Geochemistry of bitter brines in the Salar de Coipasa – Bolivia

V. Lebrun[1], P. Pacosillo[2], J. Gutierrez[2], F. Caceres[1], E. Pool[2] & E. Pirard[1]

1. Laboratoire MICA, Universitè de Liège, Avenue des Tilleuls 45, 4000 Liège, eric.pirard@ulg.ac.be
2. Universidad Tecnica de Oruro, Av. 6 Octubre 5715, Oruro – Bolivia, dpic@uto.edu.bo

ABSTRACT

The Salar de Coipasa is a 2 500 km^2 salt lake to the North of the Uyuni salt lake in the Bolivian Altiplano. Unlike Uyuni, Coipasa had not been explored systematically for the geochemistry of its brines. This paper presents results of a joint geological cooperation program between the Universities of Liege (Belgium) and Oruro (Bolivia) aiming to estimate the resources and genesis of Coipasa bitter brines.
Results indicate a noticeably higher Mg/Li ratio and a threefold sulfate enrichment in Coipasa with respect to Uyuni. The largest lithium concentrations (up to 800 mg/l) were found at the South-East border of the Salar. This region corresponds to the maximal extension of the permanent lake in the rainy season.

KEYWORDS
Altiplano, lithium, resources, salt lake

Geology of the Altiplano

The Altiplano is a 200 000 km² large closed basin situated at an altitude of 4 000 meter in the Bolivian Andes. It is limited to the East by the Cordillera Real and to the West by the Cordillera Occidental. Palaeozoic sediments (shales, sandstones, quartzites) are predominant in the Cordillera Real. They also constitute the basement of the Altiplano where they are overlaid by thick volcano-sedimentary series of Cretaceous, Tertiary and Quaternary age (sandstones, claystones, mudstones, shales and evaporites). The continental sedimentary sequence reaches a total thickness of about 15 000 meters. Gypsum diapirs of Tertiary age crop out in the North and Centre-East of the basin. The Cordillera Occidental has a volcanic origin. Strato-volcanoes, lava flows and ignimbrites overlying Tertiary formations represent the major part of this mountain range. Two wide salt crusts fill the central Altiplano: they are known as Salar de Uyuni (10 000 km², 3 653 m) and Salar de Coipasa (2 500 km², 3 656 m).

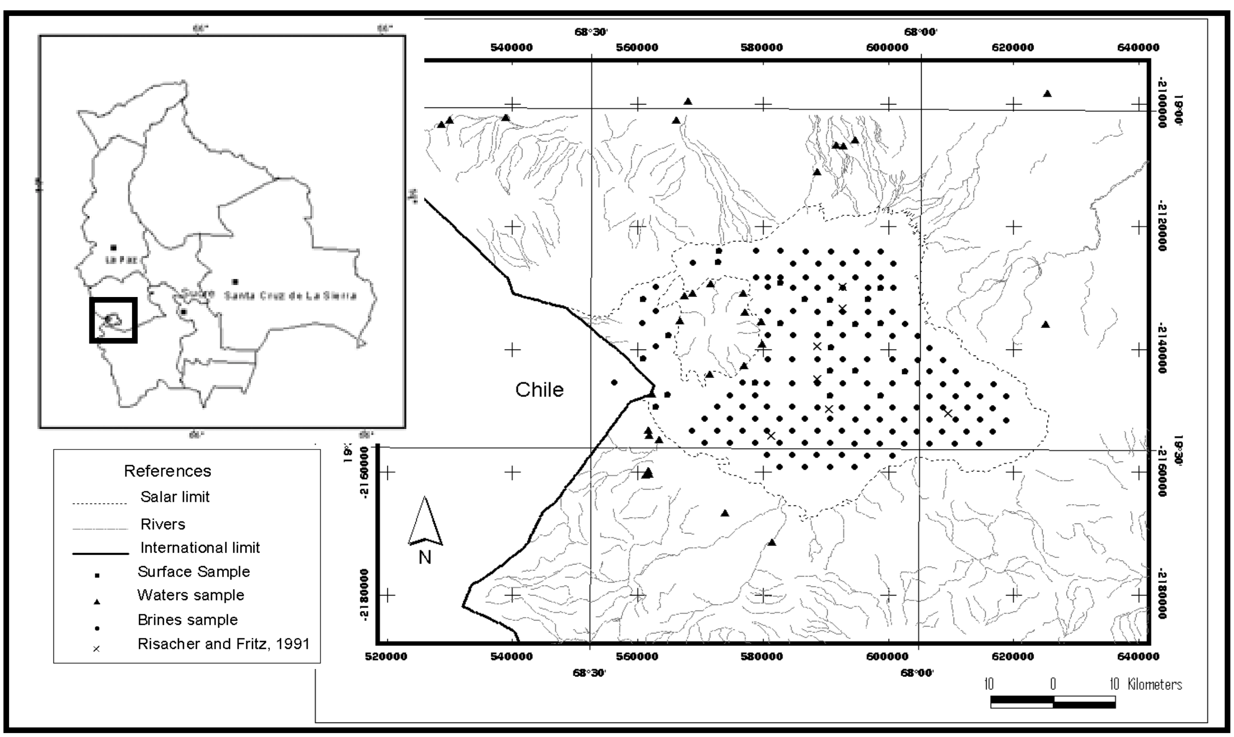

Figure 1 Location of the Salar de Coipasa at the border with Chile and sample location on the salt crust and in the tributary rivers.

