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Li-rich clays in Andean systems: the influence of geothermal activity in their genesis

Morata, D.[1]*, Maza, S.[1] and Abad, I[2]

[1]Department of Geology and Andean Geothermal Center of Excellence (CEGA), Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago, Chile. [2]Departamento de Geología y CEACTEMA, Universidad de Jaén, Campus Las Lagunillas, 23071 Jaén, Spain

E-mail address: dmorata@ing.uchile.cl

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1 INTRODUCTION

Lithium, one of the most important metals in modern society, is classified as an energy-critical element due to the increasing global demand for Li-ion batteries. Moreover, Li is considered as a key element in the transition energy policy aimed to reduce the dependence of fossil fuels pointing out to low-CO_2 emission technologies. ... The global lithium market is largely supplied by two main sources: pegmatites and brines (Bowell et al., 2020 and references therein). Currently, Australia dominates production from pegmatites, while Chile leads in lithium extraction from brines However, a third, non-conventional Li-rich source, are the claystone deposits such as volcanic clay deposits, lacustrine clays, and evaporite sequences, that are enriched in Li and mostly related with old volcanic calderas. In these volcano-sedimentary Li-rich deposits Li is mostly concentrated in phyllosilicates like hectorite (a Mg-rich smectite) and other clay minerals (illite), and these are currently the subject of intense worldwide research (e.g., Benson et al., 2017; Castor et al., 2020; Emproto et al., 2024; Putzolu et al., 2024; Kadir et al., 2025).

Warren et al (2017 and references therein) propose that the combination of the following processes are needed for the lithium rich clays formation: (1) hydrothermal alteration of volcanic ash or glass; (2) precipitation of authigenic phases from saline lacustrine pore waters; and/or (3) lithium incorporation into detrital smectite during diagenesis.

In the Andean Cordillera and in the Central Depression of Northern Chile these three key factors have been prevalent for at least the last 10-12 Ma. The massive silicic volcanism (the Altiplano Puna Volcanic Complex – APVC–) with the consequent formation of calderas, together with arid to hyper-arid climatic conditions and widespread hydrothermalism are the perfect confluence of factors for the formation of Li-rich brines that become concentrated in present day and past endorheic evaporitic basins (salars). Moreover, the presence of paleo-endorheic basins in the Central Depression of the Northern Andean Cordillera opens a new window for the presence of Li-rich claystones related with lacustrine deposits or paleosalars. This work analyzes some paleosalars deposits in the Quillagua depocenter (Figure 1) in the Central Depression of Northern Chile where Li-rich claystones have been identified. Using mineralogical (XRD, SEM. HR-TEM) studies we propose a genetic model for this non-conventional Li-rich deposits that could potentially provide a new Li resource in Chile.

2 GEOLOGICAL SETTING

The Central Depression in Northern Chile is located in one of the most arid to hyperarid regions in the world, where several non-marine intramassif fore-arc basins were formed from Tertiary time (e.g., Pueyo et al., 2001; Hartley and Evenstar, 2010). Some Upper Miocene-Pliocene paleo-lacustrine and paleosalars in the Central Depression region of the Atacama Desert evidence a strong volcanic influence on the formation of these paleolacustrine deposits and an indirect input of elements such as Li through thermal springs (e.g., Pueyo et al., 2001). The Quillagua depocenter (Atacama Desert), where the Salar de Llamara is located (Figure 1), shifted over the last 9 Ma among conditions ranging between internal drainage that created a lake which was at time fully evaporated and other times fresh water, to the erosion of a 260 m deep canyon (Jordan et al., 2022). Moreover, contemporaneous with the sedimentary history of this endorheic basin, contemporaneous volcanic activity ejected extraordinary volumes of silicic volcanic materials from calderas located only 100 to 300 km east and southeast of the Quillagua depocenter (Jordan et al., 2022). Pueyo et al. (2001) presented a detailed lithofacies description of the ancient lacustrine sedimentary sequences, where volcanic components (mostly ignimbrites) are mixed with evaporates. Following the work of Pueyo et al. (2001), high rates of volatile emission through volcanism could explain the evaporite mineral accumulations observed in these salars, which experienced persistent volcanism and arid and endorheic conditions during the Neogene. Moreover, these arid to hyperarid

conditions, for at least the last 10 Ma, has been proposed by Reich and Bao (2018) as a first order in the preservation of massive nitrate deposits (the “caliche” belt) and the Li-clay rich horizons that have been observed interlayered in the evaporite sequences.

