

## High Precision Nb/Ta, Zr/Hf and Lu/Hf Measurements by MC-ICPMS Using a Mixed Zr-Hf-Ta-Lu Tracer

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Ratios of Nb/Ta and Zr/Hf in mafic-ultramafic rocks and the continental crust of the Earth deviate little from the chondritic values that have been suggested to lie between 17 and 18 for Nb/Ta and between 36 and 37 for Zr/Hf. Realistic external precisions and accuracies that were reported for Nb/Ta and Zr/Hf measurements using spark source mass spectrometry and Quadrupole-ICPMS are not better than 10%, thus covering a significant portion of the variation of Nb/Ta and Zr/Hf in nature. Using the Isoprobe Multicollector-ICPMS in Münster, high precision isotope dilution measurements of Ta, Zr and Hf are now possible for as low as ca. 500 pg of sample. This detection limit is presently determined by the different blank levels for each element (1-150 pg), rather than by instrument sensitivity. As an isotopic tracer we use a  $^{94}\text{Zr}$ - $^{176}\text{Lu}$ - $^{180}\text{Hf}$ - $^{180}\text{Ta}$  mixture that is dissolved in dilute  $\text{HNO}_3$  and HF. Repeated measurements of standards over 8 months show that the long term stability of this isotope tracer is better than 1%. Lu, Zr-Nb, Hf and Ta are each separated from the whole rock matrix by ion-exchange chromatography. A virtually complete separation of Hf from Ta by ion-exchange chromatography is needed in order to avoid interferences of  $^{180}\text{Hf}$  on  $^{180}\text{Ta}$ .

Using the Ta tracer with 4.3%  $^{180}\text{Ta}$ , isotope dilution measurements of Ta are now possible (Weyer et al. 1999). The first Ta-results that were obtained for the ultramafic reference samples DTS-1 and PCC-1 ( $1.0\pm 0.1$  ng/g Ta and  $0.64\pm 0.06$  ng/gTa, respectively) demonstrate the high potential of this method for precise and accurate Ta measurements in mantle rocks (see also Weyer et al., 2000).

External Zr/Hf reproducibilities, as determined from multiple digestions of basalt standards, are better than  $\pm 0.5\%$ . Since Nb is monoisotopic, Nb concentrations can only be measured as Zr/Nb relative to the Zr content that is determined by isotope dilution. After quantitative extraction of Zr and Nb from the whole rock matrix by ion-exchange, we are currently able to measure Zr/Nb with an external precision of better than  $\pm 5\%$  ( $\pm 10\%$  in low abundance samples) at total Zr-yields of better than 95%. Nb/Ta ratios that were calculated from the Nb and Ta results have an external error of ca.  $\pm 5\%$  (10-20% in peridotites).

For the reference sample BIR-1 we obtained a Ta concentration of  $35.0\pm 0.6$  ng/g and a Nb/Ta of  $15.8\pm 0.8$  ( $n=5$ ), using two separately calibrated tracer solutions with different concentrations. Zr/Hf for this reference sample is  $24.1\pm 0.2$  ( $n=5$ ).

The precision of Lu isotope dilution measurements has so far been limited to  $\pm 1\%$  by the large interference of  $^{176}\text{Yb}$  on  $^{176}\text{Lu}$  and the inability to perform an internal mass bias correction. Yb and Lu both show a similar adsorption behaviour on most ion-exchange resins and are therefore difficult to separate from each other. We use the techniques of Gruau et al. (1988) and Scherer et al. (1999), where Yb is separated from Lu by a-HIBA column chemistry. The sample is then doped with Re, and  $^{176}\text{Lu}/^{175}\text{Lu}$  is normalized to  $^{187}\text{Re}/^{185}\text{Re}$ . Using this procedure, a precision of better than  $\pm 0.2\%$  for Lu/Hf measurements is routinely achieved.

In a first study, we analyzed 5 meteorites for their Nb/Ta and Zr/Hf values. These meteorites include the carbonaceous chondrite Allende, the eucrites Juvinas, Stannern and Millbillillie, and the angrite Sahara 99055. Zr/Hf values of the four eucrites and the Allende meteorite range from  $33.9\pm 0.2$  to  $34.4\pm 0.2$ , corresponding Nb/Ta range from  $17.9\pm 0.9$  to  $19.8\pm 1$ . The angrite gave slightly higher Nb/Ta and Zr/Hf of  $20.7\pm 1$  and  $35.4\pm 0.2$ , respectively. Altogether, these data confirm the suggested chondritic Nb/Ta and Zr/Hf of Jochum et al. (2000), although external precision and accuracy is improved using the isotope dilution method.

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