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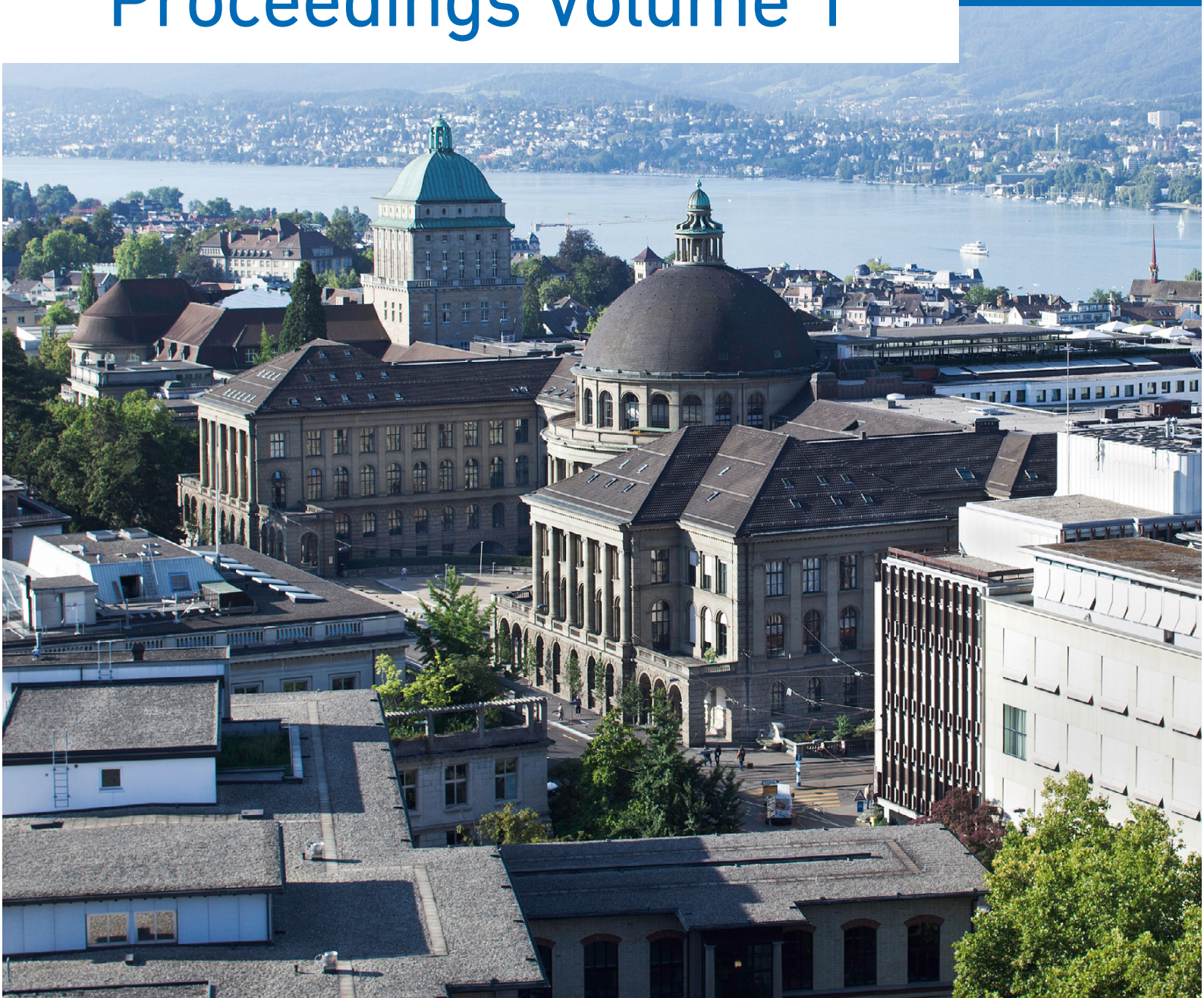
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# Lithium-bearing micas in the ‘Lithium-rich Tuff’ from the Macusani Volcanic Field, Puno, Peru

