Non-conservative behavior of bromide in surface waters and brines of Central Andes: A release into the atmosphere?

François Risacher [a,*], Bertrand Fritz [b], Hugo Alonso [c]

[a] *IRD-CNRS, Centre de Géochimie de la Surface, 1 rue Blessig, 67000 Strasbourg, France*
[b] *CNRS, Centre de Géochimie de la Surface, 1 rue Blessig, 67000 Strasbourg, France*
[c] *Universidad Católica del Norte, Departamento de Química, Angamos 0610, Antofagasta, Chile*

Abstract

The transfer of reactive bromine into the atmosphere was recently observed by Hönninger et al. [Hönninger, G., Bobrowski, N., Palenque, E.R., Torrez, R., Platt, U., 2004. Reactive bromine and sulfur emission at salar de Uyuni, Bolivia. *Geophys. Res. Lett.* **31**, doi:10.1029/2003GL018818] in a large salt pan of the Bolivian Altiplano: the salar de Uyuni. However, bromide is considered to be an excellent conservative tracer, which leads to the questioning of its actual conservation in surficial geochemical processes. The relation between bromide and lithium, thought to be a conservative component in waters and brines of the Central Andes, points to a depletion of Br relative to Li in Uyuni brines of about 50–300 kg/day, a flux close to that measured by Hönninger et al. (2004): $\geqslant 200$ kg/day. Such values are very low in regard to the size of the salar (5–30 g/km^2/day). Salt efflorescences have a much higher surface area than a flat salt crust, which should enhance the release of bromine. Leach solutions of salt efflorescences in closed basins of northern Chile are compared to their parent waters. Conservative components should have the same concentration ratios in both solutions. Actually, a strong depletion in Br is observed in the leach solutions, which could suggest a significant release of Br from the salt into the atmosphere. During the rainy season, efflorescences are leached and their dissolved components brought in saline lakes and salars. Evaporative profiles show a slight but noticeable fractionation between Li and Br which could be due to the contribution of Br-depleted leach solutions of salt efflorescences. Therefore, bromide does not behave conservatively in surface waters and brines of the Central Andes. If the loss of Br is really due to its transfer into the atmosphere, then the flux would be much higher than that estimated for the salar de Uyuni alone. Numerous salt pans, saline lakes, and widespread efflorescences covering large land surfaces would contribute significantly more reactive bromine into the atmosphere.

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1. Introduction

The geochemical study of bromide is traditionally focused on its fractionation between hypersaline brines and chloride salts, especially halite (Holser, 1966; Braitsch, 1971). The Cl/Br ratio in primary salt is related to that in the solution, which can help in the reconstruction of paleo-environments and in unravelling diagenetic processes. In dilute and brackish waters, bromide is considered to be an excellent conservative component. It is intensively used as a stream tracer in hydrological studies. Chloride also behaves conservatively in natural solutions at concentrations up to the precipitation of halite. Thus, the Cl/Br ratio is also often used as a natural tracer in waters.

In the late 1990s, the role of halogen species, especially bromine, in the ozone layer depletion became evident. For example, Vogt et al. (1996) described a mechanism for halogen release from sea-salt aerosols. Gan et al. (1998) and Baker et al. (2001a) showed that methyl bromide is emitted into the atmosphere from plants. More recently, Hönninger et al. (2004) measured a significant release of bromine monoxide (BrO) from the giant salar

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* Corresponding author. Fax: +33 03 90 24 04 02.
   E-mail addresses: risacher@illite.u-strasbg.fr (F. Risacher), bfritz@illite.u-strasbg.fr (B. Fritz), halonso@ucn.cl (H. Alonso).

de Uyuni in the Bolivian Altiplano. The question arises then as to what extent bromide behaves conservatively in geochemical processes. Can the release of bromine into the atmosphere be detected indirectly in waters and salts? Or is the release too small in comparison with geochemical contents to be observed? A new scrutiny of the bromide geochemistry becomes necessary.

In this paper, we analyze the behavior of bromide in closed basins of the Central Andes. In a first step, we examine if the release of bromine observed by Hönninger et al. (2004) from salar de Uyuni can be detected in the pore brines of the salar. The second part of the study is focused on the behavior of bromide in salt efflorescences around 116 springs in closed basins of northern Chile. In the third part, we try to determine the degree of conservation of bromide in 78 evaporative profiles of surface waters.

2. Source of data and analytical methods

Most of the data used in this study are taken from Risacher and Fritz (1991a) and Risacher and Fritz (2000) for the Bolivian Altiplano and Risacher et al. (1999) and Risacher et al. (2003) for northern Chile. Methods of analyses are described in these studies. Salt leachates, Altiplano rivers, Poopo, and Titicaca lakewaters were analyzed in this work. Cations were determined by atomic absorption spectrometry (Hitachi Z8200) and anions by ion chromatography (Dionex 4000i). Boron was analyzed by automatic colorimetry with a Technicon autoanalyzer. The error range for Br varies from $\pm 3\%$ to $\pm 10\%$ according to the concentration of Br and to the total salinity of the solution. Salt analyses were performed on approximately 500 mg of dried material dissolved in 100 ml of deionized water in a rotating shaker during 30 min. The leachates were filtered through a 0.45 µm Millipore membrane and analyzed with the same methods used for waters.

3. Bromide in waters and brines of the Bolivian Altiplano

3.1. Geology and hydrology

The Bolivian Altiplano is a high plateau enclosed between the Eastern and the Western Cordillera of the Andes. Paleozoic marine sediments (sandstones, shales) constitute the basement of the Altiplano and the bulk of the Eastern Cordillera. The basement is overlain with Cretaceous and Tertiary continental sediments (sandstones, claystones, mudstones, shales, and evaporites) including numerous gypsum diapirs. Sedimentary formations predominate in the northern Altiplano, while the southern Altiplano and the Western Cordillera are essentially volcanic.

