High-precision analysis of calcium isotopes using a Nu Sapphire collision cell (CC)-MC-ICP-MS

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This study presents high-precision analyses of calcium (Ca) isotope ratios using a collision-cell multi-collector inductively coupled plasma mass spectrometer (CC-MC-ICP-MS, Nu Sapphire). This instrument allows Ca isotope measurement in low resolution mode, requiring much less sample comparing with TIMS and conventional MC-ICP-MS, and has additional measurement capability of both radiogenic (E⁴⁰Ca) and stable isotope ($\delta^{44/40}$ Ca and $\delta^{44/42}$ Ca). The effects of several factors on the precision and accuracy of Ca isotopic data were evaluated, including total Ca concentration, Ca intensity mismatch between sample and standard, HNO₃ molarity mismatch between sample and standard, and presence of matrix elements. High precision was obtained on 100 ng g⁻¹ Ca samples (i.e., for 6 replicates ~600 ng of Ca). Accurate measurements require the following conditions: 1) Ca intensities matched within 3% between sample and standard, 2) low contents of Sr, Mg and Cr (Sr/Ca, Mg/Ca and Cr/Ca ratios need to be lower than 0.01 %, and K/Ca, Al/Ca, Ti/Ca and < 1% Cr/Ca ratios. Eleven standard reference materials analyzed using the established method, yield highly consistent Ca isotope results with literature values. The USGS standard GSP-2 with high K₂O content (5.38 %) was analyzed and yielded ε^{40} Ca =4.52 ±0.48 ‰, consistent with literature data. The long-term external precisions are better than 0.07 ‰ (2 SD) for $\delta^{44/40}$ Ca and better than 0.05 ‰ (2 SD) for $\delta^{44/42}$ Ca. The slope of the fractionation line between $\delta^{44/40}Ca$ and $\delta^{44/42}Ca$ is 1.9616 ± 0.0794 , within error of the slope value from the exponential law.