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**Abstract.** The Falchani Lithium Project has a resource of 0.9 Mt Li hosted in Neogene volcanic tuffs and breccias of the Macusani Volcanic Field. The main host is a newly-defined unit known as ‘Lithium-rich Tuff’ in which Li contents are mostly between 3,000 and 4,000 ppm. Although this tuff is pervasively altered to clays (dioctahedral smectite and kaolinite subgroup minerals) and zeolites, magmatic zinnwaldite and lepidolite crystals are preserved. The composition of the micas in the ‘Lithium-rich Tuff’ is systematically more evolved, i.e., richer in Li and other incompatible lithophile elements, relative to micas in other pyroclastic units and nearby intrusive rocks of the Macusani Volcanic Field.

## 1 Introduction

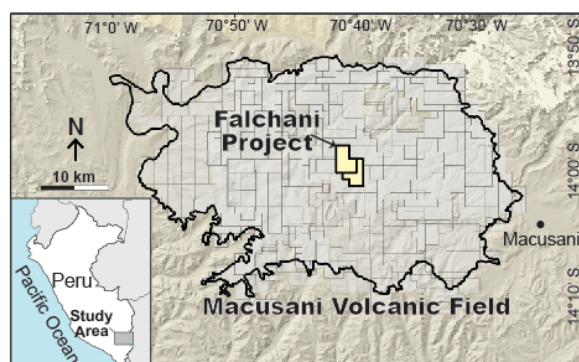
In November 2017, Macusani Yellowcake S.A.C., the Peruvian subsidiary of American Lithium Corp., announced the discovery of a major lithium resource in the Falchani Lithium Project, Puno department of south-eastern Peru (Fig. 1). As of February 2023, indicated resources amount to 0.2 Mt Li @ 2,954 ppm Li and inferred resources, to 0.7 Mt Li @ 2,706 ppm Li (<https://americanlithiumcorp.com/falchani-lithium-project>). Lithium resources are hosted by Tertiary rhyolitic tuff, breccia, and ignimbrite of the Macusani Volcanic Field (MVF), chiefly by the so-called ‘Lithium-rich Tuff’ in which Li contents are almost systematically between 3,000 and 4,000 ppm (Nupen 2019).

The general mineralogy of the ‘Lithium-rich Tuff’ is described and discussed in Segovia-More et al. (2023). It comprises relict igneous quartz, feldspar, and micas, and secondary phases such as fine-grained quartz, clays (kaolinite, dioctahedral smectites), and zeolites. In this abstract, we present the first data available on Li-bearing micas from the ‘Lithium-rich Tuff’ and nearby granites, breccias, and ignimbrites from the MVF. Variations in mica compositions are discussed focusing on their contribution to the Li endowment and source magmas.

## 2 Geological setting

The MVF (Fig. 1) is an ignimbrite basin exposed in the Quenamari Meseta, a plateau at an altitude of 4,400 m.a.s.l. in the Eastern Cordillera of southern Peru (Cheilletz et al. 1992). It is part of the Neogene ignimbrite centers of the Central Andes related to tectonic shortening, crustal thickening, and

contemporaneous lithospheric removal and thinning (Salisbury et al. 2012; Göğüş et al. 2022). The MVF 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 is underlain by Triassic syn-rift continental deposits of the Mitu Group, now exposed in the Eastern Cordillera due to tectonic inversion of the Triassic rift during Cenozoic Andean shortening.