Four basins constitute the bulk of the hydrologic system of the Altiplano (Fig. 1). From north to south: they are the Titicaca, Poopo, Coipasa, and Uyuni basins. The dilute Lake Titicaca overflows into the saline Lake Poopo through the Desaguadero River. Southward, salar de Coipasa is an active evaporative pan fed by Rio Lauca and, to
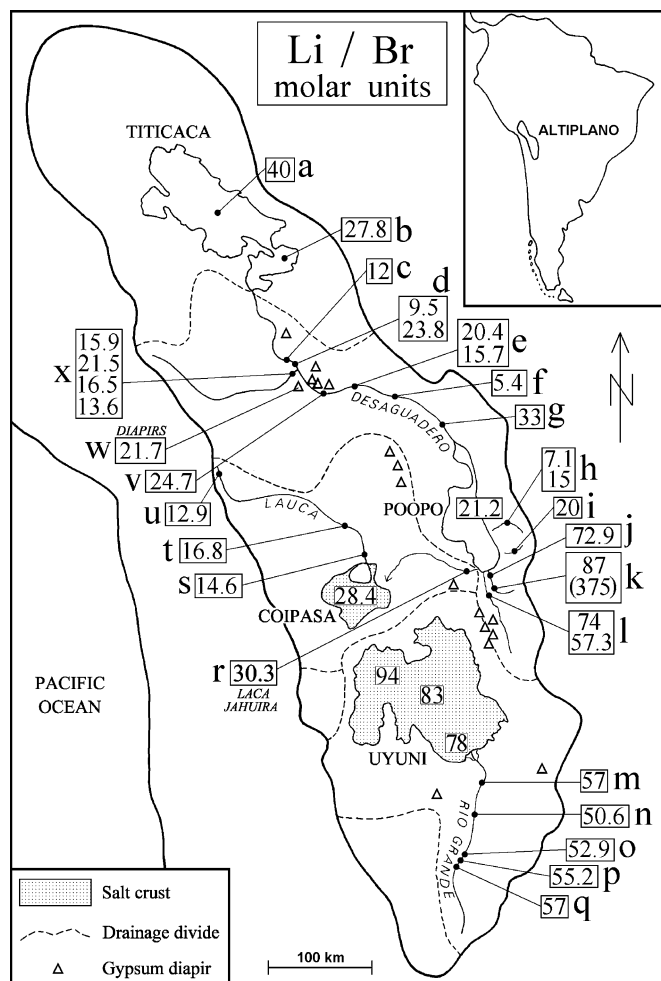

Fig. 1. Outline map and Li–Br ratio of the main hydrologic units of the Bolivian Altiplano. Li and Br concentrations of main rivers, Titicaca and Poopo Lake in Electronic annex EA-1. Data for Uyuni and Coipasa in Risacher and Fritz (1991a, 2000).

a lesser extent, by Lake Poopo through the Rio Laca Jahuira which reverses its flow during the rainy season, depending on the level of Lake Poopo. Salar de Coipasa is capped by a 2.5 m thick halite crust filled with a Na–Cl–SO$_4$ pore brine. The central trough of the Altiplano is occupied by the salar de Uyuni, a salt flat covering some 10,000 km^2 that is capped by a halite crust filled with a Na–Cl pore brine (Rettig et al., 1980; Risacher and Fritz, 1991a, 2000). The crust has a maximum thickness of 11 m and is underlain by nearly impermeable lacustrine sediments.

During the Late Pleistocene, a large saline lake (Lake Tauca) covered Poopo, Coipasa, and Uyuni basins (Servant and Fontes, 1978; Sylvestre et al., 1999; Fornari et al., 2001; Baker et al., 2001b; Fritz et al., 2004). The paleolake was fed by two major inputs: from the north by the (paleo) Lake Titicaca, as it does today via Lake Poopo, and from the south by the Rio Grande de Lipez. Paleolake Tauca receded 10,000 years ago, turning into more saline shallow lakes that eventually dried up leaving the Uyuni salt pan. Presently, the Rio Grande de Lipez is by far the main tributary to the salar. Fig. 2 shows the Br
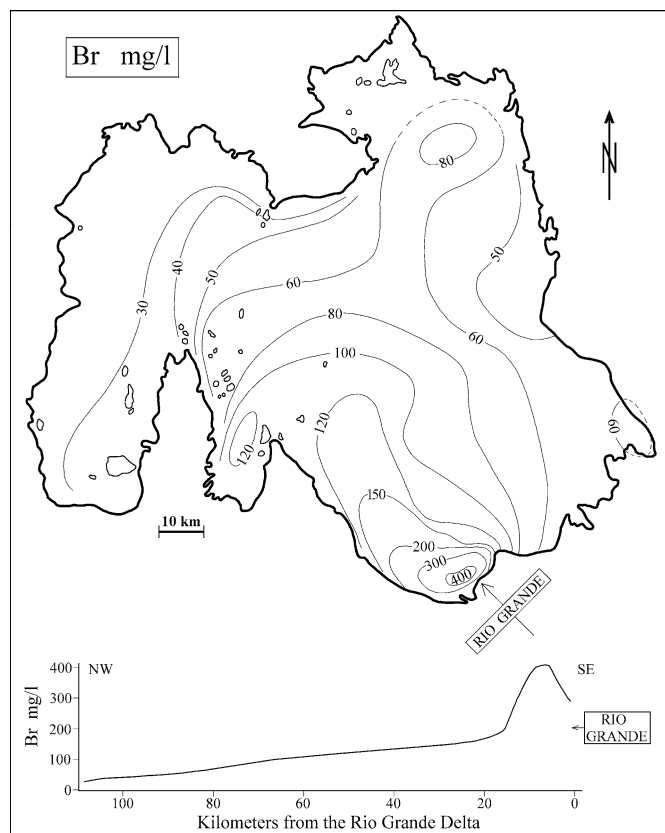
Fig. 2. Average bromide iso-concentration curves of the pore brine in the salt crust of salar de Uyuni (from Risacher and Fritz, 2000). Note the sharp increase of Br concentration just at the mouth of the Rio Grande.

