Precise determination of $\delta^{137/134}$Ba stable isotope ratios by double-spike thermal ionization mass spectrometry

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Barium has seven stable isotopes: $^{130}$Ba, $^{132}$Ba, $^{134}$Ba, $^{135}$Ba, $^{136}$Ba, $^{137}$Ba, and $^{138}$Ba. Recent researches focus on seawater, igneous rocks, carbonates, sulfates, and soil-plant systems using the Ba isotope fractionation. Barium is a large ion lithophile element and is usually incompatible in the mantle minerals. Barium is mobile in aqueous fluids and thus an important tracer of water recycling in the Earth’s mantle. Miyazaki et al. (2014) first applied stable Ba isotope ratios to igneous rocks using double-spike Multiple Collector-Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS) and observed significant difference in $\delta^{137/134}$Ba between JB-2 (slab fluid influenced) and JA-2 (slab or crustal melt influenced). They found that the ratio of BHVO-2 (oceanic island basalt) was between JB-2 and JA-2 and could not distinguish it either from JB-2 or JA-2 because of overlapping analytical errors. Although their analytical repeatability was far better than the previous reports, development of a more precise analytical method is required to apply stable Ba isotopes to igneous processes.

The double-spike method is effective for Ba isotope analyses either in thermal ionization mass spectrometry (TIMS) or MC-ICP-MS. However, isobaric interferences of Xe in Ba isotopes prevent further higher precision analyses due to instability of Xe blanks in the matrix plasma support Ar gas in MC-ICP-MS. We here report development of a high-precision Ba isotope measurement using double-spike TIMS. We modified double spike TIMS method developed for Pb isotopes by Miyazaki et al. (2009). Longer baseline measurement preformed before and after sample measurement is the key technique. This avoids unnecessary sample waste during baseline measurements within sample runs. Use of double Re-filaments and exponential law mass fractionation correction were combined to improve repeatability of $\delta^{137/134}$Ba. The measured repeatability of the Ba standard solution SRM3104a was $\delta^{137/134}$Ba = ± 0.023‰ (2SD, n = 26), 1.4 times better than that achieved by MC-ICP-MS. The SRM3104a normalized $\delta^{137/134}$Ba value of IAEA-CO-9 was 0.013 ±0.029‰ (2SD, n = 24) which is identical with the reported values 0.017 ±0.049‰ (Nan et al., 2015) and 0.014 ±0.046‰ (van Zuilen et al., 2016). Analyses of geological rock standard samples are ongoing and the results will be reported in the talk.


Keywords: Stable Ba isotope, Thermal ionization mass spectrometry, Double spike