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ISOTOPIC AND CHEMICAL COMPOSITION OF GROUNDWATER IN THE BOLIVIAN ALTIPLANO, PRESENT SPACE EVOLUTION RECORDS HYDROLOGIC CONDITIONS SINCE 11 000 Yr

Anne COUDRAIN* and Amal TALBI

1. INTRODUCTION

Research on chlorine transport in aquifers is interesting for the management of the water resources and for the understanding of the climate - hydrological cycle relation. Compared to surface water, groundwater seems better protected with respect to pollution. However it is observed that many aquifers present high chlorine concentrations and that groundwater by salinisation is increasing over the world. The processes at the origin of salt content in groundwater of a non saline rock are: sea water intrusion [1], upward from associated leakage from deep brines [2, 3], soil salinisation associated to irrigation and to the rising of the water table by deforestation [4], transport of salt by aerosols and their subsequent leaching into shallow aquifers [5]. Chemistry [6], natural isotopes [7] and modelling [8] are the main tools to identify the processes at the origin of salt content.

In most cases chlorine is conserved in the solution and groundwater velocity ranges between 1 and 10 m yr^{-1}. As a consequence, in regional aquifers where flow path are longer than several kilometres, Cl concentration may reflect hydrologic conditions over 10 thousands years or more. Climatic evolution may be marked in the spatial evolution of Cl.

The Altiplano is an endorheic catchment (Fig. 1) including the lake Titicaca (16°S, 3810 m) and the Uyuni Salar (21°S, 3653 m). The strong climatic variations of the Holocene were expressed by considerable variations in regional lake levels [9]. The chronology of these hydrologic conditions makes the Altiplano a particularly valuable source of documentation of the Holocene and its climatic variations. The aquifer under study of around 6000 km^2 is in quaternary sediments and lies in the upstream portion of the southern catchment of Uyuni. Close to present recharge area, Cl concentration in groundwater is less than 10 meq l^{-1} that may not explain the large chloride contents in groundwater that reach downward 150 meq l^{-1}. Taking into account the climatic evolution since the paleolake Tauca covered the region, mathematical modelling of Cl transport and isotopic data illustrate that hydrologic conditions since 11 ka after the paleolake Tauca retreat have to be taken into account to explain the present space evolution of the chemical composition and that the evaporative flux from the aquifer in such arid zone is important.

2. EVAPORATION FROM PHREATIC AQUIFER IN ARID ZONE AREA

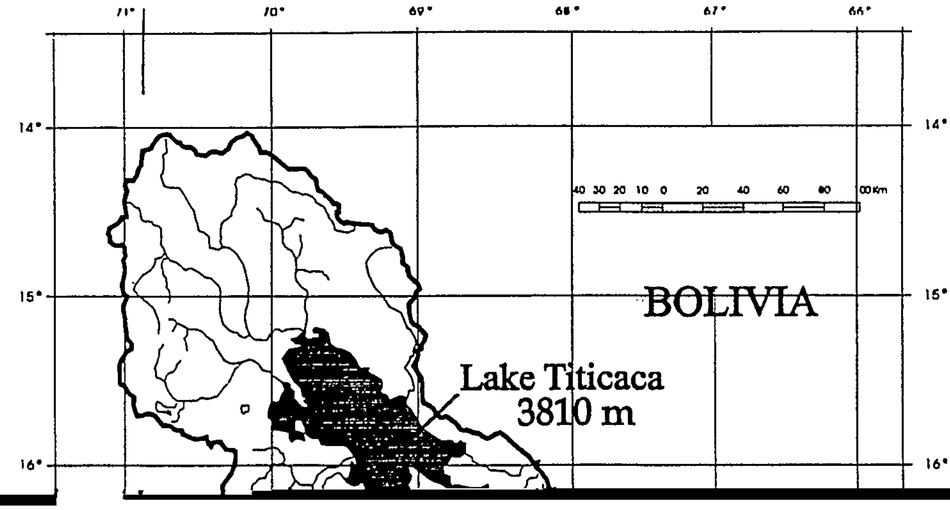
Collected data of hydraulic conductivity as a function of suction (S) up to more than 1000 m and estimations of evaporation after about 30 isotopic profiles allow to conclude [10]:

