NON MASS-DEPENDENT CALCIUM ISOTOPE EFFECTS IN AND AMONG PLANETARY MATERIALS

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Introduction: Here we report Ca isotope measurements acquired with a refined thermal ionization mass spectrometry (TIMS) method that can be used to simultaneously measure ^{40}Ca radiogenic and ^{43,46,48}Ca stable isotope effects in primitive materials. This method builds upon the those developed at Caltech, UC Berkeley, Univ. Chicago-Caltech-JPL, and NASA JSC [1-5]. Primitive meteorites often contain small radiogenic ^{40}Ca excesses in addition to rare epsilon level stable isotope anomalies that are near the analytical resolution of current mass spectrometry techniques. Calcium-Aluminum-rich inclusions (CAIs) may have larger ^{40}Ca and more resolvable ^{43,46,48}Ca isotope effects. The relative abundances of isotopic anomalies in ^{48}Ca and ^{50}Ti are believed to be correlated among some early solar system materials [e.g., 4], but the carrier of these nucleosynthetic signatures remains unknown. Measuring refractory elements that both have neutron-rich isotopes that are believed to be produced by the same nucleosynthetic process potentially provide useful constraints on their stellar origins (i.e., their correlation indicates contributions from a type Ia supernovae, [6]). Additionally, the degree to which isotopic heterogeneity exists within and among planetary materials can be used to understand the dynamics and evolution of the protoplanetary disk. Non mass-dependent calcium isotope compositions of bulk planetary materials, chondrites, and chondrite components (CAIs and chondrules) some that were measured for their ^{50}Ti isotopic anomalies by [7] are the focus of this ongoing work.

Methods: Digested materials are passed through a single-stage 2 ml TODGA resin vacuum column, which effectively separates Ti from all other major elements. This is an important step due to potential isobaric interferences between ^{46,48}Ca and ^{46,48}Ti. Following Ti separation, Ca is purified using a second TODGA column. This procedure, previously detailed in [8] has been documented to be effective for a range of sample compositions. Calcium isotope measurements are made using the Thermo Scientific TRITON mass spectrometer housed in the Center for Cosmochemistry and Geochronology (CICG) at NASA JSC. Purified Ca is dissolved in dilute HCl and loaded in 2-3 μg aliquots with dilute H_3PO_4 on outgassed Re filaments. A Parafilm dam is applied to the filament prior to loading the sample in an effort to reduce spreading and improve the consistency of loading. Filaments are slowly heated to evaporate loading acid and residual Parafilm. Calcium is analyzed using a multi-dynamic method, which is preferred to a static approach because it allows us to monitor the unavoidable cup degradation effects of large ion beams. One standard (SRM 915a) is run for ~ every 2 unknowns; normally 3 standards per barrel. A single run consists of 9 blocks of 15 ratios through four cup settings. Virtual amplifier rotation and baseline calibration are preformed preceding each block. The ^{40}Ca beam intensity is usually between 20-30 V using a 10^{11} Ω resistor. Instrumental mass fractionation is corrected using an exponential law and a ^{42}Ca/^{44}Ca value of 0.31221 [1]. Isobaric interfering elements are monitored on ^{39}K and ^{47}Ti during the analysis.

Summary of Results: Significant column and mass spectrometry calibration was required to re-establish the CICG labs for calcium isotope measurements after major renovations (>3-years). In addition to the analysis of standards used for Ca analysis (SRM 915a, terrestrial basalt BCR-2, and the Harvard peridotite TP-12), bulk dissolutions of the meteorites Allende and Sioux County have been measured. Analysis of the rock standards demonstrate comparable uncertainties to both [5] for ε^{40}Ca (~0.4, 2σ) and [4] for ε^{43}Ca (~0.4, 2σ), ε^{46}Ca (~15, 2σ), and ε^{48}Ca (~0.8, 2σ) in one instrumental setup. As seen previously, the basaltic rocks have ε^{40}Ca values that are ~0.8 e-units lower than SRM 915a [2,3,5,9]. No resolvable ε^{43}Ca, ε^{46}Ca, ε^{48}Ca isotopic anomalies were observed in Allende as previously reported by [2,3] despite resolvable effects reported in some other chondrites [4]. A ε^{48}Ca value of ~ -2 e-units for the Sioux County eucrite similar to that reported by [4] was found. Further analytical work is needed to evaluate the extent of Ca isotopic heterogeneity in and among early formed solids and bulk meteorites to address the existence of distinct reservoirs in the protoplanetary disk and the degree to which refractory inclusions and other early-formed solids were mixed during planetary accretion.

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