Supplementary Materials

for

Secondary lanthanide phosphate mineralization in weathering profiles of I-, S-, and A-type granites

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Supplementary Figures



Fig. S1. EDX spectra of secondary lanthanide phosphate phase from I-type Baynton granite containing Y and P. Refer to ei14 sp24 in Table 2 and S2 for wt% values.



Fig. S2. EDX spectra of secondary lanthanide phase from A-type Bigga granite containing Y without P. Refer to ei29 sp53 in Table 2 and S2 for wt% values.



Fig. S3. EDX spectra of secondary lanthanide aluminium phosphate from S-type Mt Disappointment granite containing Ba and REEs. Refer figure 3c for SEM of secondary phase and to ei19 sp20 in Table 2 and Table S2 for wt% values.



Fig. S4. Average upper continental crust (AUCC) rare earth concentrations plotted with rare earth concentrations in the freshest granite samples from I- S- and A-type granites. AUCC contents are from (Taylor, S.R., and McLennan, S.M. 1985).



Fig. S5. ICP-MS data of phosphate concentration in S-type weathered granite samples relative to the freshest material. Data is normalized to fresh rock to determine level of phosphate mobilisation.



Fig. S6. ICP-MS data of phosphate concentration in I- and A-type weathered granite samples relative to the freshest material. Data is normalized to fresh rock to determine level of phosphate mobilisation

Supplementary Methods

ICP-MS Analytical Details

100 mg of the samples were digested with HF-HNO₃ mixtures in high pressure bombs in an oven at 180 degrees Celsius for 60 hours. Solutions were then evaporated until dried, then redissolved in HCl for 24 hours in the oven. Next, samples were dried again and refluxed twice with conc. HNO3, then dissolved in sealed vessels with 3N HNO3 overnight. Solutions were transferred to transparent polycarbonate tubes, diluted with water and centrifuged, then inspected for undissolved fluorides. If present, the supernatants are transferred to new tubes for those samples containing fluorides, and the fluorides transferred to bombs and dissolved in HCl overnight in the oven. These solutions were then dried down, refluxed with nitric, then dissolved in 3N HNO3. These solutions were re-combined with their corresponding supernatant solutions and centrifuged to ensure no fluorides remained. An aliquot of the solution is further diluted with a 1.8% HNO3 solution containing an internal standard mixture to give a total dilution factor of 10000. Analytical and drift correction procedures are comprehensively described in Eggins et al. (1997). The method uses a natural rock standard for calibration, internal drift correction using multi-internal standards (Li⁶, Sr⁸⁴, Rh, Sm¹⁴⁷, Re and U²³⁵), external drift monitors and aggressive washout procedures. Differences from the Eggins et al. (1997) method are: 1) Tm, In and Bi were not used as internal standards as they are measured as analytes; (2) Two digestions of the USGS standard W-2 are used for instrument calibration. The preferred concentrations used for W-2 were mostly derived by analysing it against synthetic standards and a literature survey of isotope dilution analyses (Kamber et al., 2003, 2005). Because only a single calibration standard is used, data can be easily normalised to other sets of preferred values for standards. Single element solutions were analysed after each run to measure isobaric interference levels to use in interference corrections.

Samples were analysed at the School of Earth Sciences, University of Melbourne on an Agilent 7700x. The instrument was tuned to give Cerium oxide levels of < 1%. 4 replicates of 100 scans per replicate were measured for each isotope. Dwell times were 10 milliseconds, except for Be, Cd, In, Sb, Ta, W, Tl, Bi, which were 30 milliseconds.

Long sample wash-out times of 6 minutes with solutions of 0.5% Triton X-100, 0.025% HF in 5% HNO₃ and 2% HNO₃ and long sample uptake times of 120 seconds were used.

USGS granite standard GSP-2 was analysed as an unknown in each run (Supplementary Table S1). The average of these analyses agrees well with the long-term University of Melbourne average and, apart from Pr, multiple ID-TIMS and MIC-SSMS analyses by Raczek et al., 2001.

Supplementary References

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AGV-2, DTS-1, DTS-2, GSP-1 and GSP-2 by ID-TIMS and MIC-SSMS.

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