

In-situ Hf isotope ratio analysis of zircon by laser ablation-multiple collector-ICPMS

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Lu-Hf and Sm-Nd isotopic systems provide insights into the time-integrated evolution of the silicate Earth. However, in order to avoid a possible disturbance of the isotopic system due to secondary effect onto the sample, isotopic data from specific minerals, rather than bulk samples, were highly desired. Zircon, which is extremely resistant against erosion and/or metamorphic events through geological time, can be dated precisely by U-Pb chronometer. Because of high Hf content (ca. 1 wt percent) and low Lu/Hf ratio, zircon has been widely used for the geochemical study concerning the crustal-mantle evolution (Amelin et al., 1999). Recently, a new analytical technique for Lu-Hf isotopic system using multiple collector-ICPMS (MC-ICPMS) was described. The amount of Hf required for the isotopic ratio measurement was ca. 50ng for ICPMS, which was almost 1/20 level than that of conventional technique using thermal ionization mass spectrometry (TIMS). In the case of Hf isotopic measurements using ICPMS, corrections of isobaric interferences on ^{176}Hf by ^{176}Yb and ^{176}Lu highly desired in order to obtain accurate Hf isotopic data. Most of previous workers assumed that the magnitudes of mass bias are identical between Hf and Yb, and Hf and Lu, during the Hf measurement. However, as noted by Chu et al. (2002), the mass bias factors for Lu and Yb were not identical to that of Hf. Especially in the case that contribution of ^{176}Yb was greater than 10 percent, the correction of ^{176}Yb interference based on correct bias factor must be considered.

Many geochemists are increasingly interested in in-situ Hf isotopic analysis for zircons simply because of smaller risk of contamination. The combination of laser ablation technique and ICPMS has now become a fast and accurate method of in-situ isotope analysis. Thirlwall and Walder (1995) demonstrated that the potential of laser ablation-MC-ICPMS (LA-MC-ICPMS) in in-situ zircon Hf isotope analysis. Recently, Griffin et al. (2000) carried out the determination of Hf isotope ratio for zircon megacrysts by the LA-MC-ICPMS using typical ablation craters of ca. 80 micrometer diameter and ca. 40 micrometer deep. These studies have corrected the Yb isobaric interferences using a modified isotopic ratio value obtained empirically, which yield corrected $^{176}\text{Hf}/^{177}\text{Hf}$ ratio in mixed Hf-Yb solutions. However, this method is limited by the assumption that mass bias coefficients of these elements are consistent through time and between the solutions and zircon samples.

In this study, we have carefully evaluated the effect of differences in sample matrices onto the mass bias factor by means of combined sample introduction technique using desolvating nebulization and laser ablation. We will demonstrate that the mass bias factor between Hf and Yb depends on sample matrix, indicating that the Yb isobaric interference correction factor calculated using solution samples could not be applied directly to the in-situ Hf isotope ratio analysis using laser ablation technique. Moreover, in order to obtain precise Hf isotopic data from smaller crater, further enhancement of the instrumental sensitivity was strongly required. This was achieved by addition of small amount of nitrogen gas into the Ar carrier gas. The results of in-situ Hf isotope analysis from ablation crater size of ca. 30 micrometer diameter and ca. 20 micrometer depth on 91500 standard zircon show good agreement with those of previous value (Griffin et al., 2000), demonstrating the high analytical capability and versatility of the technique.