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Stable isotopes (Li, O, H) combined with brine chemistry: powerful tracers for Li origins in Salar deposits from the Puna region, Argentina.

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Abstract

Future improving of the innovative technology of Lithium air batteries correlates with an increased demand for Li-resources. We analyzed and compared stable isotopic compositions from 4 Argentinean Li rich salars. The Pozuelos (PS), Centenario (CN), Ratonés (RT) and Hombre Muerto (HM) belong to the world class brine resources of the Atacama triangle. CN has a halite core surrounded by fine grained clastic sediments, while RT comprises lesser evaporates, but coarser grained volcanoclastics. Two Cl-Na SO₄ brine aquifers (down to 250 m depth) host several hundreds of mg/l of Li. The surface waters are characterized by Li < 7 mg/l, $\delta^7\text{Li}$ of ≈ 9.5 , δD : -66 ‰ and $\delta^{18}\text{O}_{\text{SMOW}}$: -7.8 ‰. The stable isotopic composition differs slightly from the upper aquifer ($\delta^7\text{Li} \approx 9.2$ ‰, δD -47.2 ‰ and $\delta^{18}\text{O}_{\text{SMOW}}$ -0.8 ‰) to the lower aquifer ($\delta^7\text{Li}$: 9.7 ‰, δD : -51.6 ‰ and $\delta^{18}\text{O}_{\text{SMOW}}$: -1.7 ‰). The dominant source of Li is related to water-rock interactions (surface, saline waters with andesites, pegmatites, pyroclastics). The comparison of our RT and CN data to those of the close-by PS and HM, shows that each salar has its own geological, hydrological and climate history which can be defined by crossing isotope tracers. However, the development of pertinent isotopic regional and local exploration proxies, needs identical data sets on systematically defined samples of the same aquifer type, on country rocks and minerals.

Keywords: Lithium isotopes, oxygen and hydrogen isotopes, brine, salar, Argentina,

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1. Introduction

Recently Li air batteries represent an innovative technology as theoretically, its performance in high energy density could be similar as that of gasoline. Improving this technology will extend the market for electric vehicles and consequently increase the demand of Lithium. Research on Li-brine deposits is challenged by defining Li-concentrations, its sources and enrichment processes in order to develop further exploration tools. Stable isotopes (Li, O, H) may represent powerful tracers in these domains (e.g. 1, 2, 3). The Altiplano (3700-4000 m) in the Andes, hosts the world’s most important Li brine deposits. These deposits were formed during the successive aridification and final isolation of the Atacama Desert and reduced erosion, and are related to the complex tectono-magmatic history (4, 5). Variable sources (leaching of the basin host rocks, geothermal and/or hydrothermal activity related to geodynamic settings) are suggested (e.g. 2, 3, 4). Brine-rock interactions and climate variations may have modified the brine composition in time. This paper presents new results from two mixed siliciclastic-evaporite salars, the Centenario (CN) and Ratonés (RT) and compares its brine characteristics and stable isotope composition and chemistries to that of the Hombre Muerto (HM) and Pozuelos salars (PS: 2, 3, 6).

2. Geological Setting

The four salars (approximately NNE-SSW oriented; Fig. 1, 7) belong to a basin and range province, a result of thrusting, uplift and volcanic activities, originated from the large shallow Altiplano-Puna magma body scale. PS (83 km²) is limited to the NW and SE by Ordovician volcanic and sedimentary rocks, to the N, NE, W and SSW by Tertiary polymict conglomerates, salt banks and tuffs discordantly overlain by Quaternary alluviums and lacustrine sediments (halite to the N, E and W; ulexite to the N (6). E-W compression compartmentalized the basin into the sandy halite and halite basin (N), and the more clastic basin (S). The CN-RT basin (total surface: 1730 km²) is bordered to the E by Precambrian crystalline rocks, Paleozoic granites, low-grade metamorphic sedimentary rocks and volcanics, to the N and to the W by Miocene sedimentary rocks and andesites, as well as Paleozoic metamorphic rocks, to the S by Quaternary andesites. The basins are filled episodically by clastic sediments from the drainage basin (W and E), gypsum and borate evaporated under semi to arid climate conditions since Miocene. Late-stage fills (< 100 years) are calcite-gypsum-halite (7). The two salars are separated by an alluvial fan to the E. The CN and RT sub basins are separated by a rotated fault block, which are connected by a paleochannel (8). HM (≈600 km²) is a complex structure bordered by Paleozoic sedimentary rocks and locally Quaternary mafic lava to the N, W, S; to the E by Miocene sedimentary rocks and Quaternary mafic lava occur (9).

