

Calcium Isotopic Fractionation during Column Chemistry and TIMS Determination

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The observations of Calcium Isotopic fractionations of IAPSO seawater standard during column chemistry and NIST SRM 915a standard combined with a Chinese national carbonate standard GBW04412 (Original used as a Uranium Series geochronology reference) during TIMS determination were reported here. Because of the large relative mass difference of the Ca isotopes (up to 20%), significant fractionations ranged from ~ 4 to ~ 0 ($\delta^{44/40}\text{Ca}_{915a}$) were observed in different calcium cuts (i.e. 0-20, 20-40, 40-60, 60-80 and 80-100%) during elution through cation-exchange columns packed with 1 ml AG MP50 (100-200 mesh) resin. The more calcium was eluted from the column, the lower $\delta^{44/40}\text{Ca}_{915a}$ of the elution solution was found. These findings proved the earlier cognition that resin usually holds lighter isotopes more tightly than heavier isotopes. Remarkably, we also found that the fractionation of calcium isotopic compositions on the column follows exponential law very well and the weighted average value of those compositions has no difference with that of original IAPSO seawater. However, to some degree, TIMS instrumental fractionation during calcium runs are much more complicated but generally follows exponential law also in most cases. Since calcium isotopic composition determination generally requires a much higher recovery (i.e. $\sim 100\%$) from the column chemistry and well calibration on instrumental mass fractionation, our practice provided new concepts to understand the calcium activities during experimental processes and to better restore the true calcium compositions of natural samples.

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