modified either. Only two components seem to be largely conservative in the Bolivian Altiplano: lithium and bromide. Chloride is conservative only up to halite saturation, which makes it useless as a conservative tracer at Uyuni. Magnesium is removed from dilute and brackish waters, probably in Mg-calcite and authigenic smectites (Badaut and Risacher, 1983), and from the most concentrated brines as carnallite ($KMgCl_3 \cdot 6H_2O$) and polyhalite ($K_2MgCa_2(SO_4)_4 \cdot 2H_2O$). Potassium is lost throughout the evaporative process, adsorbed on active surfaces, and included in saline minerals: sylvite (KCl), carnallite, and polyhalite (Risacher and Fritz, 1992). As for boron, the Rio Grande delta contains the largest ulexite deposit in Bolivia ($NaCaB_5O_9 \cdot 8H_2O$). In contrast, lithium has never been found as a mineral phase, at least in Bolivia. Rettig et al. (1980) observed that Li is conserved in Uyuni brines. Lithium may be incorporated in clay minerals such as stevensite, saponite, and hectorite (Weaver and Pollard, 1975). However, such minerals seem to form only in alkaline brines at high pH (Starkey and Blackmon, 1979). In the Bolivian Altiplano, very few brines are alkaline (Risacher and Fritz, 1991b) and moreover the low temperatures and the high aridity prevent the formation of soils and clay minerals. Bromide replaces chloride in halite, but the loss of bromide in the solution is most often negligible. Rettig et al. (1980) used Br as a tracer throughout their study of the salar de Uyuni. To illustrate this point, the evaporation of the Rio Grande water has been modeled with and without incorporating Br in halite (program modified after Risacher and Clement, 2001). At the final concentration of 1 g/L lithium (and 336 g/L of total salinity), which is twice the average Li concentration in the whole salar, the difference between Br concentrations is only 0.6%.

3.3. Loss of bromide at central Uyuni

3.3.1. Observations

Fig. 1 shows the Li–Br ratio of the waters from the main rivers, lakes, and salars of the Altiplano (data for rivers, Poopo and Titicaca Lake in Electronic annex EA-1). There is a significant difference between the northern and the southern inflows. The northern ratios average 20–25, whereas those of the Rio Grande in the south are in the range of 50–57. The difference probably reflects the main geological features: the northern Altiplano contains extensive sedimentary and volcano-sedimentary formations. In contrast, the south is almost exclusively volcanic. The fair constancy of the Li–Br ratios of the northern and the southern waters reflects the composition of major rivers which averages many small inflows. A closer examination of Fig. 1 shows that the Li–Br ratio in Lake Poopo is in good agreement with those of the Desaguadero River, which is by far its main inflow. Coipasa pore brines have Li–Br ratios intermediate between those of the two main inflows, Rio Lauca and Rio Laca Jahuira. As for Uyuni, Li–Br is almost twice as high in the central salar than in

iso-concentration curves of Uyuni pore brines. There is a sharp increase of the Br concentration just at the mouth of the river, at the southeastern shore of the salar. The Rio Grande contributes each year about 50 tons Br to the salar (Risacher and Fritz, 2000), which corresponds to 0.003% of the total amount of Br in the salar (1,770,000 tons). As shown in Fig. 2, most of this input is stored at the mouth of the Rio Grande. The other bittern solutes (Mg, K, Li, and B) exhibit the same behavior. Thus, only the southeastern part of the salar may be considered as very active. A large part of the components stored in the rest of the salar are inherited from the past saline lakes. In other words, what should be emphasized is that salts and brines at southeastern Uyuni are significantly more recent than those of the rest of the salar.

3.2. Conservative components

Let us consider two components perfectly conserved throughout the whole salinity range of waters and brines of the Altiplano. If they do exist, their ratio in Uyuni pore brine should be in between those of the northern and southern main inflows feeding the Altiplano. The hydrologic framework of the Central Andes has not significantly changed during the Holocene, which suggests that the composition of the drainage waters has not been

the Rio Grande water. This large gap cannot be accounted for by another major inflow from the Altiplano.

Fig. 3 presents a deeper insight into the relation between Li and Br of the main hydrologic units of the Altiplano. Two regression lines characterize the whole Altiplano: the southern Altiplano line corresponds to Rio Grande waters and southeastern Uyuni brines (not central Uyuni); the northern Altiplano line fits the system Titicaca–Desagua-dero–Poopo–Lauca–Coipasa. Both lines have the same slope of 0.94, which suggests a slight decrease of Br relative to Li. They may be considered as general evaporation lines for Li and Br. If so, Poopo, Coipasa, and southeastern Uyuni brines appear to be consistently related to their main inflows. Strikingly, this is not the case for most central Uyuni brines whose points lie below the southern Altiplano line. There is a clear break between the southeastern brines, presently forming from the evaporation of the Rio Grande water, and the residual brines of the central salar. The scat-tering of the points below the line must also be noted. All of this evidence supports the suggestion that some Br has been used up in the residual brines at Uyuni. However, the possibility of an enrichment of Li cannot be ruled out. Several explanations may be addressed to account for the fractionation between Li and Br: the lack of repre-sentativity of our samples; the contribution of groundwa-ters with higher Li–Br ratio; the incorporation of Br in halite during very high evaporation stages; and the release of Br into the atmosphere.