- high dependence of evaporative flux on soil characteristics had been previously concluded on insufficient data for arid conditions,
- after recently published K(S) data reported in [10], the upper and lower bounds of this relation are :

$$28\ z^{-1.8} < E < 205\ z^{-1.6}$$

- the fitted curve determined on the base of the isotopic profiles from Algeria, Australia, Bolivia, Chile, Niger, Réunion and Tunisia [11-21] is :

$$E = 63\ (\pm 5)\ z^{-1.5} \text{ with E in mm yr}^{-1} \text{ and z in m}$$


14°
15°
16°
BOLIVIA
Lake Titicaca
3810 m

After this relation, the evaporative flow decreases from 380 mm yr^{-1} to 1 mm yr^{-1} when the water table depth increases from 0.3 m to 18 m under soil surface (Fig. 2). This relation is used in the present study to constrain the present hydrologic mass balance by prescribing the outflow by evaporative flow (section 3) and to model during 11 ka the groundwater flow and Cl transport including the Cl-accumulation in the unsaturated zone by the evaporative flow (section 4).

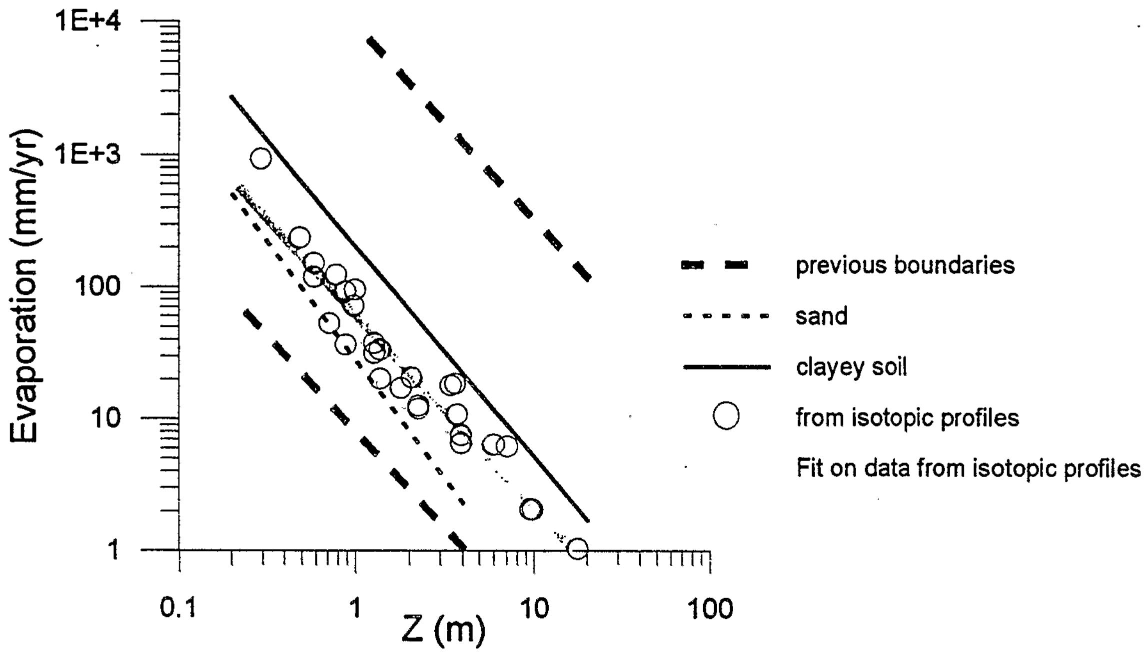


FIG. 2. Evaporation from phreatic aquifer vs. water table depth under soil surface (Z). Circles: local estimations of E from isotopic profiles; curves "sand" and "clayey soil": computed on the base of hydraulic conductivity measured for suction from saturation to very low water content; curves "previous boundaries": lowest and highest estimations of E from previous hydraulic studies based on insufficient data for arid zone area.

3. PRESENT WATER MASS BALANCE

Present precipitation, concentrated during one rainy season, is of the order of 350 mm yr^{-1}. It allows recharging the aquifer from runoff between Tertiary mountains and the hinge line with the flat plain (Fig. 3). The other present recharge is the inflow from the Rio Desaguadero, fed by the Titicaca Lake and northern tributaries (Fig. 1). The use of an hydrogeological model [22] allowed to compute for present steady state that the total outflow by evaporation from approximately 80% of the aquifer area (3550 km^2), where the piezometric head is at less than 20 m below soil surface, is of the order of 28 10^6 m^3 yr^{-1}.

