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► **To cite this version:**

Mariana Kelly Segovia-More, Lisard Torró I Abat, Cristina Villanova-De-Benavent, Johan Ramirez Briones, Jean Vallance, et al.. High-resolution mineralogy of Lithium-rich Tuff from the Macusani Volcanic Field, Puno, Peru. 17th SGA Biennial Meeting on Mineral Resources in a Changing World (2023), SGA, Aug 2023, Zurich, Switzerland. pp.303–306. hal-04251582

HAL Id: hal-04251582

<https://hal.science/hal-04251582>

Submitted on 20 Nov 2023

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High-resolution mineralogy of ‘lithium-rich tuff’ from the Macusani Volcanic Field, Puno, Peru

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Abstract. With Li contents ranging as high as ~2,000 to 4,000 ppm, the so-called ‘Lithium-rich Tuff’ in the Macusani Volcanic Field hosts the main lithium resource in the recently discovered Falchani Project in south-eastern Peru. These tuffs comprise quartz, plagioclase (albite), K-feldspar (sanidine), trioctahedral micas (zinnwaldite + lepidolite), kaolinite ± halloysite, and dioctahedral smectites, in addition to cristobalite and mordenite in a few samples. The highest Li contents (3,000-4,200 ppm Li) are found in the central portion of the ‘Li-rich tuff’ sequence, which is characterized by micas + kaolinite subgroup minerals ± mordenite. In the upper and lower portions of the tuff sequence, Li contents are < 2,000 ppm and the mineralogy is dominated by micas + dioctahedral smectite ± kaolinite ± halloysite. Li is contained mostly in zinnwaldite and lepidolite, and probably also adsorbed onto, or in interlayer positions in clay minerals.

1 Introduction

Lithium is a critical raw material for the development of eco-efficient energy technologies. Examples include Li-ion batteries for electric vehicles, much needed to promote the transition from fossil fuels to renewable energy sources in order to achieve EU’s 2025 carbon neutrality goal (IRENA 2019; European Commission 2020). Finding new conventional (e.g., granitic pegmatites, salars) and non-conventional (e.g., volcanogenic, oilfield brines) Li resources is thus essential to cover the ever-growing demand for this metal (Bowell et al. 2020; Jowitt et al. 2021; Graham et al. 2021).

In November 2017, the discovery of a major lithium resource in the Falchani Project in the central area of the Macusani Volcanic Field, located in the Eastern Cordillera of the Andes (Puno Department) in south-eastern Peru, was announced by Macusani Yellowcake S.A.C., the Peruvian subsidiary of American Lithium Corporation. As of 2023, indicated resources amount to 0.39 Mt Li₂O while inferred are 1.52 Mt Li₂O (<https://americanlithiumcorp.com/falchani-lithium-project>). Lithium mineralization occurs in Neogene breccias and tuffs. Out of these, the main lithium resource, and the higher grades – mostly between 2,000 and 4,000 ppm Li – are found in the so-called ‘lithium-rich tuff’ (The Mineral Corporation 2019).

In spite of the economic importance of these tuffs, a detailed mineralogical characterization is not available to this day. In this abstract, we present new mineralogical data, with an emphasis on clay

minerals, in order to discuss the mineralogical expression of lithium in the ‘Lithium-rich Tuff’ and a classification of the Falchani deposit.

2 Geological setting

The unit referred to as ‘Lithium-rich Tuff’ by companies exploring in south-eastern Peru belongs to the Macusani Volcanic Field (Fig. 1), a sequence of volcanic and volcano-sedimentary units mostly exposed in the Quenamari Meseta plateau, at an altitude of 4,400 m a.s.l., and is part of the Neogene ignimbrite centers of the Central Andes. Structurally, the Macusani Volcanic Field is located between the Cordillera de Carabaya and the central Andean backthrust belt, and belongs to the Macusani Structural Zone (Perez et al. 2016), previously known as the Precordillera de Carabaya (Sandeman et al. 1997). It relates to tectonic shortening/crustal thickening and contemporaneous lithospheric removal/thinning (Salisbury et al. 2011; Göğüş et al. 2022).

