcanic rock fragments are of the same type as ALT waters (except L9 and L10; cf. Fig. 6), whereas waters that have leached the whole sediment or the silt-clay fraction are impoverished in carbonate.

The diagram (alk) versus  $2(\text{Ca}) + 2(\text{Mg})$  clearly shows two groups of waters (Fig. 16). Those in contact with clean volcanic rocks are in the alkaline evolution area (except L9 and L10), whereas those in contact with the total sample or with the silt-clay fraction are all in the neutral facies area. Low alkalinity and low pH are correlated with high sulfate contents. Sulfur is apparently oxidized into sulfate. In waters in contact with the whole sample or with the silt-clay fraction, the oxidation of sulfur is able to neutralize enough alkalinity to change the ratio of (alk) to  $[2(\text{Ca}) + 2(\text{Mg})]$ . Sulfur oxidation seems to be a rapid process. The time of contact does not seem to modify the proportion of sulfate relative to salinity in the waters.

Three ephemeral streams (CAN d, e, f; location in Fig. 2, analyses in Table 3) were sampled during a rainy season in CAN basin. These very turbid streams were active for only a few hours. Two of them (CAN d, f) were draining sulfur-rich volcanic rocks. Their chemical compositions show the same trends as those of the experimental waters in contact

with colluvium samples. Strictly, all these observations only apply to the northern area, inasmuch as no colluvium samples of the southern area were studied. However, sulfur-rich volcanoes are distributed over the entire study area, and surficial sulfur enrichment is likely to occur almost everywhere.

Therefore, the addition of wind-blown elemental sulfur in dilute inflow waters seems to be a likely mechanism to account for the excess neutralization of alkalinity and the corresponding evolution in water chemistry to near-neutral as opposed to alkaline compositions.

## CONCLUSIONS

The origin of solutes in Bolivian salars may be accounted for by two major processes: (1) meteoric as well as hydrothermal alteration of volcanic rocks leading to Na-HCO<sub>3</sub> inflow waters, and (2) leaching of ancient evaporites trapped below the extensive volcanic structures. This latter process leads to Na-Cl inflow waters. Such a mixed origin of solutes has also been described by ALPERS and WHITTEMORE (1990) in nearby salars of northern Chile. Atmospheric precipitation contributes little solute material. Only Ca and SO<sub>4</sub> are carried by rainwaters in any significant amount (10% of all contributions).

The evaporative concentration of the inflow waters leads preferentially to neutral brines of the Na-Cl or Na-Cl-(SO<sub>4</sub>) type. This is often in contradiction with the calculated evaporation path based on thermodynamic equilibrium, which indicates that many inflow waters should end as alkaline brines. The most likely mechanism explaining such a shift is the oxidation of wind-blown native sulfur in the dilute waters. Acid ephemeral streams draining sulfur-enriched colluvium may also contribute to the acidification of the waters and the related reduction of alkalinity.

A relation between brine evolution and the classification system of the Bolivian salars can be inferred. Most alkaline soda salars belong to the lake type (KAR, COL, HDS, CAT). Springs and seeps are often close to the shore. Inflow waters directly enter the brine bodies without going through pre-concentration areas. One lake (HDS) is exclusively fed by

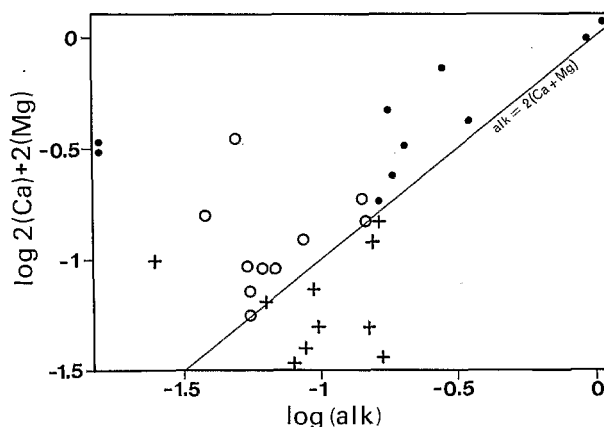


FIG. 16. Calcium ( $\times 2$ ) plus magnesium ( $\times 2$ ) concentrations versus alkalinity for leachates of three fractions of ten colluvium samples (L10 not included). Open circles = total samples (*T*); solid circles = fraction-size  $< 63 \mu$  (*F*); crosses = clean rock fragments (*R*).

underground discharge. Dilute inflow waters are not exposed for a long time to atmospheric dust, and their contact time with colluvium sediments is minimized. In contrast, neutralization of alkalinity by sulfur oxidation, and the subsequent shift in the brine evolution, occurs preferentially where dilute inflow waters remain for a long time in preconcentration areas before reaching the central low. The time of contact of water with Earth material, as a controlling factor of the chemistry of saline lakes, has been stressed previously by JONES and VAN DENBURGH (1966).

Such hydrologic control may have had a peculiar effect on the chemistry of ancient Bolivian lakes. Presently, all such lakes are at low levels. Frequently, inflow waters emerge at rather high elevation in the drainage basin and slowly flow through the colluvium before reaching the topographic low. In contrast, ancient lakes were once at higher levels and springs were therefore closer to the shore. The oxidation of sulfur may not have been effective enough to be able to neutralize the alkalinity of large volumes of inflow waters in limited contact with the atmosphere and the colluvium. Therefore, the general chemistry of some lakes may have changed during the Quaternary. Some of the present neutral lakes could be the remnants of ancient alkaline lakes. KEMPE and DEGENS (1985) speculated on a similar shift of the ocean composition in Precambrian times.

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