3.3.2. Representativity of the samples

The first question that arises to discuss the apparent loss of Br is how representative are our samples in view of the extent of the study area. The Altiplano is a wide basin (200,000 km^2) and the salar de Uyuni is the largest salt pan in the world (10,000 km^2). The sample distribution of

Uyuni brines is shown in Risacher and Fritz (1991a) and Risacher and Fritz (2000). Forty wells were drilled in the whole salar from which 140 brines were sampled at regular depth intervals. This large set of analyses (intended to esti-mate Li, K, Mg, and B reserves in the brines) is likely to be representative of the whole salar. All the major rivers of the Altiplano were sampled at several places and times (Fig. 1). They are fed by smaller streams, which themselves stem from many springs scattered in the whole Altiplano. There-fore, we may reasonably assume that they are representa-tive of the surface waters of the Altiplano.

3.3.3. Groundwater input

Groundwaters probably also enter the salar de Uyuni. Could their Li–Br ratios be very different from those of the surface waters? Schematically, we may distinguish shallow and deep groundwaters. Shallow groundwaters are fed by percolation of surface waters and circulate by gravity flow through surficial formations such as allu-vial fans. Br has not been reported to interact with such material, which makes it an excellent tracer in hydrogeo-logical studies. In contrast, Li can be incorporated in clay minerals. Up to now, such a removal has never been detected in the Bolivian Altiplano (see above, Section 3.2). However, if it would occur (or have occurred in the past), the outcome would be a decrease of the Li–Br ratio, which would lead to an apparent enrichment of Br, not a loss as observed in Fig. 3.

Deep groundwaters may reach the surface through frac-tures and convective flow. They often acquire their compo-sition by hydrothermal alteration or dissolution of buried evaporites. Their composition may then be distinct from that of surface waters. The contribution of deep groundwa-ters has been observed in a gypsum diapir in the northern Altiplano (location W in Fig. 1; analyses and discussion
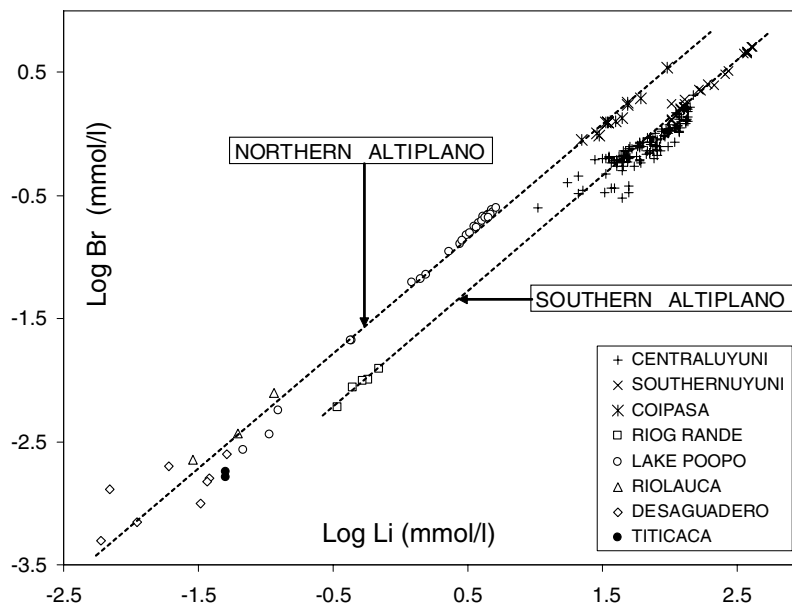

Fig. 3. Bromide vs lithium in surface waters and brines of the Bolivian Altiplano (for source of data, see Fig. 1).

in Risacher and Fritz, 1991a, 2000). Saline to hypersaline springs seep from the diapir. Their temperatures (15–20 °C) are significantly above the mean annual air temperature (8 °C) which indicates thermal heating and deep circulation. Many such diapirs are scattered across the northern Altiplano (see Fig. 1). They are probably a main source of gypsum and halite deposited in salar de Uyuni. As can be seen in Fig. 1, the average Li–Br ratio of these saline springs is in excellent concordance with the ratios of surface waters of the northern Altiplano. Therefore, the contribution of these deep saline groundwaters to salar de Uyuni cannot explain the loss of Br at Uyuni. No other evidence of major deep groundwater input has been found in the Altiplano.

3.3.4. Incorporation of Br in halite

Another possible explanation for the apparent removal of Br could be the incorporation of Br in halite. We have already shown (Section 3.2) that the present precipitation of halite removes negligible amounts of Br. However, Risacher and Fritz (2000) observed a significant increase of Br in halite of the lower part of the crust, but not in the pore brine. They relate the increase to a severe drought that affected the Altiplano during the Holocene. The pore brine evaporated leaving a residual layer of hypersaline brine that deposited Br-rich halite. Br increases from about 5 ppm in the upper halite to 20 ppm in the basal halite. This process has removed some Br from the pore brine. We have modeled the evaporation of a central pore brine to reach a content of 20 ppm Br in the precipitated halite (ua-200, from Risacher and Fritz, 1991a,b; distribution coefficient of Br = 0.072). The loss of Br in the residual hypersaline brine is 2%, which is small compared with the observed loss of about 14% in Uyuni brines (see below). The calculated hypersaline brine is quite like those found at southeastern Uyuni, which are now precipitating Br-rich halite (10–20 ppm, see Risacher and Fritz, 2000, p. 380). Thus, southeastern Uyuni brines represented in Fig. 3 have also lost a similar amount of Br. Nevertheless, they are clearly less depleted in Br than central Uyuni brines. In other words, the loss of Br from the southeastern Uyuni brines is already included in the regression line in Fig. 3. From this discussion, it appears that the incorporation of Br in halite can hardly be accounted for its loss in central Uyuni brines.