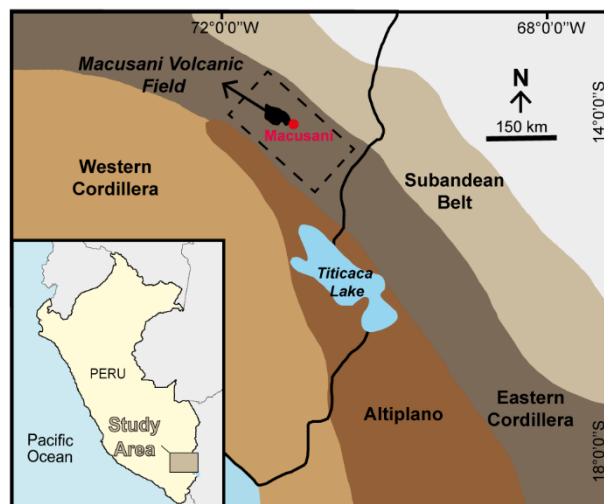


Figure 1. Location of the Macusani Volcanic Field within the geomorphotectonic map of the Central Andes.

Late Oligocene to late Miocene volcano-sedimentary sequences exposed in the Macusani Volcanic Field were grouped by Sandeman et al. (1997) under the Crucero Supergroup and subdivided into the Quenamari and Picotani groups. Rhyolitic ash-flow tuffs of the late Miocene (6.8 – 10.5 Ma) Macusani Formation, in which the studied ‘Lithium-rich Tuff’ is found, are part of the

Quenamari Group. The Macusani Formation comprises whitish-grey, poorly consolidated, lapilli-crystal tuffs mineralogically consisting of quartz, sanidine, plagioclase, sillimanite, andalusite, muscovite, biotite, and tourmaline (Sandeman et al. 1997). Geochemically, they are characterized by felsic and highly peraluminous signatures, with 71.5-75 wt% SiO₂, high Al₂O₃ (normative corundum >2%), and high alkalis, with an enrichment in lithophile trace elements (e.g., Li, Be, Cs, Nb; Pichavant et al. 1988). López (1996) renamed the Macusani Formation as Quenamari Formation and proposed its subdivision, from bottom to top, into the Chacacuniza, Sapanuta and Yapamayo members. In the Falchani Project, rocks of the Sapanuta Member, including the 'Lithium-rich Tuff', are widely exposed (The Mineral Corporation 2019).

3 Analytical methods

Thirty-two representative samples of 'lithium-rich tuff' were analysed by powder XRD using a Bruker D8 Discover diffractometer in Bragg-Brentano $\theta/2\theta$ geometry of 240 mm radius, at the Centro de Caracterización de Materiales of the Pontifical Catholic University of Peru (CAM-PUCP). Also, seventeen mica- and clay-rich samples, eleven of which from drill core, were analysed by XRD on oriented mounts using the same equipment and setup as for powdered samples, in air dried, ethylene glycol-saturated (ETG), heated (at 400 °C to 550 °C) preparations. Three samples were studied using a Quanta 650 FEI scanning electron microscope (SEM) equipped with an EDAX-Octane Pro Energy Dispersive Spectrometry (EDS) microanalysis system at CAM-PUCP. Three more samples were studied by Transmission Electron Microscopy (TEM), using powder specimens deposited onto formvar-covered Cu grids, to determine the mineral composition by Analytical Electron Microscopy (AEM) in the Thalos microscope of the CIC of the University of Granada, calibrated with natural standards.

4 Results

Powder XRD results show that the tuffs are mainly composed of quartz, plagioclase (probably albite), K-feldspar (probably sanidine) and mica (zinnwaldite and lepidolite; see Torró et al. 2023), with variable proportions of clay minerals (kaolinite subgroup minerals and smectites), mordenite, and cristobalite. The tuffs can be grouped into four categories according to their prevalent mineralogy: i) mica with no zeolite nor clay minerals, ii) mica with kaolinite subgroup minerals (Fig. 2a), iii) mica with smectite (Fig. 2b), and iv) mica with mordenite.

According to oriented-mount XRD data, the clay mineral peaks with $d_{(001)}$ spacing of 12 to 15.1 Å correspond to smectite. The $d_{(001)}$ spacing expands with ETG to 16.6 to 17 Å, and contracts to ~10 Å with oven-dried treatment at 400°C and 550°C. Moreover, the clay presenting peaks with $d_{(001)}$

spacing of 7.1 to 7.2 Å at 2 θ ~12.3° for air dried samples corresponds to kaolinite subgroup minerals. ETG and 400° heat treatments have no effect on the diffractogram of this mineral, but the $d_{(001)}$ spacing peak was destroyed by heat treatment at 550°, which is consistent with the aforementioned subgroup.

