

Transition metal stable isotopes in komatiites

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Komatiites represent large degree partial melts of the mantle (30-50%), which segregated from their sources at high temperatures (>1500°C) and pressures (>5GPa), and are thus largely restricted to the Archaean. As the magnitude of stable isotope fractionation decays according to $1/T^2$, the difference in the stable isotope composition between komatiites and their mantle source is negligible (Dauphas et al., 2009). This permits the characterisation of the stable isotopic composition of the mantle source, provided the effects of alteration and fractional crystallisation can be accounted for.

We present high precision Cu, Zn and Fe isotope analyses for a suite of Early Archaean komatiites (3.5-3.2Ga) from the Pilbara craton, separated from a single dissolution. Fe isotopes bracket a range of compositions from $\delta^{57}\text{Fe}$ (vs. IRMM-014) of -0.17‰ to +0.17‰. Zn isotopes show a more restricted range of compositions, with $\delta^{66}\text{Zn}$ varying from -0.1‰ to -0.16‰ (vs. IRMM-3702), consistent with the smaller range hitherto observed in igneous rocks (Albarède, 2004). A well defined increase in both $\delta^{57}\text{Fe}$ and $\delta^{66}\text{Zn}$ with decreasing Cr and MgO is attributed to a strong olivine control on their stable isotope composition. Cu isotopes scatter around 0‰ (vs. SRM-976), lacking any systematic trend with indices of differentiation. Nevertheless, confirmation of $\delta^{65}\text{Cu}$ values near 0‰ in other igneous rocks (Li et al., 2009) indicates no discernible change in the Cu isotope composition of the Earth over time.

While $\delta^{66}\text{Zn}$ and $\delta^{65}\text{Cu}$ values are representative of current-day mantle, the komatiite array has $\delta^{57}\text{Fe}$ that extends to $\approx -0.15\%$ lighter than the contemporary mantle value. At a given stage in their differentiation, the Pilbara komatiites are also 0.1‰ lighter than komatiites from Alexo (Dauphas et al., 2010).

Compared to carbonaceous chondrites, the Zn composition of the Earth lies at the volatile-poor end of a volatile-depletion trend, where $\delta^{66}\text{Zn}$ becomes lighter with decreasing Zn/Mg. This is the opposite trend to that expected if Zn were being lost by vaporisation.

[1] Dauphas et al., (2009) *EPSL* **288**, 255-267. [2] Albarède (2004) *RiMG* **55**, 409-427 [3] Li et al., (2009) *Chem. Geol.* **258**, 38-49 [4] Dauphas et al., (2010) *GCA* **74**, 3274-3291

Use of MC-ICPMS for laser ablation U/Pb geochronology of baddeleyite

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Microbeam analyses by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) are increasingly used for U-Pb geochronology of zircon. LA-ICPMS is a powerful method for U-Pb geochronology because grains can be dated directly in thin section, avoiding time-consuming laboratory procedures involving heavy liquid separations and ion exchange chromatography. In many silica-poor terrestrial rocks such as mafic dikes, anorthosites, gabbros and carbonatites as well as lunar rocks and Martian meteorites, baddeleyite (ZrO₂) rather than zircon is present. Unlike zircon, the baddeleyite tends to form very small elongate grains, typically no more than 30-50 μm in the longest dimension and less than 20 μm in the smallest dimension. This makes U-Pb analyses of baddeleyite by LA-ICPMS more challenging than for zircon because smaller laser spot sizes (<20 μm) and shorter ablation times (<30 sec) are required, reducing analytical precision significantly compared to zircon analyses.

High-precision thermal ionization mass spectrometry (TIMS) is commonly used for U-Pb baddeleyite geochronology of Large Igneous Provinces (LIPs), particularly where mafic magmatic events need to be determined with a precision better than 5 Ma. In cases where ages with uncertainties of approximately 20 Ma provide useful data for LIPs, however, it would be desirable however to apply LA-ICPMS to U-Pb baddeleyite geochronology.

We report a U-Pb dating method for baddeleyite by LA-multi-collector-ICPMS using a Thermo Scientific NEPTUNE MC-ICPMS. The collector array consists of six Channeltron ion counters allowing for the simultaneous collection of ²⁰²Hg, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb and ²³⁵U isotopes. The use of a collector array consisting only of ion counters eliminates the need of cross-calibration between ion counters and Faraday detectors. Standard – sample – standard bracketing is employed to correct for instrumental mass bias using Forest Center baddeleyite (FC-4b; TIMS age = 1095.42 \pm 0.16 Ma) as a standard. A slow line scan ablation is used where a 4 μm laser beam with an energy density of 9 J/cm² and a repetition rate of 5 Hz scans across the sample surface at a rate of 1 $\mu\text{m}/\text{sec}$. Using the method described, after 30 sec (150 pulses) of ablation, the ²⁰⁷Pb/²⁰⁶Pb age determined for the ca. 2060 Ma Phalaborwa baddeleyite is 2058.9 \pm 18 Ma (2 σ , n = 6) with an external precision of 0.9 % (2RSD). While this result is comparable to U-Pb zircon and analyses by single-collector LA-ICPMS, the smaller volume of material consumed and the shorter ablation time required to achieve such precision during multi-collector analyses is more suitable for, typically smaller, baddeleyites. The described method can be used as a reconnaissance tool to screen baddeleyite grains prior to physical separation for further high precision TIMS analyses, in order to identify critical samples that can be used for paleocontinental reconstruction in LIPs.