**Figure 1.** Location of the study area in SE Peru (inset) and of the Falchani Lithium Project concessions in the MVF.

Extrusive and intrusive suites exposed in the Macusani and neighboring volcanic fields represent the youngest igneous events recorded in the Macusani Structural Zone (Clark et al. 1990) and were grouped by Sandeman et al. (1997) into the Crucero Supergroup and the Crucero Intrusive Supersuite, respectively. Volcanic units, including lavas and pyroclastic deposits, were subdivided by these authors into the late Oligocene–early Miocene Picotani Group – comprising medium- to high-K calc-alkaline basalts, shoshonites and S-type rhyodacites and rhyolites – and the mid- to late Miocene Quenamari Group – comprising exclusively silicic peraluminous rocks. In the MVF, volumetrically dominant extrusive rocks belong to the Macusani Formation, the youngest unit of the Quenamari Group. This formation comprises a ~280 to 450 m-thick sequence of strongly peraluminous, rhyolitic, whitish-grey, poorly-consolidated, crystal-rich (~ 45 vol.%), ash-flow tuffs deposited between ca. 10.1 and 6.5 Ma (Cheilletz et al. 1992; Sandeman et al. 1997).

The lithium mineralization in the Falchani project is hosted by rocks of the Macusani Formation. The 'Lithium-rich Tuff' unit has a thickness comprised between 50 and 140 m and is sandwiched between an Upper and a Lower breccia, which are interpreted as deposited in a volcano-sedimentary environment and are also mineralized with average Li contents of ~1,400 and 1,900 ppm, respectively (Nupen 2019). The 'Lithium-rich Tuff' is interpreted to have deposited sub-aerially in an active crater-lake volcano (Nupen 2019).

### 3 Analytical methods

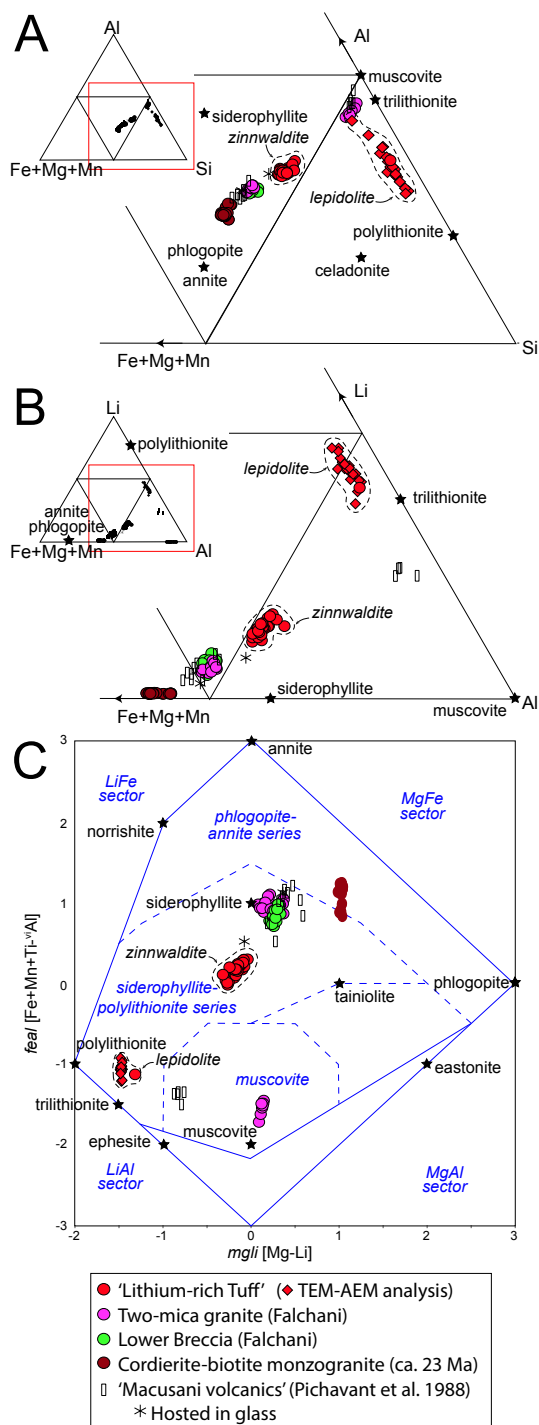
Point analyses of minerals of the mica group were performed using a CAMECA SXFive electron microprobe (EMPA) at the Centre de Microcaractérisation Raimond Castaing, Toulouse. X-ray (compositional) maps were acquired using a five-channel JEOL JXA-8230 electron microprobe at the Centres Científics i Tecnològics of the University of Barcelona (CCiT-UB). The structural formula of micas was normalized to 11 O, H<sub>2</sub>O was determined by assuming (OH+F+Cl) = 2 atoms per formula unit (apfu), and lithium contents were calculated using equations tri1 [SiO<sub>2</sub> > 34 % and MgO < 6 %] and tri2 [SiO<sub>2</sub> > 34 % and MgO > 6 %] of Tischendorf et al. (1997). Raman spectra were obtained on polished thin sections with a HORIBA JobinYvon LabRam HR 800 dispersive spectrometer equipped with an Olympus BXFM optical microscope at the CCiT-UB. Mica grains from a 'lithium-rich tuff' sample were studied by Transmission Electron Microscopy (TEM) to determine the mineral composition by Analytical Electron Microscopy (AEM) in the Thalos microscope of the CIC of the University of Granada, calibrated by natural standards.