The Uyuni and Coipasa salt lakes

The scientific discussion about the origin and chemistry of the Uyuni and Coipasa salt lakes began when Ericksen *et al*. (1978) first published the analyses of superficial brines. Rettig *et al*. (1979) and later Risacher and Fritz (1991) further studied these giant salt crusts and the entrapped brines. Both works largely contributed to the understanding of the general mechanisms of evaporite formation in the Altiplano.

The Uyuni salt crust has a maximum thickness of 11 m. It is made out of 95% halite and 5% gypsum with an average porosity of 30 to 40%. It contains interstitial brines whose table lies 10 to 20 cm below the surface (Risacher and Fritz, 1991). The Coipasa salt crust never exceeds 2.5m and is made out of porous halite passing towards more and more abundant mirabilite ($Na_2SO_4.10H_2O$) in the basal part (Risacher, 1992).

Numerous chemical analyses of brines from Uyuni pumped at various depths have been published (Risacher and Fritz, 1991). In the major part of the superficial crust, the Li and B contents vary from 0.1 to 1 g/l with a gentle northwards-decreasing gradient. An enrichment area has been discovered in the contact zone between the salt crust and the deltaic sediments of the Rio Grande Delta. In this region, the Li and B concentrations reach values up to 2 g/l and even 4 g/l locally . Mg and K contents also indicate a sharp increase. Until today, the number of chemical analyses available for Coipasa brines was insufficient to allow any consistent study. It is the aim of this paper to fill the lack of data on the Salar de Coipasa and to contribute to the description of the upper part of the lacustrine sediments.

Sampling strategy in the Salar de Coipasa

During the exploration survey of the Salar de Coipasa, a systematic grid with a mesh of 2 by 2 km has been superimposed on the salt crust for sake of gravity measurements. The same reference system has been used for the collection of superficial brines (Figure 1). Most brine samples have been taken by breaking the salt crust with an iron rod until reaching the brine table level (5 to 20 cm below the salt crust). For sampling at depth, a specific sampling method has been designed to avoid mixing brines originating from different levels. Nine bore holes were drilled with a percussion hammer (Atlas Copco Cobra) suited for drilling in soft terrains. In addition to the brine samples, waters from the tributary rivers and sources have been sampled all around the Salar.

The salt crust and the superficial lacustrine sediments

Risacher (1992) described a 2.5 meters thick salt crust, constituted by halite in its upper part and mirabilite ($Na_2SO_4.10H_2O$) in its lower part. In the nine bore holes of this study, we have only found 20 to 40 cm of halite crust. The lower 1 to 1.5 meters are invariably constituted of lacustrine sediments. These sediments are made of more or less sandy clays and sometimes sand in alternation. They contain gypsum and mirabilite crystals in variable proportions. At 1.8 meter deep in bore hole 7 and at 1.3 meter in bore holes 4a, 4b and 4c, we reached a muddy cluster of mirabilite crystals. This muddy cluster is up to 1 meter thick in bore hole 4c. In addition, in all the points where superficial brines were taken, the halite crust has been perforated and never exceeded 40 cm. Under the crust, we invariably found a black clay layer.

Geochemistry of Coipasa brines and waters

Tracing the evolution of the evaporative process

In the context of evaporative concentration, it is important to chose a parameter to trace the evolution of the system. Usually a conservative element known to remain in solution is used for this purpose. Because brines obviously reach halite saturation, the chloride ion cannot be used for this purpose. In Coipasa, Li^+ reaches important concentrations and appears to be the best candidate for tracing the evaporation. Li^+ has theoretically a strong affinity for ion-exchange sites on clay minerals, especially smectite. But, the lacustrine sediments extracted from the nine bore holes of this study are very poor in smectite (similar observations have been done in Uyuni (Shuler *et al*. 1995)). One could also argue that smectite with a large quantity of incorporated lithium ions could be confused with the pattern illite on the Xray diffraction. To verify this hypothesis, a normal smectite has been dipped into a brine from Coipasa but no noticeable change of the XRD pattern has been noticed after a few days.

Table 1 : Chemical analyses of the main tributary rivers from Coipasa and Uyuni.