4. MODELLING Cl TRANSPORT OVER THE PAST 11 000 YEARS

On the base of recent quaternary studies [9, 23, 24], it can be assumed that the aquifer was covered by the paleolake Tauca (12 ka BP) during a period long enough to allow diffusion between both water bodies. Geochemical data collected in the zone under study also argue in favour of this hypothesis : *(i)* ^{14}C activities of inorganic carbon dissolved in groundwater range between 59 and 4 pmC, (ii) δ^2H *vs.* $\delta^{18}O$ graph of saline groundwater [25] suggests that evaporation occurred prior to infiltration, *(ii)* saline groundwater and reconstructed composition of paleolake Tauca present low values of Li/Cl [26, 27]. In order to test if chloride in solution of the Quaternary aquifer may remain since the paleolake covered the area, modelling of the Cl transport during 11 ka has been undertaken.

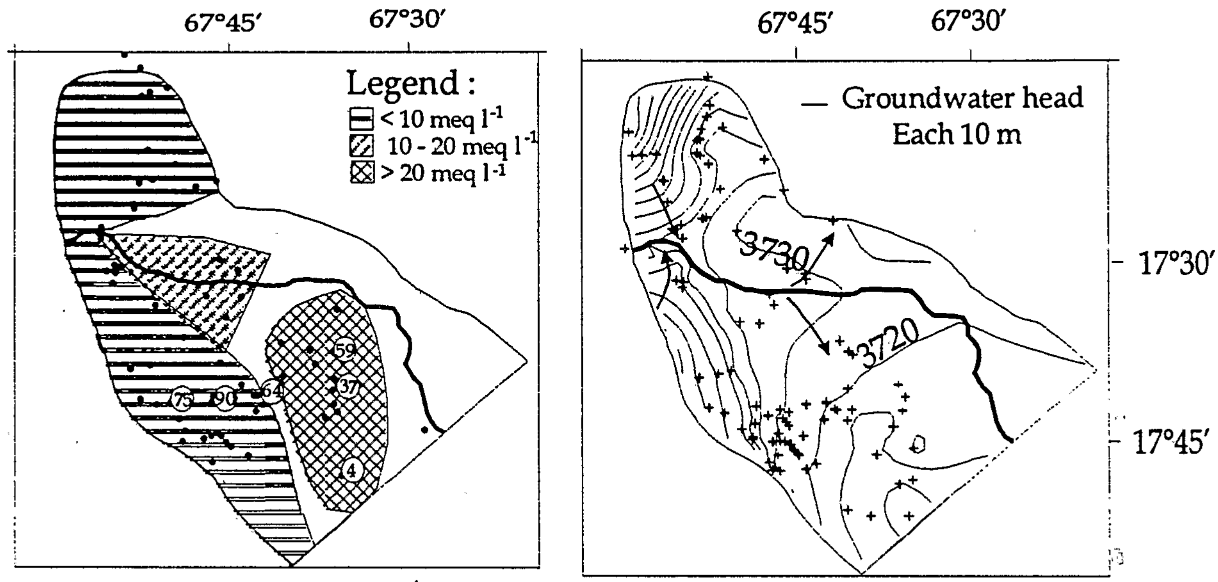


FIG. 3. Maps of present Cl concentration and piezometry of the phreatic aquifer in the central Altiplano. Cl concentrations increases from upstream (0.5 meq l^{-1}) in the recharge zone to downstream (150 meq l^{-1}) where 4 pmC were analysed for ^{14}C.

Modelling has been performed by using the NEWSAM code [28] that has been modified to take into account the outflow by the evaporative flow from the aquifer. For the groundwater flow modelling, input data are evolution of the infiltration, presence or lack of the Rio Desaguadero, hydraulic parameters (thickness 50 to 100 m; transmissivity 0.5 10^{-3} to 10^{-2} m^2 s^{-1}) of the aquifer. Output data computed by the simulation are the time and space evolution of groundwater head, outflows by evaporation and toward south and flow between the Rio Desaguadero and the aquifer.

