Optimize the double-spike technique for accurate calcium isotope measurements by thermal ionization mass spectrometry (TIMS)

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Metal stable isotopes geochemistry is one of the research priorities in the Earth Sciences. It has been proven to be a powerful tool in elucidating many major scientific issues such as the origin of the Earth and the Moon, and the evolution of life and the driving force of climatic changes. Importantly, to perform accurate measurement of isotopic compositions is a prerequisite for all kinds of applications. Thus, correct understanding and proper calibrations on laboratory background, isotopic fractionations, matrixes and/or isobaric interferences during mass spectrometry and/or the column chemistry must be considered seriously. To issue such problems, many correction methods/techniques such as internal normalization, element doping, standard-sample bracketing, and double-spike technique have been proposed. Obviously, double-spike technique is a robust one for calibrating instrumental and chemical isotopic fractionation.

Up to now, the double-spike technique has been widely applied in isotopic analysis of many elements such as Ba, Ca, Fe, Cd, Hg, Mo, Se, etc. However, practical use of double spiking is hindered by the perceived difficulties in proper double-spike calibration, mathematical inversion and data reduction. In this study, we will refer to Ca double spike on how to yield excellent Ca isotopic compositions. The composition of double spike is a key factor that have a big impact on the accuracy and precision of isotopic data, which must be carefully calibrated. According to our long-term observation, the composition of $^{42}$Ca-$^{43}$Ca double spike with relatively low-concentration (~35ppm) has been changing over a period of 5 years. Overall, to facilitate the adoption of the double-spike technique, we take Ca isotope spike for example and aim at providing a practical guide when working with double spikes, especially for researchers in new isotopic systems.

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