3.3.5. Release of Br into the atmosphere

The best mechanism so far reported that may account for the fractionation between Li and Br is the loss of bromide as reactive bromine into the atmosphere as described by Hönninger et al. (2004). However, these authors measured the loss of Br from the salt crust during the dry season, not from the brine. Each year, the salar of Uyuni is flooded during the wet season, mainly by direct rainfall. The upper crust is redissolved and mixed with the shallow pore brine. When the salar dries up, the upper crust precipitates again and incorporates new Br from the pore

brine. This process may ensure a steady-state transfer of Br from the brine to the atmosphere. A continuous loss of Br without replenishment would deplete the upper crust in Br. However, the surface halite is not depleted in Br as compared with deeper samples (Risacher and Fritz, 2000, p. 380). Moreover, during the dry season, the pore brine evaporates through polygonal cracks leaving salt efflorescences. As will be shown in the next section, salt efflorescences seem to be a major cause of Br transfer to the atmosphere. Therefore, the loss of Br from the salt crust observed by Hönninger et al. (2004) also affects the pore brine.

It is possible to give a gross estimate of the loss of Br corresponding to the shift of the points below the southern line. The vertical projection (at constant Li) of each point on the southern line leads to an initial concentration of Br before the loss. The average of all these initial concentrations is about 1.06 mmol/L. The present average concentration of all brines that plot below the line is 0.91 mmol/L, which corresponds to a reduction of 14%. The brine volume of the central salar has been estimated at 15.8×10^9 m^3 (Risacher and Fritz, 1991a). The loss of Br would then be about 191×10^6 kg. This leads to a flux of 52 kg/day Br, if we assume a continuous loss since Paleolake Tauca retreated 10,000 years ago. However, Paleolake Tauca was also fed during its highest stages from the north of the Altiplano. An isotopic budget of Paleolake Tauca based on Sr isotopes supports this contention (Grove et al., 2003). It is more likely that just after the drying the representative points of Uyuni brines plotted in between the northern and southern lines, as some presently do (see Fig. 3). By increasing Br concentrations up to an intermediate and equidistant line, the flux of Br lost by the salar would be 280 kg/day. These fluxes are in excellent agreement with that measured by Hönninger et al. (2004), at least 200 kg/day, which strongly suggests that the fractionation of Br relative to Li observed at central Uyuni is due to the release of reactive bromine into the atmosphere during the last 10,000 years.

Actually, such fluxes are very low. The yearly loss of Br is only 0.005% of the total amount in brines. They can be detected from Uyuni brines only because of the long time span involved. We will see now if a loss of Br can also be detected in more rapid processes. It has already been observed that the slope of the two Li–Br evaporation lines in Fig. 3 is slightly below one (0.94), suggesting a general loss of Br at the Altiplano scale. Vogt et al. (1996) measured a bromide deficit as high as 90% in marine aerosols due to its transfer into the gas phase. Such a high value suggests that the surface area of the material from which Br is released is an important factor. Uyuni crust, dry or flooded, is flat and compact, while aerosols have fractal dimensions. We have therefore looked for geochemical materials with large surface areas in which the behavior of Br could be easily monitored. The best candidates are salt efflorescences.

4. Bromide in salt efflorescences in closed basins of northern Chile

4.1. Formation of salt efflorescences

Salt efflorescences result from the complete evaporation of groundwaters. Brine films ascend by capillary draw along vegetation and rock debris depositing all dissolved salts. Components that do not usually precipitate due to the very high solubility of their salts are included in fluid inclusions or may form labile, ephemeral salts. Efflorescent salts are tiny, friable, porous crystal aggregates. Under very arid climate, with almost no rain, efflorescences coalesce into a hard crust. In more humid regions, like that of the Andean Highlands, rainfall dissolves the salt efflorescences almost completely each year. Only minerals of low solubility (calcite, Mg-silicates) may remain partially in place. Therefore, the most soluble salts containing Cl, Li, and Br have necessarily precipitated after the last rain. They are too labile to be preserved during a rainy event. Theoretically, the concentration ratios between the soluble components Cl, Li, and Br should be identical in the parent groundwater and in the leachate of the efflorescent salt.

4.2. Loss of bromide in salt efflorescences

A set of 116 freshly precipitated salt efflorescences has been sampled around springs in closed basins of northern Chile. Fig. 4 shows the study area. All spring waters have been analyzed as well as the leachates of their salt efflorescences. The composition of the leach solutions and that of the parent waters are given in Electronic annex EA-2. Precise location, description of each basin, and complete analyses can be found in Risacher et al. (1999, 2003). The leaching process was performed on disaggregated salts (not crushed) for 30 min to try to reproduce, as far as possible, a strong rainfall. The ratios between Br and each main component in springwaters and salt leachates are compared in Fig. 5. If Br and another component (X) are perfectly conserved, the representative point plots on the iso-ratio line $(Br/X)salt = (Br/X)water$. Points below the iso-ratio line correspond to a loss of Br in the salt relative to the other component. As can be seen, Br is depleted in salts with respect to all components. No other component shows such a systematic behavior. The depletion is particularly pronounced relative to Cl, Na, K, Li, SO_4, and B. The retention of Ca and Mg in low-soluble minerals could explain the lower depletion of Br relatively to these components. As an overall average, about 70% Br is missing in salt leachates. There is no definitive evidence that the missing Br has been transferred into the atmosphere. However, it is for now the simplest possible mechanism.