Reconstitution of possible infiltration towards the aquifer has been computed as follows. The water levels in a lake situated in an endhoreic catchment make it possible to calculate the associated rainfall rate by the use of the water balance over the whole catchment. The evolution during the Holocene of water levels in lake Titicaca, previously published, shows that in the most arid period, between 8000 yr and 4000 yr BP, the average level was 50 m lower than today. The rainfall associated with this low level is 635±50 mm yr^{-1} i.e. about 18% lower than the present amount [29]. Assuming a similar ratio of rain amounts between both catchment area than the present one, it has been computed in this study that lowest rain amount close to the zone under study (17°30 S) was about 290 mm during the arid period from 8000 to 3000 yr BP. The evolution of the infiltration towards the aquifer has been computed proportionally to this reconstructed rainfall amount.

Modelling takes also into account the lack of perennial flow of the Desaguadero between 10 ka and 2 ka B.P. when the low level of water in lake Titicaca did not allow outflow towards the Rio Desaguadero [24]. Results show that between 10 ka and 2 ka, during lack of perennial flow in the Rio Desaguadero, the hydraulic head of the aquifer is decreasing and evaporative flux decreases. Reversibly, after 2 ka when infiltration from the Rio Desaguadero is again possible and that infiltration from local runoff increases, evaporative flux and underground flow towards South increase progressively. Outflow by evaporation is always close to 2/3 of the total outflow, which again demonstrates how important it is to take it into account. The local maximum Darcy velocity, at each time step, is always of the order of 1 m yr^{-1}.

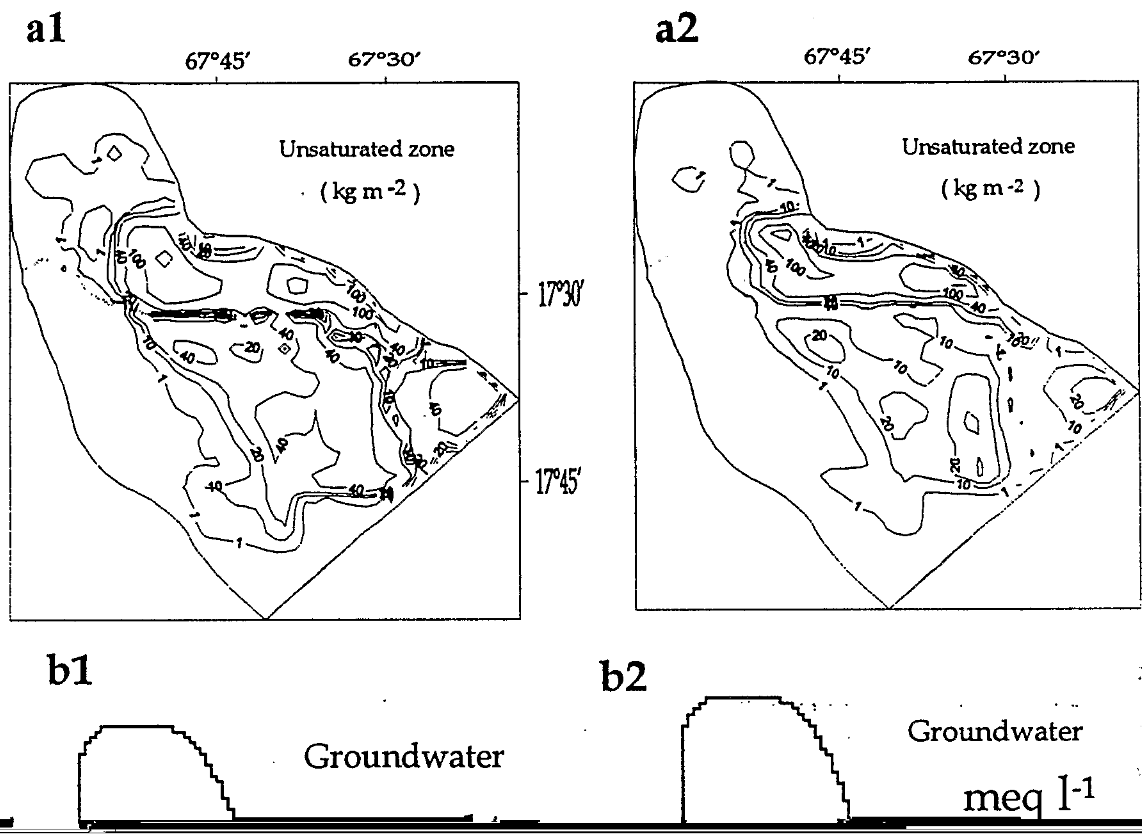
Associated to groundwater flow, the transport of chloride has been simulated by NEWSAM, assuming a mean value of 0.25 for the porosity. Initial concentration of chloride was assumed to be of 200 meq l^{-1} where the soil surface is below 3740 m and of 0.5 meq l^{-1} above this elevation. This corresponds to the hypothesis that the paleolake Tauca covered the aquifer during sufficient time (2 ka) to allow diffusion between the lake and the aquifer so that the concentration in the aquifer reached 200 meq l^{-1}. The Cl concentrations associated to inflow by runoff and by the Rio Desaguadero are 0.5 and 10 meq l^{-1} respectively.