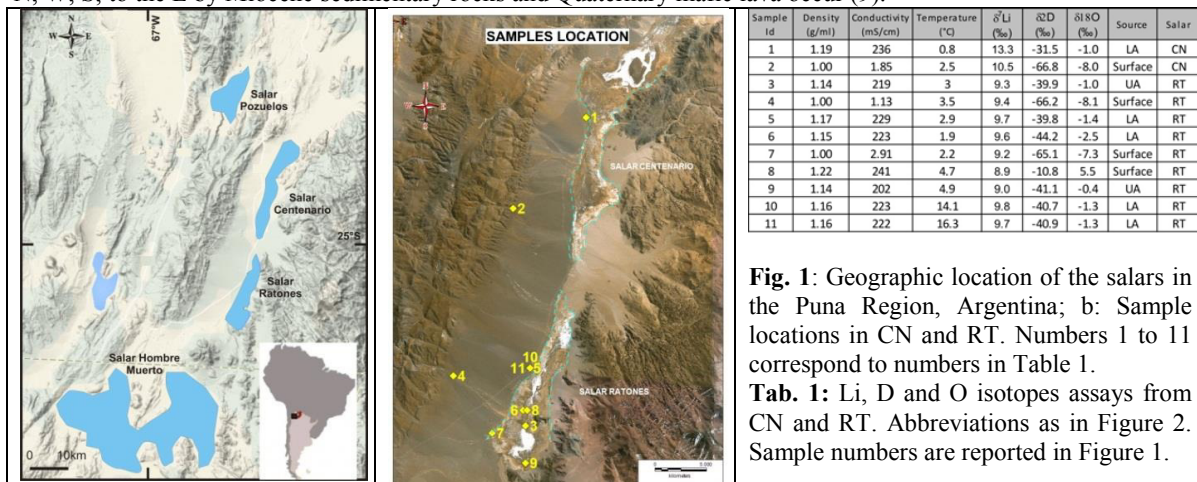


Fig. 1: Geographic location of the salars in the Puna Region, Argentina; b: Sample locations in CN and RT. Numbers 1 to 11 correspond to numbers in Table 1.

Tab. 1: Li, D and O isotopes assays from CN and RT. Abbreviations as in Figure 2. Sample numbers are reported in Figure 1.

The basin is filled with ≈ 1000 km³ of ignimbrite and recent scoria (e.g. 10 and papers therein). The salar is compartmentalized with a halite depot center to W of the major NNW-SSE oriented fault. The Li contents of PS, CT, RT vary from ≈250 to ≈800 mg/L (6), lower than those of HM (≈ 400 - 950 mg/L (2)).

3. Analytical Methods

Brine densities and temperatures were measured in situ together with conductivity and pH (titration method with methyl orange indicator) (Tab. 1). Chemical analyses were performed at Alex Stuart laboratory (Mendoza, Argentina) for major cations and anions (ion chromatography, ICP). Samples were analysed for stable isotopes at BRGM. Sample preparation and analytical methods are described in (1). The reproducibility for each $\delta^7\text{Li}$ measured is $\pm 0.5\%$, $\delta^{18}\text{O}_{\text{SMOW}}$: $\pm 0.2\%$ and $\delta\text{D}_{\text{SMOW}}$: $\pm 1.2\%$. $\delta^{18}\text{O}$ and δD were corrected empirically for the salt effect.

4. Results

Surface waters are diluted and characterized by low contents of Na (< 0.4 g/l), Cl (< 0.2 g/l), SO_4 (< 0.7 g/l) and Li (< 10 mg/l), low δD (-66 ‰) and $\delta^{18}\text{O}$ (-7.8 ‰). They have an average $\delta^7\text{Li}$ of 9.5 ‰. However, one surface sample from RT show unusual high Na, Cl, Li and SO_4 contents (> 10g/l). This sample has highest δD (-26.3 ‰) and $\delta^{18}\text{O}$ (+5.9 ‰), and lowest $\delta^7\text{Li}$ values (8.9 ‰). The brines of both salars can be classified as Cl-Na ($\approx 70\text{g/l Na}$, $\approx 150\text{g/l Cl}$) with high SO_4 contents (>10 g/l). Lithium contents of a few hundred mg/l are positively correlated with the Cl content and the total cation contents. However, $\delta^7\text{Li}$ values in the upper aquifers are slightly lower (9.2 ‰) compared to the lower aquifers (9.7 ‰). However the CN upper aquifer shows highest $\delta^7\text{Li}$ value of 13.3 ‰. δD and $\delta^{18}\text{O}$ are slightly higher in the upper aquifer (-47.2 ‰ and -0.8 ‰, respectively) compared to the lower one (-51.6 ‰ and -1.7 ‰, respectively).