River	Code	Cl mg/l	SO_4 mg/l	SO_4* mmol/l	HCO_3 mg/l	Na mg/l	K mg/l	K* mmol/l	Li Mg/l	Ca mg/l	Mg mg/l
r. Lauca	L33	191.1	146.97	12.8	268.07	154	17.2	3.7	0.48	60.0	33.5
r. Lauca	L28	585.1	417.66	15.8	271.18	484	37.6	3.5	1.1	80.0	45.6
r. Lauca	L27	954.4	409.22	12.2	383.27	808	38.7	2.8	1.4	56.4	33.7
r. Grande	UL-1	1580	313	3.3	-	908	41,9	1.1	4	202	56

Geochemistry of inflow waters

Chemical analyses of waters from the main tributary rivers of the Salar de Coipasa give some indications about the geographical origin of elements present in the brines (Table 1). As a point of comparison an analysis from the Rio Grande in Uyuni (UL-1 from Risacher and Fritz, 1991) is given. Results of normalisation with Li are shown here for SO_4 and K. The strong enrichment of rio Lauca with respect to rio Grande in sulfates is very noticeable. The much larger Mg/Li ratio in Coipasa waters with respect to Uyuni is already remarkable as will be observed in brines.

Geochemistry of brines

Table 2 displays basic statistics obtained from superficial brines of the Coipasa salt crust during this campaign. Statistics for Uyuni brines are given for comparison and were selected from the U series of Risacher and Fritz (1991) after elimination of deep brines and deltaic sediments. Uyuni brines have a noticeably higher Li content but rather similar K and lower Mg contents as compared to Coipasa. As already suspected from the rio Lauca analyses and the observation of sodium sulfates in the crust, the sulfate content of Coipasa is about three times larger than the one in Uyuni.

Iso-concentration curves for the spatial distribution of Lithium were computed using an inverse squared distance algorithm (Figure 2). The lowest concentrations are found at the West of the volcanic Island of Coipasa. This region is also the driest as it does not receive a lot of water from tributary rivers. On the contrary, the Eastern part of the salar is the more concentrated and the gradient increases when approaching the permanent lake fed by the Lauca River to the North and by the Laca Jauira River to the East.

Discussion

Mg, K, Li and B find their source in the leaching of rocks from the drainage basin and do not precipitate massively into evaporitic minerals. In Uyuni, it is most probable that ions transported by the Rio Grande during the dry season are concentrated at the interface between the salt crust and the deltaic sediments. Only ions brought to the salar during the rainy season, when the crust is flooded, can further diffuse. But due to the absence of a permanent lake only very little quantities of Li, K, Mg or B do reach areas that are distant from the Rio Grande delta. In the case of Coipasa, a permanent lake is established and operates a concentration of the bitter elements during the dry season but such a process is less efficient than it is in the deltaic sediments of Uyuni. During the rainy season, a sheet of water floods the entire salt crust. It is at the opposite of the Lauca delta, in the south eastern part of the Salar where evaporation is the most intense, that the highest concentrations are reached.

Conclusion

This paper presents a geochemical study, including original data, of the Salar of Coipasa, Bolivia. The analysis of these data allows to specify the nature of the brines and sediments found in the Salar. Among the new elements that have been put in evidence are : the enrichment of the brines in the mouth areas of rivers, and their impoverishment in the western part of the salt crust; the relatively low gradient of concentration in the brines; the higher Mg/Li ratio and sulfate concentration of Coipasa in comparison with Uyuni.

Table 2 : Descriptive Statistics for Coipasa (unpublished data) and Uyuni (data from Risacher and Fritz, 1991, U series except deep brines and deltaïc sediments). All data are in mmol / l.

	Mg	**K**	**Li**	**Ca**	**Na**	**SO_4**	**Cl**
	Coipasa (23 brines)						
Minimum	169	98	15	8.2	4303	326	5278
Maximum	1086	489	82	55	3480	158	5052
Mean	599	272	46	120	5150	523	5424
Coeff. Var. (%)	46	43	44	20	12	27	2

	Uyuni (36 brines)						
Minimum	122	79	6	3	1622	49	5303
Maximum	2098	760	188	26	4915	463	5839
Mean	527	291	42	14	4259	144	5432
Coeff. Var. (%)	86	64	107	37	19	72	2

