

Investigating instrumental mass bias in MC-ICP-MS using isotope ratio plasma profiles

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In multi-collector inductively-coupled-plasma mass spectrometry (MC-ICP-MS) heavy/light isotope ratios are fractionated to high values relative to the true value. Accurate and precise correction of this instrumental mass bias is a prerequisite for accurate MC-ICP-MS isotope ratio data. However, understanding of this phenomenon is limited.

As a step towards gaining insight into the processes involved in generating instrumental mass bias we have measured the variation of heavy/light isotope ratios as sampling depth in the plasma is varied. These axial plasma profiles were measured at ~250 μm intervals over a sampling depth of ~3.5 mm. Each experiment consisted of 6 profiles sampled over the same sampling depth range but tuned at different sampling depths.

Pb and Mg were chosen as the analytes. These elements though very different in mass have similar first and second ionisation potentials, therefore any differences in heavy/light isotope ratios variation with sampling depth should be mass dependent. All profiles were curvilinear. For Pb the heavy/light isotope ratio (²⁰⁸Pb/²⁰⁶Pb) increased with decreasing sampling depth, whereas for Mg (²⁶Mg/²⁴Mg) it decreased. ²⁰⁸Pb/²⁰⁶Pb values on individual profiles varied by 0.56 – 0.70% of the average value measured on the profile and the magnitude of variation increased as the tuned sampling depth decreased. Variation in ²⁶Mg/²⁴Mg was much greater, 1.1 – 1.3% of the average value measured on each profile and increased dramatically to 7.1% for the profile tuned at the shallowest sampling depth. If only ratios measured at the tuned sampling depth on each profile are considered, the trends are reversed e.g. ²⁰⁸Pb/²⁰⁶Pb generally decreases with decreasing sampling depth.

These apparent variations in instrumental mass bias with sampling depth in the plasma result from a combination of processes occurring during transport of the analyte through the plasma (e.g. radial mass dependent dispersion of ions and atoms and ionisation potential effects) and additional mass dependent effects produced during sampling and transport through the interface. The contrast in apparent mass bias response between Mg and Pb allows us to speculate on the relative significance of plasma versus interface processes in producing the instrumental mass bias.

Subduction channel or fossil rifted margin? Serpentinite geochemistry of the Punta Rosa Unit, Western Alps

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The Punta Rosa unit (PR), now stacked in the Valaisan domain (Western Alps) preserves evidence of Mesozoic mantle exhumation at the seafloor, despite having undergone pervasive Alpine deformation/metamorphism. Serpentinites are overlain by slivers of continental basement or meta-sedimentary breccia and have been interpreted as an ocean-continent transition (OCT) based on structural data [1]. However, similar lithological associations throughout Alpine-type orogens are often interpreted as subduction-related “tectonic mélanges” [e.g., 2]. Here we present the first geochemical study of PR serpentinites to further test the interpretation of their tectonic setting.

Stable isotope and major and trace element compositions of PR serpentinites with varying distances from the contact with meta-sedimentary material were determined. $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and δD values range from +1.1 to +2.7‰, +7.0 to +8.5‰, and -50 to -73‰, respectively. $\delta^{37}\text{Cl}$ values are some of the highest reported for serpentinites and increase towards the contact with the metasediments, indicating interaction with metasediments/altered oceanic crust during Alpine subduction/exhumation. O and H isotope data are consistent with low-T interaction with seawater (with partial resetting of H by meteoric fluids) or slab-derived fluids. Bulk serpentinite samples have high REE concentrations, compared to typical mid-ocean ridge serpentinites, with nearly flat to slightly convex up REE patterns ($\text{La}_N/\text{Sm}_N = 0.38 - 0.62$; $\text{La}_N/\text{Yb}_N = 0.20 - 0.47$; $\text{Sm}_N/\text{Yb}_N = 0.41 - 0.89$). These high REE concentrations are similar to those observed in OCTs (Iberia Abyssal Plain; Newfoundland) [3] and the Malenco and Platta peridotites (Switzerland), which are the type localities for preserved OCTs [4]. Serpentinite geochemistry supports stratigraphic and structural evidence for an abyssal origin of the PR serpentinites, providing a powerful tool to determine tectonic setting in poorly exposed/highly deformed metamorphic units.

- [1] Beltrando *et al.* (2012) *Tectonophysics* **579**, 17-36. [2] Gerya *et al.* (2002) *Tectonics* **21**, doi:10.1029/2002TC001406. [3] Kodolányi *et al.* (2012) *J Petrology* **53**, 235-270. [4] Müntener *et al.* (2010) *J Petrology* **51**, 255-294.