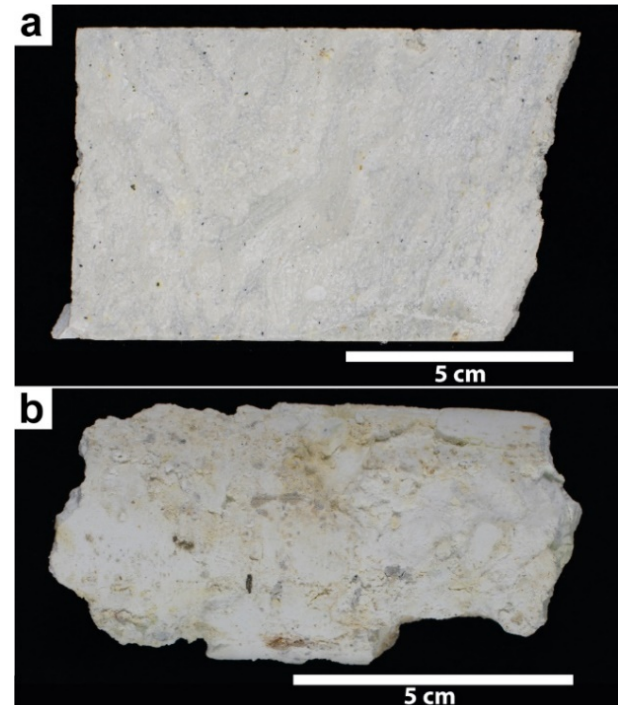


Figure 2. Lithium-rich samples from Macusani Volcanic field. a) 2021-MAC-040: mica (scattered black grains) with kaolinite subgroup minerals. b) 2021-MAC-051: mica with smectite.

In Figure 3, the diffractograms obtained from powder XRD analysis of samples of three drill core samples (i.e., mica- and clay-rich samples corresponding to 2021-MAC-035 to 2021-MAC-053) are ordered according to their relative depth,

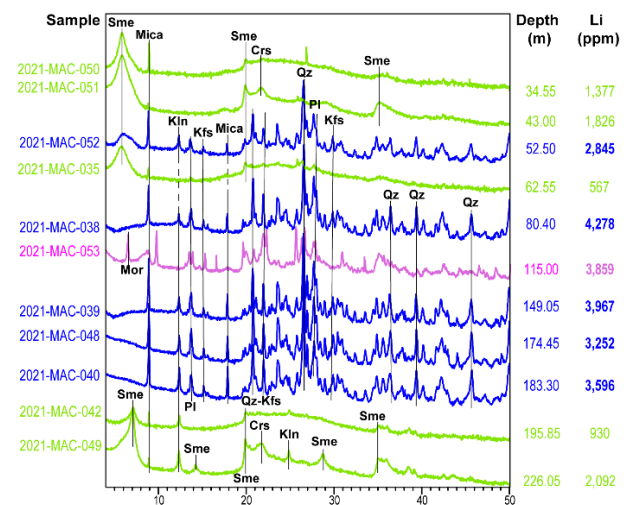


Figure 3. Drill core samples classified according to the prevalent mineralogy (color) and ordered according to their relative depth. Key: plagioclase (PI), mica (Mica), quartz (Qz), K-feldspar (Kfs), kaolinite (Kln), smectite (Sme), cristobalite (Crs), and mordenite (Mor).

with their corresponding lithium contents. A vertical mineral zoning comprising three main layers is observed: i) the upper tuff zone (UTZ), ii) the central tuff zone (CTZ), and iii) the lower tuff zone (LTZ). The UTZ presents Li contents in the range of 567 to 1,826 ppm and is dominantly composed of smectite and micas. The CTZ has the highest Li contents – ranging from 2,845 to 4,278 ppm – and is dominated by micas and kaolinite. Finally, the LTZ presents Li contents between 930 and 2,092 ppm and the mineralogy consists predominantly of smectite, micas ± kaolinite.

