

Appendix 2: U-Pb CA-ID-TIMS titanite dating – analytical methodology

All sample preparation, geochemical separations and mass spectrometry were done at the Pacific Centre for Isotopic and Geochemical Research in the Department of Earth and Ocean Sciences, University of British Columbia. Minerals were separated from samples using conventional crushing, grinding, and Wilfley table techniques, followed by final concentration using heavy liquids and magnetic separations. Mineral fractions for analysis were selected on the basis of grain quality, size, magnetic susceptibility and morphology. Masses were determined with a Sartorius SE2 ultramicrobalance. Grains were transferred into 300 μL PFA microcapsules (crucibles) and 0.1 mL subboiled ^{29}N HF and 14N HNO_3 in a 10:1 mixture was added. Each fraction was spiked with a $^{233-235}\text{U}$ - ^{205}Pb tracer solution (typically 2 μg), capped and placed in a 125 mL teflon liner (8-13 microcapsules per liner), which in turn went into a Parr-style stainless steel high pressure dissolution device for 7–10 days at 240°C. Sample solutions were then dried to salts at $\sim 130^\circ\text{C}$ and residues were redissolved ~ 1 mL of sub-boiled 6.2 M HCl in oven in high pressure devices for 12 hours at 210°C. These solutions were again dried to salts and were again redissolved in 3.1 N HCl in high pressure devices for at 210°C for 12 hours. Purification of Pb and U employed ion exchange column techniques modified slightly from those described by Parrish et al. (1987). Pb was eluted into a PFA beakers and U into a second set of beakers and further purified by passing through columns a second time. U was then eluted into beakers containing Pb. Elutants and dried in 7 mL screwtop PFA beakers on a hotplate at $\sim 120^\circ\text{C}$ in the presence of 2 μL of ultrapure 0.2N phosphoric acid (H_3PO_4). Samples were loaded onto degassed, zone-refined Re filaments in 2 μL of silicic acid emitter (Gerstenberger and Haase, 1997). Isotopic ratios were measured using a modified single collector VG-54R thermal ionization mass spectrometer equipped with an analogue Daly photomultiplier.

Measurements were done in peak-switching mode on the Daly detector. Analytical blanks during the course of this study were 0.2 pg for U and 8 pg U. Fractionation was determined directly on individual runs using the $^{233-235}\text{U}$ tracer, and Pb isotopic ratios were corrected for fractionation of 0.23%/amu, based on replicate analyses of the NBS-982 Pb standard and the values recommended by Thirlwall (2000). Data reduction employed the Excel-based program of Schmitz and Schoene (2007). Standard concordia diagrams were constructed and regression intercepts, weighted averages calculated with Isoplot (Ludwig, 2003). Unless otherwise noted, all errors are quoted at the 2σ or 95% level of confidence. Isotopic dates are calculated the decay constants $\lambda_{238}=1.55125\text{E-}10$ and $\lambda_{235}=9.8485\text{E-}10$ (Jaffey et al. 1971).

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