New analytical technique for determination of minor and trace element in zircon by using solid mixing calibration technique with multiple spot-laser ablation-ICP-MS

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Zircon ($ZrSiO_4$) has acted as “robust timekeeper” in the Earth science. In igneous rocks, elements with trivalent (*e.g.,* rare earth elements: REEs) or tetravalent states (*e.g.,* Hf, Th and U) were principally incorporated in the zircon, and the abundance data for these elements could reflect condition of the crystal growth, and thus, trace-element abundances and/or distributions in zircons have been used as a thermometer based on Ti concentration (Ti-in-Zircon), a proxy for the redox state (e.g., Ce and Eu anomalies), and an indicator of source rock type (e.g., REE patterns). Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is widely used for *in-situ* determinations of minor and trace elements in zircon. However, development of minor- to trace-elements analysis in zircon with high precision and high accuracy is still key issue. The availability and application are limited by developments of microanalytical technique under present circumstances. This study aims to open the window to a zircon geochemical tracer using solid mixing calibration technique by a multiple spot-LA-ICP-MS (msLA-ICP-MS).

The major drawback of the conventional LA-ICP-MS technique is lack in proper calibration standard that requires (a) highly homogeneous, (b) similar matrix composition, and (c) similar concentration ranges of the analytes to the sample. In strike contrast, with the present msLA-ICP-MS system, its high-repetition laser (> 10 kHz) achieves better sensitivity and enables mixing of sample aerosols removed from more than two solid materials during the same ablation. For example, analytes in the homogeneous reference materials (e.g., NIST SRM glasses) can be added to the unknown sample, which allows for acquirement of standard addition calibration. Moreover, the dilution of the analytes by the addition of the pure materials results in significant improvements in a dynamic range of calibration curve.

In our study, three commercially available glass materials (NIST SRMs 610, 612, and 614) were added to a laboratory synthesized zircon with various proportions, and now calibration standard with a zircon matrix could be prepared within the sampling cell through the solid sample mixing. The msLA-ICP-MS analysis was conducted by coupling of the Jupiter Solid Nebulizer (ST Japan) to the ICAP TQ (Thermo Fisher Scientific). The ablated region was totally 150 ×210 μm^2 per ablation, and mixing ratios of each NIST SRM glasses to the synthesized zircon is about 2%, 5%, and 33%. The linear regression calculated by IsoplotR is used for determining a best-fit calibration line. In order to evaluate the validity of our analytical method, we also conducted measurements of three different Harvard 91500 zircon grains which were known as a well-characterized standard.

Our analysis of the zircons using msLA-ICP-MS exhibited ten times better LOD and LOQ in most analyte than previous studies. We succeeded in the accurate quantification of P, Ti, V, Fe, Y, Nb, REEs, Ta, Pb, Th, and U concentrations above LOQ. Unfortunately, Mg, Cr, Ni, and Sr abundances were equal to the detection limit. In the case of Ti analyses, their precisions ranged from 7% to 35% at 2 relative standard deviations, and sample heterogeneity between three 91500 zircon grains was insignificant. On the other

hands, Fe, Y, REEs, Th and U concentrations indicated sample heterogeneity between the 91500 zircon grains. In our presentation, we will present details of analytical procedures using the msLA-ICP-MS technique and also discuss the reliability of the analytical results on the Harvard 91500 zircon grains.

Keywords: Zircon, Trace element quantification, Solid mixing, multiple spot-LA-ICP-MS