Output of the Cl transport modelling is the time evolution of Cl concentration in the groundwater and inflow and outflow of chloride. Roughly, half of the initial quantity of chloride in the aquifer is leaving out from the aquifer by underground flow towards South and the other half by evaporation that lead to salt accumulation in the unsaturated zone with a weighted mean value of 19.7 kg m^2 (Fig. 4-a1). The computed present concentration is in the right riverbank less than 30 meq l^{-1} (Fig. 4-b1).

Subsequent infiltration of the chloride accumulated in the unsaturated zone toward the aquifer should have occurred with a small amount of water. Such process would keep agreement with the low and decreasing ^{14}C activity toward South (57 to 4 pmC). The Cl profiles of the unsaturated zone [22] show that very probably no infiltration occurred toward the aquifer in the flat plain since around two thousand years. Another simulation of Cl transport has been conducted where the Cl accumulated in the unsaturated zone between 11 ka and 2 ka is locally added to the groundwater solution (Fig. 4).

The model allow to reproduce the special pattern of observed chloride concentration similar to an ellipsoid in the right river bank where the more saline water are the older one with concentration as high as 80 meq l^{-1}. The Cl accumulated close to the point with a value of 37 in ^{14}C activity is 18 kg per m^2 of soil surface; the computed one is 15 kg m^{-2} (it is 39 kg m^{-2} when injection of Cl at 2 ka is not taken into account). In the left riverbank, the observation of very saline soils and non-permanent surface water is in good agreement with this second simulation.

However, at this stage the absolute values of chloride concentrations may not still be compared between observed and computed values. A study by electromagnetic investigation is now undertaken to get data on the spatial evolution of the aquifer thickness.



groups of distinct geochemical compositions extending on different geographical area. The relevant parameters to distinguish these groups are Cl, Na/Cl, $^{87}Sr/^{86}Sr$, U/As, U/Rb.

The first group corresponds to the brines (1.8 mol l^{-1} of Cl) of some localized dacitic domes drilled by a gold mine exploitation. The value of their Sr isotopic ratio is as high as 0.719. Two other groups correspond to the present recharge area of the aquifer (Fig. 5). The saline waters at the center and south center of the area displayed specific compositions distinct from the three other groups, supporting a distinct origin of these waters. Diagrams such as (C_x, C_{Cl}) and ($^{87}Sr/^{86}Sr$, C_x/C_{Sr}), where C_i is the concentration of the chemical element i, were used for discussing the origin of the groundwater salinity. In these diagrams the saline samples of groundwater display linear trends congruent with the hypothesis of a mixing between two end member components, one of low Cl content and the other one of high Cl content. The end member with low Cl content is associated with the recent recharge waters. The Cl enriched end member does not correspond to any identified group of present water. Various characteristics (SO_4/Cl, Li/Cl, K/Cl, Na/Cl, $^{87}Sr/^{86}Sr$ compositions) lead us to identify the Cl enriched end member as the paleolake Tauca or some more recent laguna.