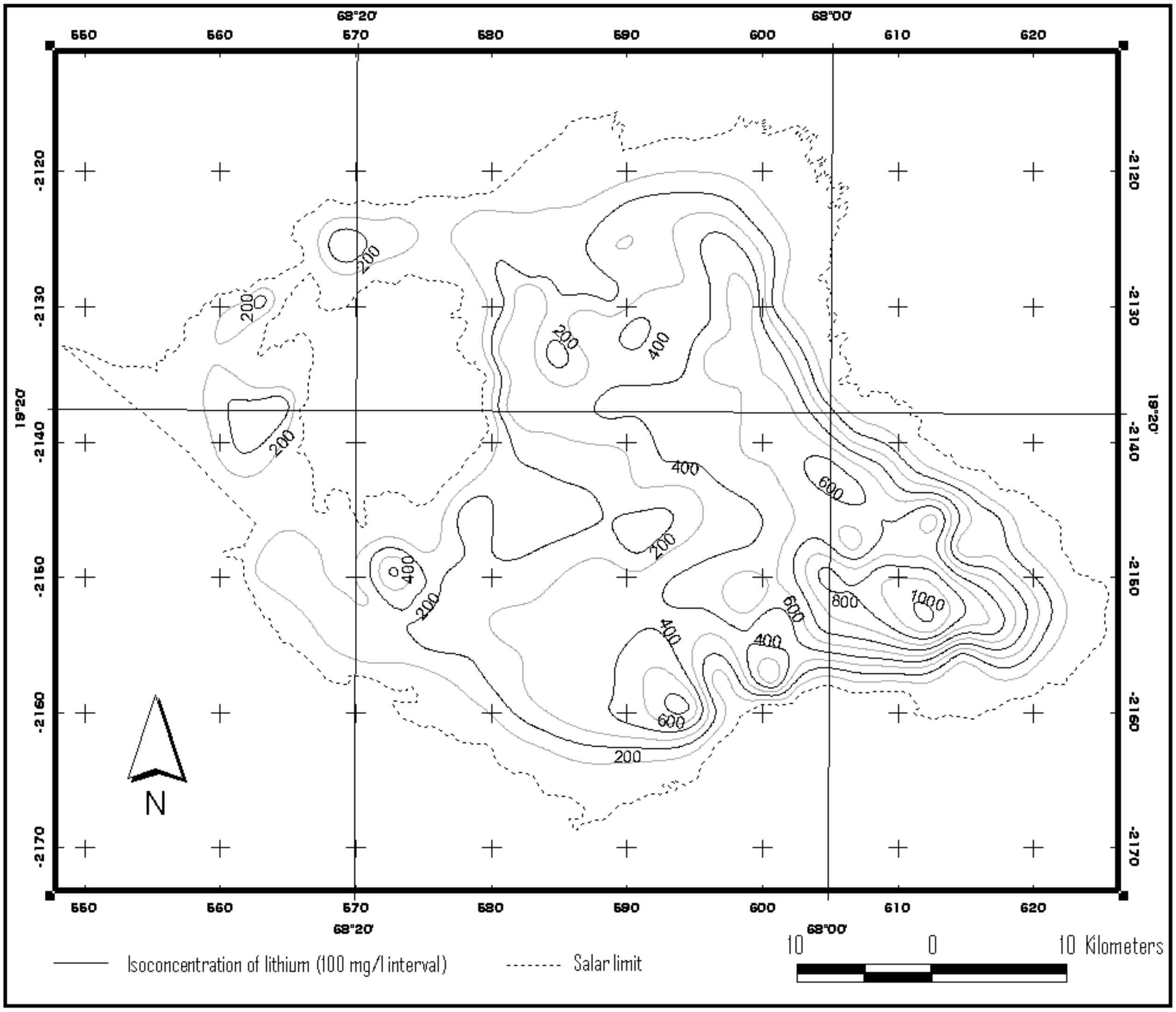

Figure 2 Iso-concentration curves for lithium in the Salar de Coipasa.

Acknowledgements

This study has been made possible through a joint cooperation project between Bolivia and Belgium funded by the university co-operation program of the belgian agency for development (DGCI). The authors wish to thank Sophie FIS, André LANNOYE, Charles-Etienne HOUSSA, Pierre FRANCUS and Guy WANSARD for their fruitful contribution to this project.

REFERENCES

ERICKSEN, G.E., VINE, J.D. & 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.

RETTIG, S.L., DAVIS, J.R., SMITH, R.L., SMITH, K.A. & ERICKSEN, G.E. 1979. Bolivia. *U.S. Geological Survey Professional Paper*. p. 321.

RISACHER, F. 1992. Géochimie des lacs salés et croûtes de sel de l'Altiplano bolivien. *Sci. Géol. Bull.* **45, 3-4,** 219pp.

RISACHER, F. & FRITZ, B. 1991. Quaternary geochemical evolution of the salars of Uyuni and Coipasa, Central Altiplano, Bolivia. *Chemical Geology* **90**, 211-231.

SHULER, M., BLANC-VALLERON, M.M. & RISACHER, F. 1995. La matière organique des alternances sel-marne du salar d'Uyuni (Altiplano, Bolivie) : études géochimiques et palynologiques. *Sci. Géol. Bull.* **48, 4,** 211-247