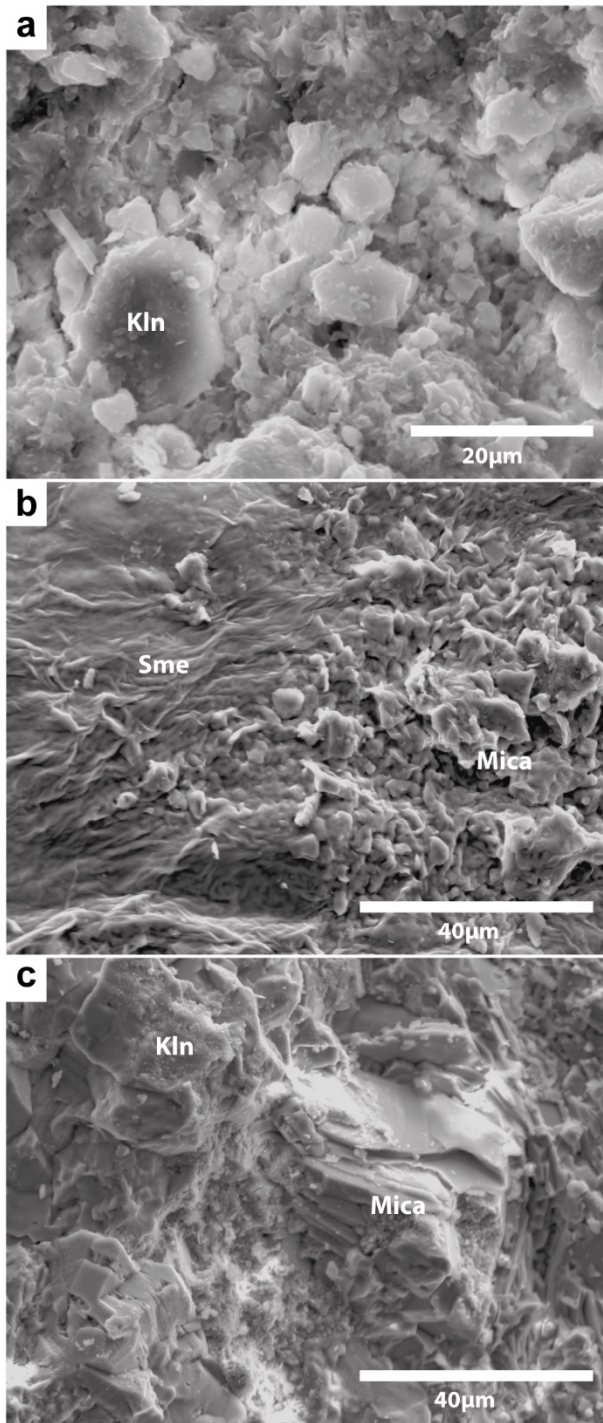


Figure 4. Secondary-electron SEM images of samples from the ‘Lithium-rich Tuff’. a) Pseudo-hexagonal plates of kaolinite with sheet-like masses probably corresponding to mordenite. b) Hybrid morphologies of tightly interwoven

flakes with areas with scalloped edges characteristic of smectite and mica. c) Flaky grain of mica and kaolinite aggregates.

Secondary-electron SEM images of samples 2021-MAC-026, 2021-MAC-035, and 2021-MAC-039 show the morphologies of clay minerals, micas, and zeolites. In sample 2021-MAC-026, small plates of variable thicknesses are observed, most probably corresponding to kaolinite subgroup minerals, according to their pseudo-hexagonal morphology (Fig. 4a). In addition, some grains yield high contents of O and Si in EDS spectra, compatible with the zeolite mordenite. In sample 2021-MAC-035, tightly interwoven and wavy flakes with curved-edges are distinctive of smectite (see Keller et al. 1986), whereas mica grains show scalloped edges (Fig. 4b). SEM-EDS analyses in smectite reveal relatively high contents of Si and Al and minor proportions of Mg, Ca, and Na. Finally, in sample 2021-MAC-039, a flaky grain of mica and kaolinite subgroup minerals are observed (Fig. 4c).

The TEM study (Fig. 5A) shows that the fine fraction of samples 2021-MAC-049 and 2021-MAC-050 is majorly composed of smectite showing dioctahedral characteristics in the electron diffractions (Fig. 5B), and chemical compositions with the octahedral population approaching 2 atoms per formula unit (apfu). Iron and Mg contents are low, with some analyses showing a slight octahedral deficit. Interlayer occupancy is deficient and composed of small quantities of Na, K, and Ca. The fine fraction of sample 2021-MAC-038 contains predominantly mica and kaolinite subgroup minerals. Mica consists mostly of Si, Al, and K, with very scarce Mg and Fe, and its composition can be adjusted to that of ‘lepidolite’. Assumption of the normal values of Li for this type of mica brings the octahedral occupancy to values in the range of 3 apfu.