### 3 Results

In the 'Lithium-rich Tuff' unit of the MVF, mica-bearing tuff displays a variety of structures including fine, often contorted, alternating light and dark laminae, as well as nodular, porous, and massive layers. They consist mostly of igneous micas, quartz, and feldspars in a matrix composed of quartz plus clay minerals (see Segovia-More et al. 2023). Mica grains are dark brown to black in color and their size ranges between 0.5 and 5 mm. They commonly disrupt the laminations in the tuff and are enclosed in sag structures. Although these mica grains are largely subhedral with straight outlines, some show embayments filled with clay and quartz. In the powder sample studied by TEM, mica appears without a definite morphology or size, but grains have high-crystallinity electron-diffraction and are larger than the co-existing clay minerals.

Mica grains from the 'Lithium-rich Tuff' are characterized by an octahedral occupancy > 2.8 apfu, which classifies them as tri-octahedral. Two contrasting compositions, labelled as zinnwaldite and lepidolite, were found. Zinnwaldites plot in the field of the siderophyllite-polyolithionite series close to

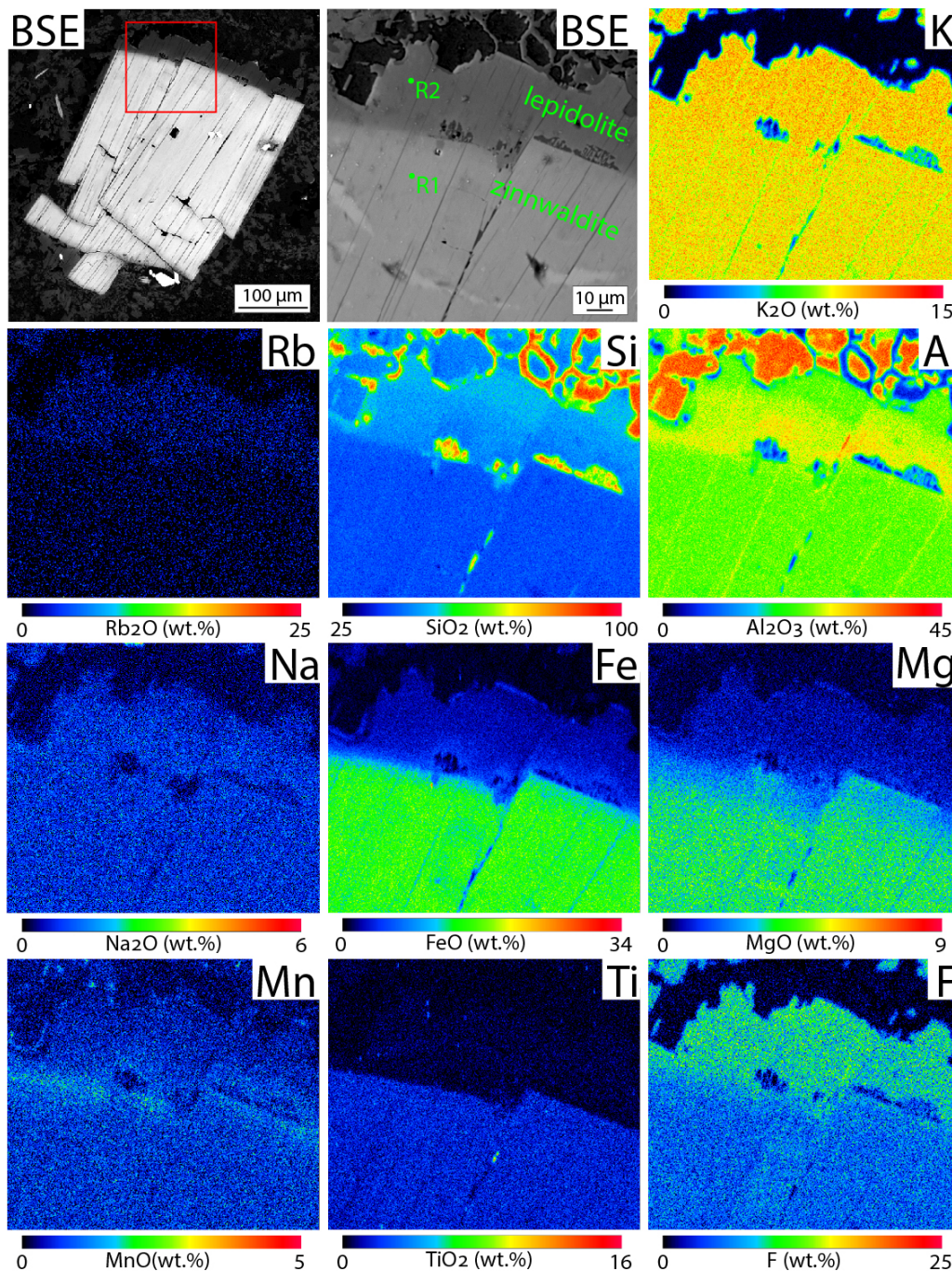
the siderophyllite end-member (Fig. 2). They yield higher Fe (0.85-1.02 apfu; EPMA data) than Mg (0.26-0.38 apfu) contents, relatively high Ti (0.04-0.09 apfu), and much lower Mn (0.02-0.04 apfu) and Zn (<0.02 apfu). Calculated Li contents are in the range of 0.41 to 0.61 apfu. In the interlayer position, K (0.81-0.90 apfu) is more abundant than Na (0.06-0.10 apfu), whereas the contents of Rb (0.01-0.02 apfu) and of Ca, Cs, and Ba (<0.01 apfu) are much lower. Their F content is of 1.01-1.51 apfu.



**Figure 2.** Classification of mica from the MVF in the ternary diagrams after Monier and Robert (1986) (A-B) and the binary diagram after Tischendorf et al. (2007) (C). TEM data were adjusted assuming Li = 1.5 apfu.