5. Discussion and conclusion

The isotopic differences of the aquifers and surface waters for the four salars are shown in Fig. 2 (2). Generally, in semi-arid regions, evaporation dominates due to an upward hydraulic system, thus it can be suggested that the surface water at RT, with highest Na, Cl and Li contents, represent most likely discharge ponds/seeps rather than recharge areas (11). Upper aquifers have higher $\delta^{18}\text{O}/\delta\text{D}$ ratios than the lower ones, while lowest ratios are observed in the surface waters and the highest ratio in the RT “seep/pond water”. All points are located on the evaporation line (Fig. 2). A systematic evaporation trend was also observed for the brines from the PS (3) and the surface waters of HM (2). However the HM subsurface waters plot close to the meteoric water line, which is explained by an evaporation delay related to the lowering of the water table, and water entering HM except the lagoon (2). The surface waters of the western border of the RT and the CN upper aquifers show increasing $\delta^7\text{Li}$ with increasing Cl/Li ratios with a high slope, tracing precipitation of secondary minerals (incorporating lithium and preferentially ^6Li). The RT pond water, lower and upper aquifers show also a positive correlation, but with a lower slope, indicating its minor effect on Li isotopic fractionation. The HM Cl/Li ratios in the subsurface waters are higher than in the surface brine reflecting again an evaporation delay due to water influx. Surface waters of the RT/CN salars are low in Cl with variable SO_4 contents, which may reflect interactions with gypsum at the western border of the basin. The CN surface pond has high Cl and very low SO_4 indicating different sources of these elements. The samples of lower and upper aquifers in the RT region are roughly positive correlated, reflecting similar sources of Cl and SO_4 and its enrichment due to evaporation. One sample from the upper aquifer at RT is off this evaporation line, which may imply a higher contribution from sulfides or sulfates. Highly varying Li-isotopic compositions (+12‰ to +20 ‰) from the PS indicate that Li is derived from different sources through water-rock interaction with variable magmatic, metamorphic and sedimentary host rocks. In contrast, the RT and CN $\delta^7\text{Li}$ values are lower and more homogenous; only the RT surface pond water show similar values (3). The HM $\delta^{18}\text{O}$ and δD isotopic compositions show a strong influence of wet and dry climate conditions, but also of freshwater influence which was related to Li-brine pumping, and Li may be rapidly accumulated during pluvial climate conditions (2). Analyses of Li and $\delta^7\text{Li}$ of the HM country rocks and minerals show that highest Li values are recorded in ignimbrites ($\approx 1000\text{ ppm}$), and Li-micas and Li-phosphate from the basement rocks near Mina de Patos (2). For the RT and CN, the dominant source of Li seems to be derived from leaching of andesites and pegmatites by surface waters and the interaction of brines with the pyroclastic material of the host aquifer. As low $\delta^7\text{Li}$ signatures are not associated to high Li contents, a deep and hot hydrothermal origin can be excluded as a main Li source. Further analyses at RT and CN on the host rocks and minerals, on brines and geothermal springs including Sr isotopic composition would provide further

proxies for Li exploration. This study shows that, even belonging to the same geographical/geological province, each salars has its own geological, hydrological and local climate history. In order to use the here studied isotopic tracers as more powerful exploration tools in modern and fossil Li-brine regions, it would necessary to compare identical data sets (waters, brines, rocks and minerals) on systematically defined samples.

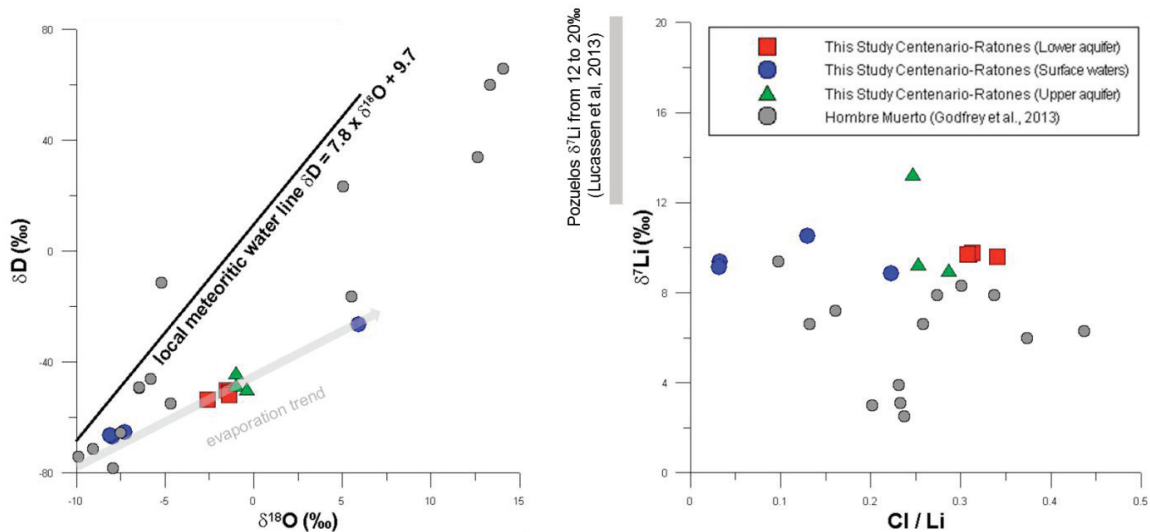


Fig. 2: δD versus $\delta^{18}O$, and Cl/Li versus δ^7Li show distinct populations: surface waters (blue dots), the brines (red squares: lower aquifers, green triangles: upper aquifers). Meteoric water line (12). Data from HM (grey dots): (2)

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