5. Bromide in surface brines of Chilean salars

Whatever the reason for the loss of Br in salt efflorescences, it is clear that during the rainy season surface waters that have leached these salts are impoverished in
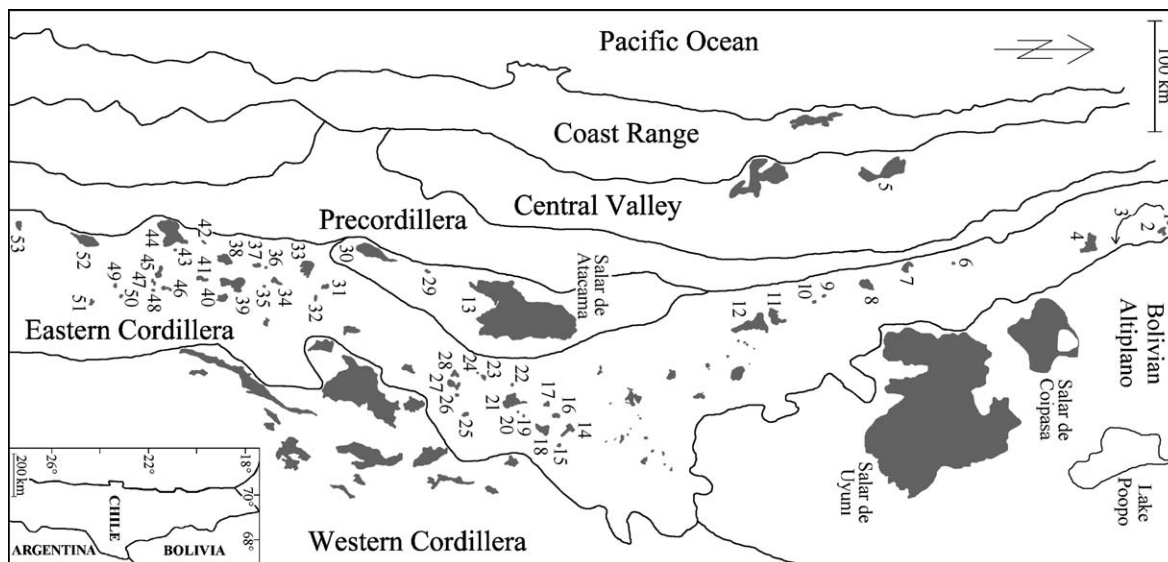

