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Biotites as recorders of the magmatic-hydrothermal transition

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With lithium (Li) increasingly sought after for new technologies, understanding how Li is focused into economically relevant deposits is of increasing importance. Despite an intimate link between Li deposits (brine or pegmatite) and silicic magmatic systems the behaviour of Li in shallow magmatic systems remains poorly understood. Melt inclusions suggest that Li is typically lost from the melt between inclusion entrapment and quenching of the groundmass glass, but the fate of this 'lost lithium' remains unknown.

We studied products of 3 trachytic to phonolitic systems (the Granadilla from Tenerife, and the Campanian Ignimbrite and Astroni tephra from the Campi Flegrei) and 3 rhyolitic systems (Kos Plateau Tuff; Bishop Tuff; Caetano Tuff) concentrating on biotite compositions. Within the rhyolitic suites, Kos and Bishop Tuff biotites are distinguished by unusual swirly textures in BSE imaging and electron microprobe analyses return low totals (~90 wt.%). LA-ICPMS analyses reveal that biotites with low-totals contain appreciable amounts of lithium, with maxima at 323 ppm (Kos) and 1,364 ppm (Bishop). These values are one to two orders of magnitude higher those in biotites from the Caetano Tuff and alkaline systems (c. 10-20 ppm Li). Groundmass glass Li contents are similar across all samples (<50 ppm Li). The low-total, high-Li biotites have extremely low δ^7Li, reaching as low as -27.6‰ (values among some of the most negative δ^7Li values in silicate phases measured by dissolution), whereas bulk rock δ^7Li values approximate typical crustal values. X-ray diffraction (XRD) spectra of biotites from all samples are identical precluding the involvement of another (high-Li) mineral phase.

We speculate that the enrichment in Li and negative δ^7Li values reflect magmatic fluids trapped within the biotite interlayers. If correct, this suggests that Li partitions strongly into the co-existing fluid rather than into silicate melt. This effect, seen in the Kos Plateau Tuff and Bishop Tuff rhyolites, has not yet been observed in phonolitic systems. This is potentially due to the relatively earlier crystallisation of biotite in phonolitic and trachytic magmas as opposed to rhyolites where biotite crystallises relatively later, at a time when melt and magmatic fluid co-exist.