A complete description of the stratigraphy of the sedimentary formations of the Quillagua depocenter was published by Pueyo et al. (2001) and Jordan et al. (2022). Along the Loa Canyon, north of Quillagua village (Figure 1), the Miocene to Pliocene stratigraphic units presented belonging to the Quillagua depocenter are named as Quebrada Amarga (Upper Oligocene-Lower Miocene), Hilaricos (Upper Miocene), Quillagua (Upper Miocene-Pliocene) and Soledad (Pliocene) formations (Jordan et al., 2022; Vásquez et al., 2018). These sedimentary units are composed by of evaporites, evaporitic sands, sandstones, siltstones, and gravel sequences, where Li-rich evaporites drilled by 2008 (454 up to 1161 ppm) were obtained in several sectors of the Soledad Formation north-east of Quillagua. Based on available geochronological ages, Jordan et al (2022) proposed an age for the Soledad Formation of 4.1-2.6 Ma, contemporaneous with the voluminous volcanic explosive deposits (some of them exceeding 1000 km^3 volumes) proximal to areas now draining into the Quillagua depocenter. For the present work, only rocks from Soledad Formation, sampled along the Loa canyon, and composed by lacustrine evaporitic sequences, will be considered.

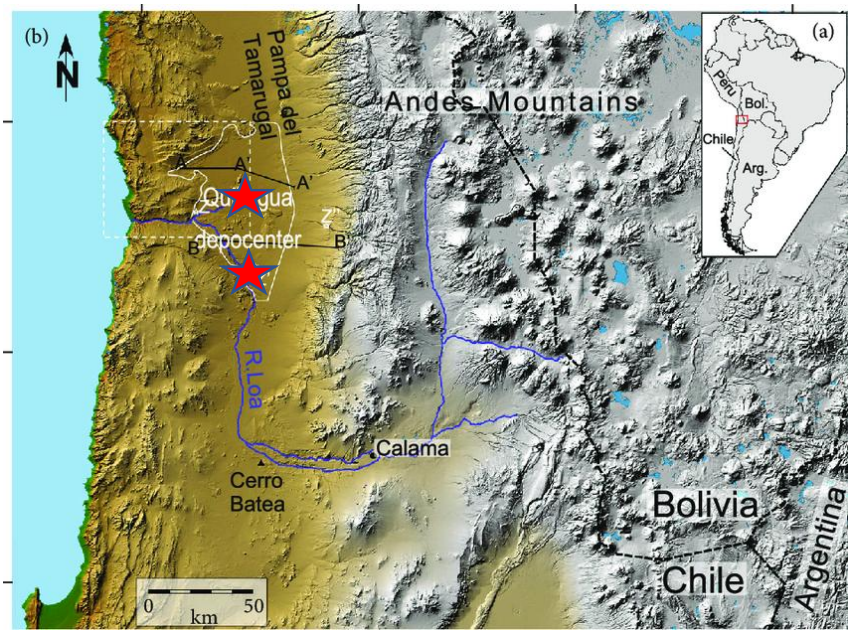


Figure 1. Location of the Quillagua depocenter (taken from Jordan et al., 2022) and location (red stars) where studied samples from Soledad Formation come from.

3 METHODOLOGY

Representative samples of the evaporitic and siltstone units were selected for mineralogical and geochemical analyses. X-ray diffraction (XRD) analyses were obtained from whole unoriented powdered samples and also from oriented aggregates prepared by sedimentation on glass slides from the < 2 μm fraction. Clay fraction analyses were performed after washing with distilled water to remove salts. X-ray diffractograms were obtained using a Bruker D2 Phaser diffractometer at the CEGA XRD laboratory. Mineral identification was performed using the Diffrac.EVA v5.2 software and the mineral quantification was obtained using the TOPAS-6 software with the Crystallography Open Database. Chemical analyses of whole-rock were also performed at the CEGA geochemical laboratories. Trace elements (Li, Sr and Ba) for the clay-rich layers were analyzed in a Thermo Scientific iCAP Q quadrupole mass spectrometer (Q-ICP-MS). Anions (chlorine, sulphate, nitrate, bromide, phosphates and fluorine) were analysed by ionic chromatography (IC) using a Metrohm 861 Advanced Compact IC. Intercalated tephra deposits into the evaporitic Soledad sequence were examined in a scanning electron microscope (SEM) FEI Quanta 250 at the CEGA laboratory.