Fig. 4. Salt crusts and saline lakes of the Central Andes. Main morphostructural units are outlined. Code numbers refer to north Chilean salars (the same than in Risacher et al., 2003). Most are used in this study (lag = laguna; if nothing before the name = salar): 1, lag. Cotacotani (cot); 2, lag. Chungara (chr); 3, rio Lauca (laa); 4, Surire (sur); 5, Pintados (pin); 6, Lagunilla (lgu); 7, Huasco (hua); 8, Coposa (cop); 9, Michincha (mic); 10, Alconcha (alc); 11, Carcote (car); 12, Ascotan (asc); 13, Atacama (ata); 14, Tara (tar); 15, lag. Helada (hel); 16, Aguas Calientes 1 (ac1); 17, Pujsa (psa); 18, loyoques (loy); 19, Trinchera (tri); 20, Chivato Muerto (mue); 21, Aguas Calientes 2 (ac2); 22, lag. Lejia (lej); 23, lag; Miscanti (mis); 24, lag. Miñique (min); 25, Laco (lac); 26, lag. Tuyajto (tuy); 27, Aguas Calientes 3 (ac3); 28, Capur (cpr); 29, Imilac (imi); 30, Punta Negra (pun); 31, Aguas Calientes 4 (ac4); 32, lag. de la Azufrera (laz); 33, Pajonales (paj); 34, Gorbea (gor); 35, Ignorado (ign); 36, salar de la Azufrera (azu); 37, Agua Amarga (ama); 38, Aguilar (agi); 39, Isla (isl); 40, Las Parinas (par); 41, Salar Grande (gra); 42, Infieles (inf); 43, La Laguna (lgn); 44, Pedernales (ped); 45, Piedra Parada (pie); 46, lag. Bravas (bra); 47, lag. del Jilguero (jil); 48, lag. del Bayo (bay); 49, Wheelwright (whe); 50, lag. Escondida (esc); 51, lag. Verde (lav); 52, Maricunga (mar); 53, lag. del Negro Francisco (fra). The three-letter codes are the same than those used in Electronic annexes EA-2 and EA-3.
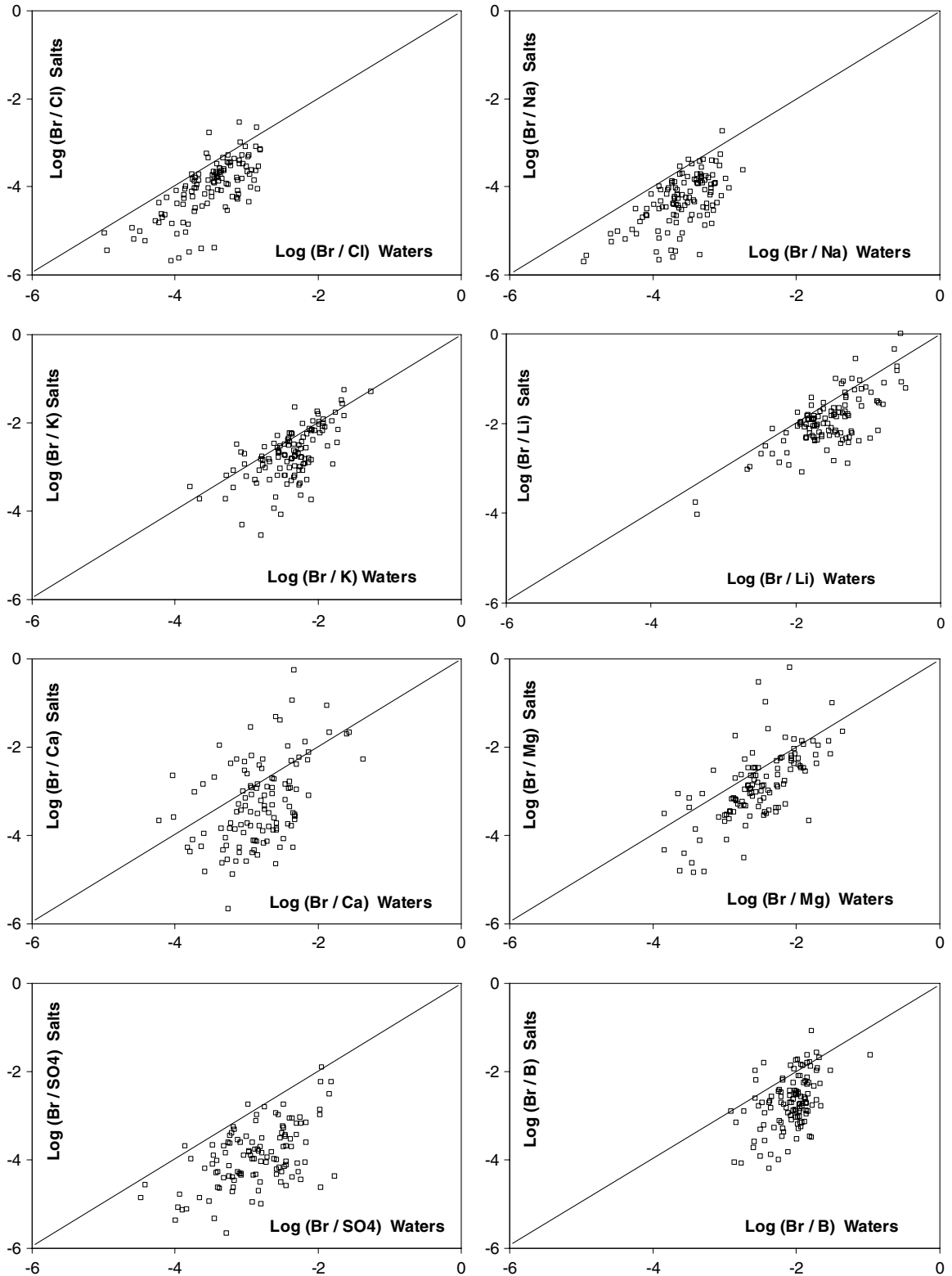
Fig. 5. Composition of salt leachates compared to that of their parent waters. If Br and another component X are perfectly conserved, then the ratios Br/X in the leachate and in the parent water are identical, and the representative point plots on the iso-ratio line. Most points plot below this line, suggesting a loss of Br in the leach solutions. Data in Electronic annex EA-2 (concentrations in mmol/L).

Br relatively to other surface waters. Therefore, Br should also be depleted in salt lakes where all inflow waters mix and evaporate. The question is to what extent the loss can be detected. For this, we have scrutinized 78 evaporative profiles of saline ponds and lakes in the same basins of northern Chile. Analyses are given in Electronic annex EA-3. Former studies are in Risacher et al. (1999, 2003).

Most evaporative profiles were sampled in ponds and lakes fed by a single and well-defined inflow pouring into the salar. Ponds fed by several inflows were excluded, except when inflows have similar composition. The number of samples in each profile ranges from 2 to 7. Almost all brines are undersaturated with respect to halite, which allows the use of Cl as a conservative component. For each evaporative profile the regression lines, in log scale, relating Br to Cl and Br to Li were calculated. A slope of one indicates perfect conservation of Br with respect to Cl or Li. A slope below one reflects either a loss of Br or an enrichment of the other component. Fig. 6 shows all slopes as a function of the highest salinity observed in the profiles. A rather clear trend can be noticed: the slopes tend to drop below one as the salinity increases. Table 1 gives the average slopes in a low and a high salinity range. Note that they are similar to those of the two Br–Li general evaporation

Table 1
Mean slopes of the regression lines of log(Br) vs log(Cl) and log(Br) vs log(Li) for 78 evaporative profiles of surface waters in north Chilean salars

Salinity range (g/L)	Log(Br) vs Log(Cl)	Log(Br) vs Log(Li)
0–100	0.96	0.98
100–350	0.92	0.94
0–350 (whole range)	0.94	0.96

lines of the Bolivian Altiplano (0.94). Two mechanisms may be invoked in explaining the lowered slopes. The most obvious is the input of leached salts during the rainy season. As shown in the previous section, Br is clearly depleted in salt efflorescences. The second possible mechanism is a direct loss of bromine from the lake brines in a process similar to that described at salar de Uyuni by Hönninger et al. (2004). However, a direct loss could be efficient only in very shallow lakes in which Br has a long residence time. Otherwise, Br would be renewed too rapidly and only evaporative concentration would be measurable.