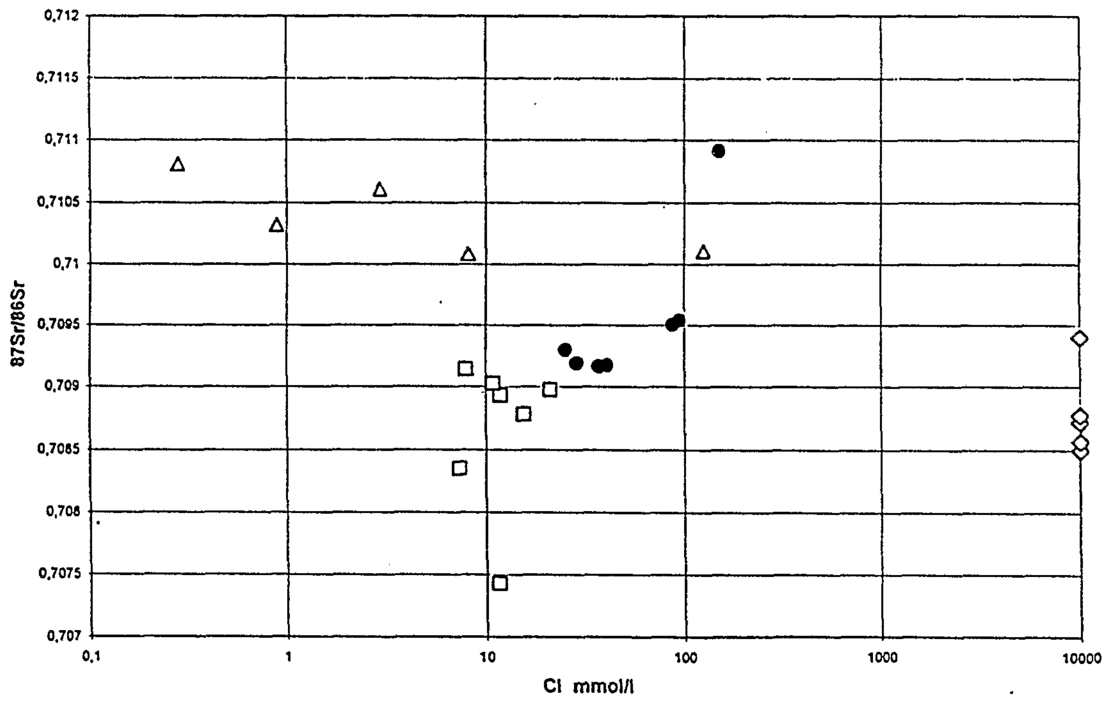


FIG. 5. $^{87}Sr/^{86}Sr$ versus Cl content of waters, and $^{87}Sr/^{86}Sr$ composition of stromatolites from Bolivian Altiplano. White triangle: surface and groundwater corresponding to local runoff and western tributaries recharge. White square: surface and groundwater corresponding to recharge from northern catchment. Black circle: saline groundwater in the aquifer under study. White diamonds: stromatolites sampled in various parts of the Altiplano.

6. DISCUSSION AND CONCLUSION

One part of this study, on evaporation from aquifers under arid climatic conditions, is an example of the usefulness of comparing different approaches. Results from isotopic approach allowed re-analysing the previous accepted and erroneous results from hydraulic approach. Finally the simple relation proposed by this study may be used for local or regional and present or past estimation of evaporation from aquifers in any arid zone area where evaporation is a major outflow process.

On the dynamics of the aquifer of the central Altiplano, present groundwater flow, spatial evolution of geochemical parameters (^{14}C, δ^2H, $\delta^{18}O$, Li/Cl, trace element and Sr isotopic compositions) and results of modelling groundwater flow and Cl transport allow to conclude that the present concentration of chloride in the aquifer may be bound to the paleolake Tauca (12 ka B.P.). Temporary accumulation of salt in the unsaturated zone due to evaporation over long arid periods and subsequent leaching into the aquifer may also have occurred, probably at 2 ka B.P. This secondary process might have delayed the transfer of salt towards South.

The functioning proposed on the base of the available data is the following. When the aquifer was covered by the paleolake Tauca (maximum level at 12 ka BP), diffusion of salt from the saline lake allowed to increase chloride concentration in the aquifer. It is assumed today, as a working hypothesis, that this concentration might be around 200 meq l^{-1}. Since the lake retreat, around 11 ka BP convection pushes the bulk of saline groundwater toward southeast. This movement was very slow during the very dry period between 8 ka and 2 ka. Since the lake retreat, evaporation from the aquifer led to accumulate salt in the unsaturated zone over the aquifer. This salt remains in general in solution that is under saturated with respect to halite. A humid period could have taken place between 4 and 2 ka when the level of the lake Titicaca is recorded to have increased rapidly. Subsequently, such humid period could have allowed the leaching of the salt into the aquifer by a small amount of water. Such process would not modify the ratio of lithium/chloride or the isotopic ratio of strontium.

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