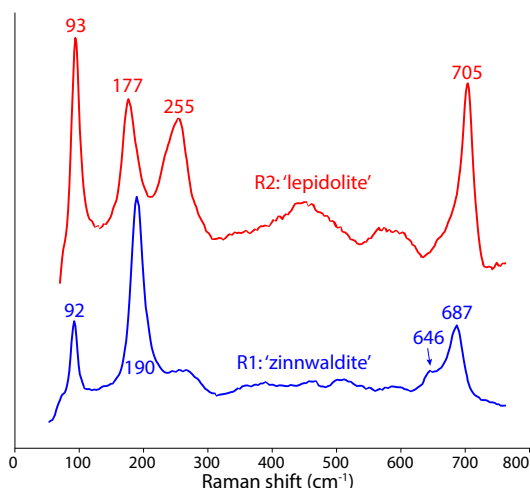
Only one EMPA analysis of lepidolite was obtained so far. Its composition plots close to the polyolithionite end-member in the classification scheme of Tischendorf et al. (2007). It has a Li content of 1.35 apfu and much lower contents of Fe (0.13 apfu), Mg (0.04 apfu), Mn (0.02 apfu), Ti (0.01 apfu), and Zn (0.01 apfu). The K content (0.85 apfu) is higher than the Na (0.06 apfu), Rb (0.03 apfu), and Cs (0.01 apfu) contents and F is very high, at 2 apfu. This composition agrees nicely with the analyses obtained on TEM on another sample in which zinnwaldite was absent and lepidolite was the only mica present (Fig. 2).

The X-ray maps in Figure 3 show a subhedral mica grain from the 'Lithium-rich Tuff' that is compositionally zoned with a zinnwaldite core and a lepidolite rim. The latter is richer in F and Rb and poorer in Ti than the zinnwaldite core. Micro-Raman spectra obtained on the core and the rim of the same grain are shown in Figure 4. Zinnwaldite displays one strong band at 190, two weaker bands at 92 and 687, and a shoulder at 646  $\text{cm}^{-1}$ , whereas lepidolite is characterized by four strong bands at 93, 177, 255, and 705  $\text{cm}^{-1}$ . The latter, at 705  $\text{cm}^{-1}$ , is often observed in the lepidolite series, and in the trilithionite and polyolithionite endmembers (RRUFF).



**Figure 3.** SEM (BSE mode) and quantitative X-ray images of a zoned mica grain from the 'Lithium-rich Tuff' in the Falchani Lithium Project, comprising a zinnwaldite core and a lepidolite rim.





**Figure 4.** Raman spectra measured in a mica grain from sample 2021-MAC-11, for 20 s (5 accumulations) using a 532 nm laser, a 50x objective and a 50% grating. Location of point analyses (R1 and R2) shown in Fig. 3.

## 4 Discussion

The correlation between the lithium mineralization and rocks of volcanic origin ascribes the Falchani Lithium Project to the volcanogenic lithium deposit type (Bowell et al. 2020). In volcanogenic lithium deposits, Li enrichment from pre-enriched volcanic or volcanogenic rocks occurs during intense alteration that arises from the circulation of fluids of magmatic and/or meteoric origin in restricted basins such as volcanic calderas (Benson et al. 2017). These authors argue that the large volumes of Li-enriched rhyolites that are needed to form volcanogenic lithium deposits are typically emplaced in intracontinental settings through partial melting or assimilation of thick, felsic crust and, particularly, in strongly evolved melts through fractional crystallization.

The compositions of micas in the 'Lithium-rich Tuff' from the MVF contrast to those of micas in granites and ignimbrites in the area (new data plus published mica analyses in 'Macusani Volcanics' by Pichavant et al. 1988; Fig. 2). In particular, micas from the 'Lithium-rich Tuff' are systematically enriched in Li, Rb, and F relative to micas in the Lower Breccia (Nupen 2019) and nearby two-mica granites. All of them, in turn, are enriched in these elements compared to micas in older (ca 23 Ma; Sandeman et al. 1997), late Oligocene, cordierite-biotite monzogranites found in the southern margin of the MVF (Fig. 2). The marked enrichment in Li and other incompatible elements such as Rb in mica grains preserved in the 'Lithium-rich Tuff' would illustrate crystallization in equilibrium with a highly evolved rhyolitic magma during a particular period of magmatism in the Neogene MVF.

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