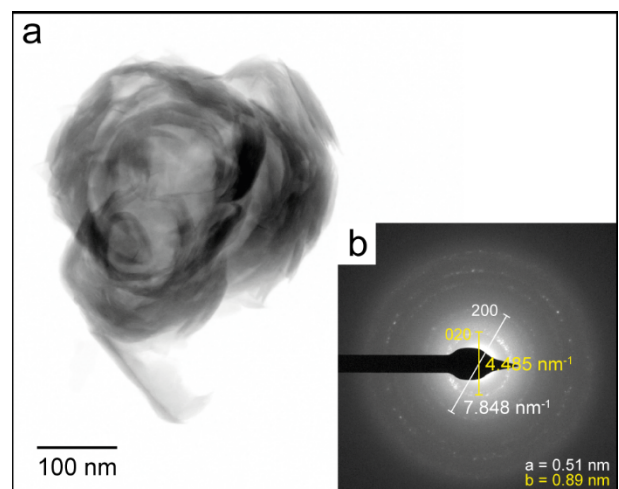


Figure 5. a) TEM image showing a flower-shaped smectite aggregate with curved morphologies. b) Electron diffraction pattern showing the crystal parameters ($a = 5.1 \text{ \AA}$, $b = 8.9 \text{ \AA}$) indicative of dioctahedral smectite.

5 Discussion

A close correlation between lithium mineralization and pyroclastic units would ascribe the Falchani project in the Macusani Volcanic Field to the volcanogenic lithium deposit type. Volcanogenic deposits stand as 'non-conventional' Li resources – in front of 'conventional' LCT pegmatites and hydromorphic ('salar') deposits (Bowell et al. 2020). Enrichment in lithium to economic grades in volcanogenic deposits is considered to result from the interaction of pre-existing volcanic rocks enriched in lithium and atmospheric or hydrothermal fluids in rhyolitic calderas, triggering the deposition of secondary, Li-rich minerals (Benson et al. 2017; Bowell et al. 2020).

Volcanogenic lithium deposits are subdivided into clay, ion-clay, and jadarite subtypes depending on the nature of prevalent lithium-bearing phases (Bowell et al. 2020). From a mineralogical point of view, the best studied volcanogenic lithium deposits are those in the McDermitt Caldera in Nevada (USA). Castor and Henry (2020) concluded that, in the Thacker Pass deposit of the McDermitt Caldera, lithium occurs in hectorite (Li-smectite), in an illitic clay that is chemically similar to tainiolite, and in a mixed-layer smectite-illite clay. These authors reported a vertical mineral zonation consisting of i) illitic clays in the lower sedimentary section (~ 3,000 ppm Li), ii) a transitional zone with mixed smectite-illite (tainiolite?) clays (~ 2,000 ppm Li), and iii) an overlying upper sedimentary section dominated by hectorite (< 2,000 ppm Li).

Based on the XRD, SEM-EDS, and TEM data presented here, the mineralogy of the 'Lithium-rich Tuff' unit in the Macusani Volcanic Field consists of quartz, plagioclase, K-feldspar, trioctahedral micas, mordenite, cristobalite, and clay minerals (kaolinite ± halloysite and dioctahedral smectite). The trioctahedral micas correspond to zinnwaldite and lepidolite and are interpreted as igneous in origin (see textural and compositional details in Torró et al. 2023). No other lithium-bearing minerals have been identified in the studied samples. However, preliminary metallurgical tests on 'Lithium-rich Tuff' from the Falchani Project reported by The Mineral Corporation (2019) describe Li recovery as high as 90 % by leaching with sulfuric acid at 90–95°C, thus suggesting that Li may also occur adsorbed or in interlayer positions in smectite and/or kaolinite subgroup minerals. Our ongoing mineralogical work on samples from the Falchani Project will help assess the contribution of relict (i.e., zinnwaldite-lepidolite) and secondary (i.e., smectite, kaolinite subgroup minerals) phases to the bulk lithium resource and refine the classification of the deposit.

Acknowledgements

We wish to thank the geologists from Macusani Yellowcake for their help and hospitality during fieldwork. This research work was financed by the Peruvian PROCENCIA-FONDECYT project 1122-

2020 E041-2020-01-01, and logistically supported by the 2021 SGR 00239 project of the Agència de Gestió d'Ajuts Universitaris i de Recerca de Catalunya.

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