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In situ garnet Lu–Hf via LA-ICP-MS/MS: new reference materials and approaches to enhance instrument sensitivity

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Garnet is arguably the most versatile mineral used to decipher the Earth's tectonic evolution, as its chemical composition is sensitive to small changes in pressure and temperature conditions of geological processes. Importantly, garnet also encompasses key radiogenic geochronometers such as Sm–Nd, U–Pb and Lu–Hf. Recent advances in tandem mass spectrometry have bolstered the application of in situ garnet Lu–Hf geochronology, providing a rapid and spatially resolved alternative to conventional garnet geochronology via isotope dilution techniques. However, well-characterised reference materials suitable to evaluate data quality and analytical factors such as laser-induced instrumental matrix effects, long-term reproducibility, and uncertainty components on isochron dates, are rare. We present two well-characterised reference materials for in situ garnet Lu–Hf dating (almandine-grossular GWA-1, and almadine-spessartine GWA-2). Detailed microstructural and chemical characterisation of both garnet indicate that they grew in a single growth event. Isotope dilution Lu–Hf analysis yields isochron dates of 1267.0 ± 3.0 Ma with $^{176}Hf/^{177}Hf_i$ of 0.281415 ± 0.000012 for garnet GWA-1, and 934.7 ± 1.4 Ma with $^{176}Hf/^{177}Hf_i$ of 0.281386 ± 0.000013 for garnet GWA-2. In both cases, the isotope dilution Lu–Hf dates are interpreted to date the timing of closure to radiogenic Hf diffusion coeval with garnet crystallisation.

The results from in situ Lu–Hf analysis commonly yielded older isochron dates compared to isotope dilution Lu–Hf reference dates, likely due to matrix effects between the NIST-610 calibration reference material and garnet, and to session specific ICP–MS/MS tuning conditions used to maximise sensitivity. Both GWA-1 and GWA-2 behave similarly throughout multiple analytical sessions, reinforcing their usefulness to be employed as reference materials to account for matrix effects on Lu/Hf ratios. These garnet reference materials can yield isochron dates with uncertainties as low as ~1 % (depending on instrument sensitivity) on converted Hf isotopes. We also show that ICP-MS/MS sensitivity can be significantly improved by flushing the reaction cell with high NH_3 flow prior to commencing analysis, increasing the converted $^{188+82}Hf$ signal by 100 %. This sensitivity increase results in lower Lu/Hf and Hf/Hf measured ratio uncertainties, down to 4 and 6 %, respectively.