Finally, detailed clay mineral analyses were performed on selected samples by high-resolution transmission electron microscopy (HR-TEM) at the Centro de Instrumentación Científica (CIC) of the Universidad de Granada (Spain) using a HAADF Thermo Fisher Scientific TALOS F200X microscope, operating at 200 kV and with a point-to-point resolution of 0.12 nm in the TEM mode and 0.19 nm in the STEM mode. The quantitative micro- to nano-chemical analyses, in the STEM mode, were obtained by means of the AEM-EDX (energy dispersive X-ray microscopy), using the Super-X system.

4 RESULTS AND DISCUSSION

Soledad Formation whole-rock XRD analyses identified anhydrite, halite, gypsum and bassanite as major phases, coupled with glauberite, nitratine and strontianite as accessory evaporitic minerals. Detritic, authigenic and diagenetic minerals are dominated by quartz, feldspars, clay minerals and clinoptilolite. Separate clay fraction geochemistry confirms the presence of Li-bearing phases, with ICP-MS Li content ranging from 130 to 931 ppm. High chlorine, sulphate, nitrate, and bromide content confirm the presence of evaporitic phases even in the clay fraction samples. The careful determination by XRD of the Li-rich claystone layers highlights the presence of hectorite and illite/smectite (I/S) as the probable Li-hosted minerals. After ethylene-glycol treatment observed the characteristic ~11.5-12.5 to 16.1-16.9 Å hectorite shifting coupled with a R0 I/S with illite proportion <50%. Illite and chlorite were also identified in minor amounts.

Finally, EDX-HR-TEM microanalyses in Mg-rich trioctahedral smectite reflect charge deficiency in the octahedral site that could be interpreted as indirect evidence of Li in the smectite (hectorite) structure (Fig. 2). For the illite/smectite clays, less frequent in the analysed samples that smectite, illitic component could be assumed as trioctahedral and, in this case, cation deficiency could also be an indirect indicator of Li in their structure as substitution of Mg in the octahedral sites. Benson et al. (2023) also observed a Li-enrichment in illites with respect to smectites in volcano-sedimentary intracaldera illite-bearing claystones from the McDermitt caldera (USA).

