High precision Ca isotope measurements by collision cell MC-ICPMS

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Calcium isotopes are very interesting in cosmochemistry. For instance, excesses in radiogenic ^{40}Ca can be produced from the decay of radioactive ^{40}K, while the mass-independent nucleosynthetic variability in the neutron-rich ^{48}Ca in the solar protoplanetary disk allows genetic relationships to be established between planetary bodies [e.g., 1, 2, 3]. Analyses of calcium isotopes are typically made by thermal ionisation mass spectrometry. This allows all Ca isotopes to be measured but requires intense ion beams on ^{40}Ca to have appreciable ion beams on the minor isotopes, leading to rapid degradation of the Faraday cups. Measurements can also be made by multi-collector inductively coupled plasma source mass spectrometry where, typically, only the ^{42}Ca to ^{48}Ca isotopes are measured since the intense $^{40}Ar^+$ ion precludes the measurement of isobaric $^{40}Ca^+$.

In Bristol, we have developed a method to measure both mass-independent ($\Delta^{40/44}Ca$ and $\Delta^{43/44}Ca$) and stable ($\delta^{44/40}Ca$) calcium isotopes using the prototype collision cell MC-ICPMS, Proteus. In particular, we use helium and hydrogen gases in the collision cell and the well characterised resonant charge exchange between Ar^+ ions and H_2 molecules to almost completely remove the $^{40}Ar^+$ ion, permitting the measurement of ^{40}Ca isotope by MC-ICPMS without resorting to 'cold' plasma. This technique allows typical precisions better than 15 ppm (2se, n=8) to be reached on both mass-independent $\Delta^{40/44}Ca$ and stable $\delta^{44/40}Ca$ using a ^{42}Ca-^{43}Ca double spike, when analyzing various reference materials covering a wide range of matrices (e.g., various terrestrial rocks, seawater, bone ash, coral).

This technique was used to analyse a suite of bulk chondrites, including carbonaceous (CI, CO, CM, CK, CV), ordinary (H and LL) and enstatite chondrites (EH and EL), as well as CAIs and diogenites to investigate potential variabilities at a precision 4 times better in average than the literature data. The data will be presented at the conference.

[1] Schiller M. et al. (2018), Nature 555, 507-510. [2] Dauphas, N. et al. (2014), EPSL 407, 96-108. [3] Chen H.-W. et al. (2011), ApJL 743, L23.