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Assessment of Zr/Hf Fractionation in Oceanic Basalts During Petrogenetic Processes

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Introduction

Zirconium and Hafnium are two High Field Strength Elements with the same chemical and geochemical properties. They behave similarly as incompatible elements due to their ability to form stable complexes in silicate melts. Consequently, Zr/Hf ratios in terrestrial rocks were considered uniform, equal to the chondritic value (Jochum et al., 1986). This was true until recent high-precision measurements by ICP-MS of significant Zr/Hf ratio variations for oceanic basalts from Pacific Seamounts (Niu and Batiza, 1997). Thus, the uniformity of Zr/Hf ratios in oceanic basalts has been questioned as well as its potential as a quasi isotopic ratio to infer the present-day composition of the Earth's mantle and its evolution. In this study, we present a new compilation of precise Zr/Hf ratio measurements for terrestrial and extraterrestrial samples in order to assess the Zr/Hf ratio of the major geochemical reservoirs on the Earth. These include oceanic basalts, continental materials such as shales and river sediments and the CI1 carbonaceous chondrite Orgueil. By using the isotope dilution with a mixed Zr-Hf spike by thermal ionisation mass spectrometry and magnetic sector multiple-collector ICP-MS, Zr/Hf ratios have been measured with an external reproducibility of 0.5% (David et al., 1999).

Results

Orgueil, representative of the Bulk Earth gave a value equal to 36.5, close to the published data of 36.3 (Jochum et al., 1986). We have observed that MORB and OIB samples display Zr/Hf ratios significantly different from the chondritic value. MORB and continental materials display the same range of Zr/Hf ratios, irrespective of the element concentrations, with average values [Zr/Hf=37±1 (1σ), Zr/Hf=37.5±0.8 (1σ)] quite similar to that given by Orgueil. In contrast, OIB display higher Zr/Hf ratios for a given Zr concentration and ranging from. 36.9 to 63.7. The C1-chondritic Zr/Hf ratios observed for MORB and continental materials indicate that the extraction of the continental crust from an initially primitive Earth's mantle did not result in a large Zr/Hf fractionation as observed in OIB. Consequently, the large variations in Zr/Hf for both MORB and OIB call into question their significance, in particular whether the measured Zr/Hf ratio values reflect magmatic process variability, primary mantle variations or a combination of the two processes. Zr/Hf ratio in oceanic basalts as indicator of petrogenetic processes or source heterogeneities: By carefully selecting OIB with a large range of chemical composition, from relatively primitive basalts (Mg#54) to trachytes (Mg#11), we observed a negative correlation between Zr/Hf ratios and Sc contents. The absence of such relationship between Zr/Hf ratios and Ni concentrations suggest that Zr/Hf ratios in OIB are controlled by the precipitation of clinopyroxene. This result is reinforced by $D^{cpx/melt}_{Hf} > D^{cpx/melt}_{Zr}$ (Fujinawa and Green, 1997). Although clinopyroxene is the major phenocryst phase, $D_{Hf} > D_{Zr}$ for amphibole/sphene-alkaline melts implies that minor mineral phases such as sphene and amphibole are also able to fractionate Zr/Hf ratio in highly evolved alkaline suites (Weaver, 1990).

After filtering data for such fractionation effects, the positive correlation between Zr/Hf ratios and Zr concentrations for MORB and undifferentiated OIB may also suggest that Zr and Hf concentrations are mainly controlled by a simple process such as partial melting or source heterogeneity. However, because the residual garnet influence will result in the generation of OIB with lower Zr/Hf ratios and recycling of continental and oceanic crust materials in the sources of OIB will not strongly modify their Zr/Hf ratios, we argue in favour of a partial melting effect. Therefore, the preferred explanation for the observed MORB-OIB trend in a Zr/Hf vs Zr diagram is that $D_{Zr} < D_{Hf}$ during progressive melting of mantle sources with similar Zr/Hf ratios.

Conclusion

The data have clearly shown that the Zr/Hf ratio fractionates during fractional crystallisation and partial melting. Thus, the use of the Zr/Hf ratio as geochemical tracer to map the characteristics of mantle reservoirs requires an assessment of the change in this ratio during petrogenetic processes.

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