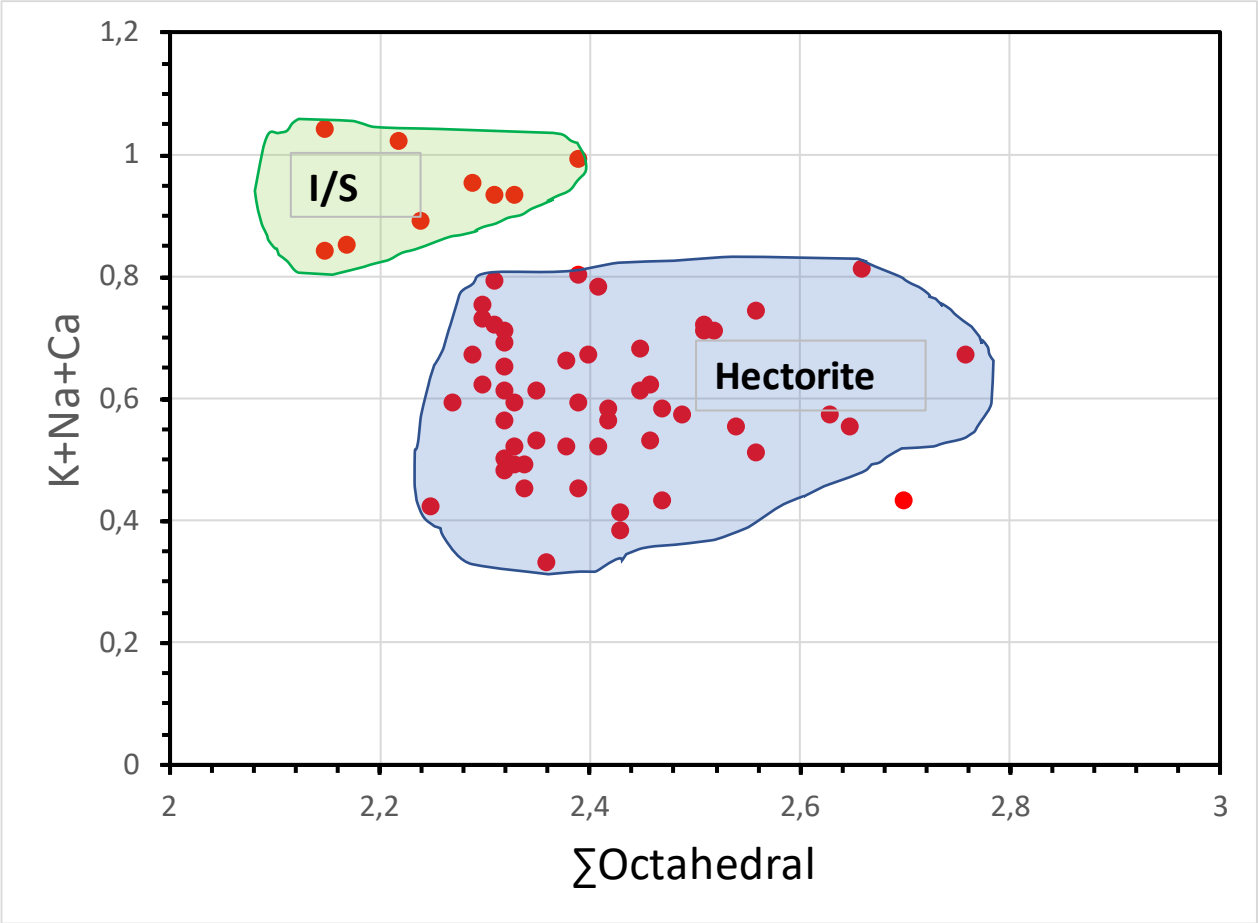


Figure 2. Chemical composition diagram of smectites (hectorite) and illite/smectite (I/S) clays analyzed in the studied samples by EDX-HR-TEM, showing >80% of the analyses a sum of octahedral cations ($Fe+Mg+Al^{VI}$) between 2.2 and 2.5 atoms per formula unit suggesting presence of Li in octahedral position.

The origin of these Li-rich clay deposits is considered to be controlled by the confluence of factors critical for the formation of volcano-sedimentary Li-rich claystones: (1) hyperaridity climatic conditions, (2) high evaporitic rate, and (3) intense volcanic activity (ignimbritic deposits) coetaneous with closed basin formation and geothermal activity. Our working hypothesis assumed that intense acid volcanism, during the explosive APVC events, favoured the formation of pyroclastic rocks that were altered because hydrothermal activity related with past geothermal systems. Available data of geothermal fluids from production wells from the only one geothermal power plant existing in the Andes (Cerro Pabellón, Chile, see Morata & Arancibia, 2025) show Li content in the

geothermal brine of *c*. 60 mg/l. This Li content is assumed to have an origin as consequence of interaction between hot geothermal fluids with ignimbritic deposits hosting the geothermal reservoir. And recently, Ayaz Alam & Muñoz (2024) propose the association between geothermal fluids and lithium-rich brines in the Laguna Verde (N. Chile) hypersaline lake and salt flats.

In this sense, Miocene-Pliocene caldera collapse and ash-flow deposits would favour Li-rich hydrothermal fluids that mix with meteoric water in closed, topographically low caldera basin, generating a hybrid diagenetic fluid. Fluid-rock interactions, enhanced by the high geothermal gradient in the APVC, will increase these Li leaching processes. Such fluids would be mobile and flow west to the Central Depression where under arid climatic conditions, where evaporation will be strongly favoured in closed isolated lacustrine environments, and Li could be concentrated in Li-rich saline brines in surface waters and sub-surface brines. Some of this Li will be incorporated in neoformed smectite by surface sorption mechanisms together with the precipitation of evaporitic minerals. Finally, diagenetic, solid-state mineralogical transformations (enhanced by high geothermal gradient) in these saline basin sedimentary units would favour the released of Li from brines to be mostly incorporated in hectorite and the zeolitization of acid volcanic fragments. Water from the Loa catchment would have included sources with direct contact to hydrothermal systems at the margin of calderas (Jordan et al., 2022). In this same way, a $(^{40}Ar/^{39}Ar)_{biotite}$ age from a tephra deposits intercalated in evaporites from Soledad Formation (Vasquez et al., 2018) supports the coincidence in time between the evaporitic sedimentation with voluminous Tara (3.5 Ma) and Pastos Grandes II (2.89) ignimbrites (Jordan et al., 2022), suggesting a mostly volcanic origin for Li in these sedimentary deposits.

The high-Li content of active geothermal systems in northern Chile and the presence of Li-rich clays in some salars and paleosalars in the same geographical location aims to propose a genetic link between Andean Li-rich clays and active (and fossil) geothermal activity.

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