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Unusually low Zr/Hf and Nb/Ta Ratios in the Depleted Mantle: Precise ID Analysis of Ultra low Concentrations by MC-ICPMS

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The geochemistry of mantle rocks allows valuable insights into melting processes in the sources of basaltic magmas. In particular, ratios of the High Field Strength Elements (Nb/Ta, Zr/Hf) can be used to constrain degrees of partial melting, source depletion and mantle evolution. We present a new method for the precise determination of HFSE concentrations and Hf isotope compositions (IC) in low abundance mantle rocks, including peridotites and cumulate pyroxenite dikes. The samples are from the well investigated Balmuccia peridotite body in the Italian Alps

The sensitivity of the Micromass Isoprobe MC-ICPMS in Münster is sufficient to perform precise isotope dilution (ID) concentration measurements of Zr, Hf and Ta even at ppb abundances in rocks. Only 0.5-1 ng of an element is required for an ID analysis with a precision of < 1%. About 20 ng are sufficient for an IC analysis of Hf with a precision of < 0.5 ε (2σ). The Nb concentration can be determined relative to Zr by measurement of $^{93}Nb/^{90}Zr$, after quantitative extraction of Zr and Nb from the whole rock by ion exchange. The first isotope dilution Ta concentrations are presented using a tracer enriched in ^{180}Ta.

The peridotites have present day ε_{Hf} values of 20-35 and the dike rocks display ε_{Hf} values of 8-15. The $\varepsilon_{Hf}(T)$ values of four peridotite samples, based on a Nd isochron age of 270 Ma (Voshage et al. 1988) range from 14.0-15.2 and overlap within analytical uncertainty.

The Ta concentrations in depleted peridotites from the Balmuccia peridotite vary between 0.4 and 1 ppb for most of the samples. Typical Nb concentrations for the peridotites are 3-10 ppb. These results can be duplicated within 5-10%. There is a weak correlation between the Ta or Nb concentration and the Zr concentration but no correlation between the Nb/Ta ratio and the Zr concentration. Most samples have clearly subchondritic Nb/Ta ratios of between 7 and 10. Only some peridotite samples that are located close to the dikes have Nb/Ta ratios higher than the chondritic value of 17. However, the dikes themselves have also subchondritic ratios.

The Zr and Hf concentrations in the peridotites range from 0.5-3 ppm and 50-130 ppb respectively. The Zr/Hf ratios vary between 26 and 10 and are always lower than the chondritic value of 36. There is a strong correlation between Zr/Hf and the Zr concentration for most of the peridotites. Assuming the trend of Zr/Hf and in particular the extremely low Zr/Hf ratios are caused by partial melting processes and controlled by melting of cpx our data confirm the experimental results of Hart & Dunn (1993) and Blundy et al. (1998) that Zr is more incompatible than Hf. Ta/Zr ratios are more constant and increase slightly rather than decrease with the degree of depletion. In spite of the ultra low concentrations, Nb and Ta seem to be slightly enriched or the concentration is "buffered" in the depleted peridotites. As a results, these elements appear to display a more compatible behaviour than Zr in the depleted mantle, which is inconsistent with cpx controlled melting. Once the mantle is depleted by partial melting processes, the budget of Nb and Ta (and possibly also other highly incompatible elements) is likely controlled by small amounts of metasomatic fluids or melts.

The high precision data of this study demonstrate that the "geochemical twins" Zr and Hf can behave remarkably different during melting and metasomatism in the mantle, resulting in extremely low Zr/Hf and Nb/Ta ratios in the restitic mantle.

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