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Biotite as a recorder of an exsolved Li-rich volatile phase in upper crustal silicic magma reservoirs

Ben Ellis¹, Julia Neukampf², Olivier Bachmann¹, Chris Harris³, Francesca Forni⁴, Tomas Magna⁵, Oscar Laurent⁶, and Peter Ulmer¹

¹ETH Zurich, Zurich, Switzerland (ben.ellis@erdw.ethz.ch)

²CNRS, Centre de Recherches Pétrographiques et Géochimiques, 15 rue Notre Dame des Pauvres BP 20, F-54500 Vandœuvre les Nancy, France

³Department of Geological Sciences, University of Cape Town, 13 University Avenue, Rondebosch 7701, South Africa

⁴Department of Earth Sciences, Università degli Studi di Milano, Via Festa del Perdono 7, 20122 Milano, Italy ⁵Czech Geological Survey, CZ-11821, Prague, Czech Republic

⁶CNRS, Géosciences Environnement Toulouse, Observatoire Midi-Pyrénées, F-31400 Toulouse, France

The fate of many economically important elements is controlled at the magmatic-hydrothermal transition, where the co-occurrence of melt and magmatic fluid may significantly change partitioning. With increasing usage of batteries across a range of appliances the requirement for lithium (Li) is growing. Despite this, the behaviour of Li in silicic magmatic systems remains poorly known. Here, we illustrate how compositionally unusual biotites from the Bishop and Kos Plateau tuffs may contain a magmatic volatile phase trapped between layers of biotite crystals. These biotite crystals come from pristine volcanic deposits, appear fresh under the binocular microscope and return oxygen isotopic compositions that, taken together with other phases in the same sample, indicate high-temperature equilibrium. Biotite separates show expected XRD specta indicating the absence of other crystalline phases and yet these biotites return low (< 95 wt.%) analytical totals via electron microprobe (EMP) consistent with the presence of considerable amounts of light elements (non-measurable by EMP). Lithium abundances of these biotites are remarkable with values reaching >2,300 ppm with similar results from both spots and line analyses. Lithium isotopic compositions in these biotites are exceptionally light (δ^7 Li as low as -27.6‰) and large isotopic fractionation between biotite and corresponding bulk samples (Δ^7 Li_{bt-bulk} as low as -37.3%). Groundmass glasses, melt inclusions and other mineral phases from the Kos and Bishop systems do not support an extremely Li-rich melt prior to eruption. In contrast, biotites from the phonolitic systems of Campi Flegrei and Tenerife do not exhibit such extreme compositions with bioites and melts having approximately equivalent Li contents with $\Delta^7 \text{Li}_{bt-bulk}$ to a maximum of -10.9%. We infer this difference in behaviour to the appearance of biotite in alkaline systems occurring prior to the widespread exsolution of a magmatic volatile phase in the magma reservoir. In the rhyolitic suites, biotite crystallises at lower temperatures and so most biotite growth occurs in the presence of an exsolved fluid phase allowing such a fluid to be trapped within the biotites.