Evaluation of acid and alkali-fusion digestion techniques for determination of high field strength elements of geological samples by ICP-MS

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The high field strength element (HFSE) concentrations and their ratios, such as Zr/Hf and Nb/Ta in mantle-derived rocks provide a useful tool for characterizing mantle reservoir, crust genesis and subduction processes. The element pairs of Zr-Hf and Nb-Ta are identical in charge, ionic radii and chemical properties, consequently show more congruent geochemical behavior than previously used incompatibility-based element pairs (for example, Ce/Pb, Nb/U). However the main impediment to use these elements is analytical difficulties and high uncertainty.

For analyzing HFSE in rock samples with ICP-MS of external calibration, complete decomposition of refractory mineral is always the controversy point, because these elements are thought to reside mainly in refractory minerals (e.g., zircon, rutile and ilmenite) that are resistant to acid attack and are not chemically stable in simple nitric solution which is preferred in ICP-MS analysis. Mixed acid attack and alkali-fusion are two commonly used decomposition methods when determination of these elements. We improved both the methods for analyzing HFSE in rock samples, and evaluated their efficiency.

The acid decomposition procedure used here is enhanced with a HF/HNO₃ treatment of pulverized rock in ultrasonic bath prior to attack by mixed acids of HNO₃-HF-HClO₄. Major silicate structure was broken in beforehand HF/HNO₃ treatment; the followed mixed acids thus can effectively attack residual refractory minerals. Alkali-fusion digestion was performed using LiBO₂-Li₂B₄O₇ as flux and sample/flux ratio of 1:5. Molten glass was dissolve directly with diluted HNO₃/HF other than HNO₃ only to prevent formation of undissolved polysilicic acid. The resulted sample solutions were diluted with HNO₃/HF and added internal standard (¹¹⁵In, ²⁰⁹Bi) shortly before ICP-MS measurement.

The measured results for basaltic and andesitic reference (JB-3, BHVO-1, BCR-2 and JA-1) and rock samples show that HFSE concentrations obtained from the two techniques agree generally within analytical uncertainty. But it should be noted that for rocks with extremely low Ta (for example Ta<0.1 µg g⁻¹ in rock as in JB-2), Ta concentration measured from alkali-fusion method is about 3-5 times higher than that from acid digestion. This is hard to be explained as procedural blank contribution of fusion method.

For analysis of granitic rocks (JG-3 and JG-1a), however, the results are quite complicated. Recoveries yielded from acid decomposition are less than 50-65% for Zr and Hf, and 80-90% for Nb and Ta, indicating that the mixed acids are not sufficient to decompose granitic rocks for HFSE analysis. While from alkali-fusion decomposition, Zr and Hf are almost quantitatively recovered, but the values of Nb and Ta are even less than that of acid decomposition. It seems Ta and Nb partly coprecipitated with the polysilicic acid formed when dissolving fused glass, and this coprecipitation was less profound for Zr and Hf. As a future attempt, removal of Si from rock sample before fusion or before dissolving fused glass may suppresses the formation undissolved polysilicic acid, and improve the efficiency of alkali-fusion method for analysis HFSE of granitic rocks.