The scattering of the slopes suggests that additional processes are affecting the concentrations of Cl, Li, and Br. Underground inputs cannot be definitely excluded. They are very difficult to measure directly. Actually, it is the irregular behavior of conservative components that permits the detection of such inputs. Dry fallout on the lake surface may also modify the water composition (Rech et al., 2003; Risacher et al., 2003). Diffusional exchange of components between surface waters and pore waters of bottom sediments could be an additional fractionation process (Lerman and Brunskill, 1971; Wardlaw and Valentine, 2005). Cl and Br have similar diffusion coefficients at infinite dilution (Li and Gregory, 1974). They will probably not fractionate significantly. Li, however, diffuses twice as slowly as Cl and Br. The depth of the water body also has an influence. Large, deep lakes are less sensitive to small perturbations because of the large mass of their dissolved components. As an extreme example, even if 90% of Br in marine aerosols is lost into the atmosphere, the impact on the Br content of the oceans is not detectable. In contrast, in dilute and shallow waters small gains or losses may have a relatively larger effect on the low concentration of dissolved components. This is probably the main reason of the high variability of the slopes at low salinity.

6. Conclusions

Bromide does not behave conservatively in surface waters of the Central Andes. The residual brines of salar de Uyuni are depleted in Br relative to all main inflow waters and active brines of the Bolivian Altiplano. If the loss has been continuous since the paleolake dried up 10,000 years ago, the flux of Br out of the salar would be in the range of 50–300 kg/day (5–30 g/km²/day). This is in excellent agreement with the flux of at least 200 kg/day
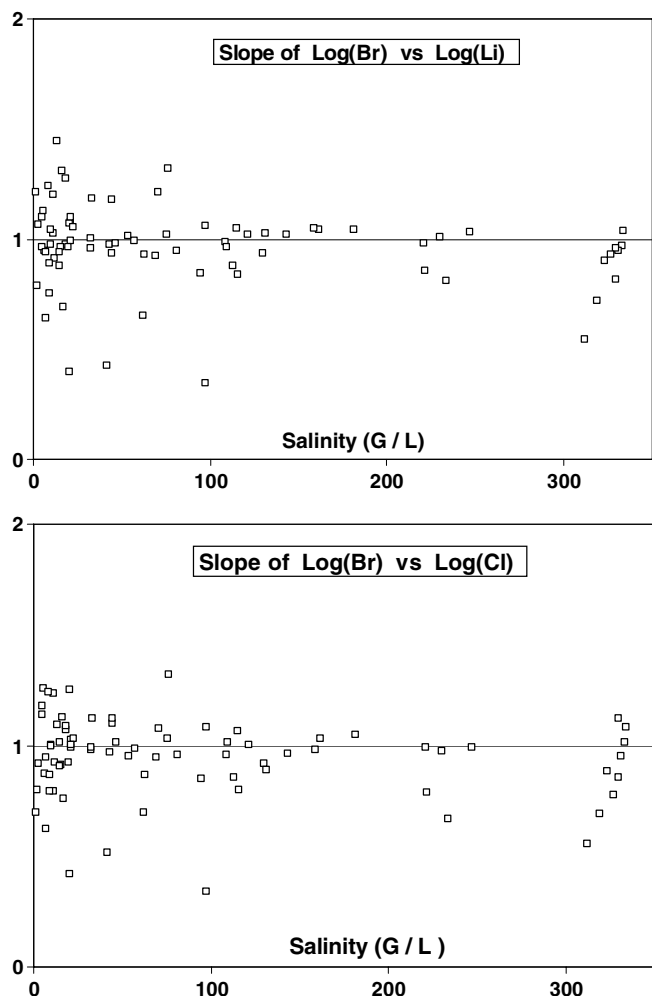

Fig. 6. Slopes of the regression lines for the relations between log(Br) vs log(Li) and log(Br) vs log(Cl) in 78 evaporative profiles of surface waters and brines of Chilean salars. The salinity is that of the most concentrated solution of the profile. A slope of one indicates a perfect conservation of the two components. Data in Electronic annex EA-3 (concentrations in mmol/L).

of reactive bromine emitted to the atmosphere by the salar as measured by Hönninger et al. (2004).

Leach solutions of efflorescent salts in closed basins of northern Chile are depleted in Br as compared to the waters from which they have precipitated. The loss averages 70% of Br, but with large variations from one sample to the other. The only known mechanism that can explain such a loss is the transfer of bromine in the atmosphere as observed at salar de Uyuni.

Efflorescent salts are redissolved each year during the wet season and feed terminal saline lakes in the central depression of the closed basins. Their contribution lowers the Br–Cl and Br–Li ratios of the lake brines mainly fed year-round by springs, rivers, and underground waters of higher ratios. The lowering is small but noticeable, especially in shallow lake brines. A direct loss of Br from the water surface may also occur.

Although not a certainty, it is likely that the loss of Br in efflorescent salts and lake brines is due to its transfer as reactive bromine into the atmosphere. However, if true, it would mean that the flux of bromine emitted into the atmosphere from saline formations in the Central Andes is much higher than the flux measured by Hönninger et al. (2004) only from the salar de Uyuni. Efflorescent salts not only forms close to springs and rivers, but also on dry playas and on large land areas where the groundwater table is less than a few meters deep. As can be seen in Fig. 4 (where only the largest are represented), the Central Andes are densely covered with salars often surrounded by a halo of efflorescent salts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2006.01.019.

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