

MASS-DEPENDENT CA ISOTOPIC DIFFERENCES BETWEEN CHONDRITES AND THE EARTH

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Introduction: Small mass-dependent isotopic differences among meteorites and terrestrial igneous rocks have been reported for iron, silicon, and chromium (e.g., [1-7]). Larger isotopic differences in oxygen exist (e.g., [8]). Here we report mass-dependent calcium isotopic compositions for chondrites. Differences may reflect an incomplete mixture of initial isotopic heterogeneity in the solar system, mass-dependent evaporative losses during accretion, or parent body differentiation processes.

Approach: This study reports calcium isotope data for 6 chondrites. All data were obtained on ⁴²Ca-⁴⁸Ca spiked samples using thermal ionization mass spectrometry. Further measurements of terrestrial and extraterrestrial materials are in progress.

Chemical separation. Samples were dissolved in a mixture of hydrofluoric and perchloric acids (HF-H₃ClO₄), followed by nitric acid (HNO₃), and centrifuged; a mixed ⁴²Ca-⁴⁸Ca spike was added to an aliquot of each dissolved sample. Unspiked sample aliquots were measured previously [9]. Calcium was purified on standard cation exchange columns [10, 11]. It was found that a second pass through the cation exchange resin (AG-50W-X8) reduced aluminum, allowing for greater beam stability and intensity in samples with high Al/Ca ratios. For consistency, the second column pass was used for all samples. The separated calcium was loaded in dilute HNO₃ onto rhenium filaments with dilute phosphoric acid (H₃PO₄) for mass spectrometric analysis.

Mass spectrometry. Calcium isotope ratios were measured with a Thermo-Finnigan Triton multi-collector mass spectrometer. The ³⁹K, ⁴⁰Ca, ⁴²Ca, ⁴³Ca, ⁴⁴Ca, ⁴⁶Ca, ⁴⁸Ca, and ⁴⁹Ti beams were measured in a multi-step cup configuration in order to obtain all calcium isotopes. The magnitude of mass interference from potassium and titanium was monitored and found to be insignificant; no corrections for potassium or titanium were applied. Double spike subtraction and determination of the unspiked sample isotopic composition were obtained by an iterative technique (cf. [12]). Variations in calcium reported as $\delta^{44}\text{Ca} = \left(\frac{{}^{40}\text{Ca}^{44}\text{Ca}_{\text{normal}}/{}^{40}\text{Ca}^{44}\text{Ca}_{\text{measured}}}{47.153} - 1\right) \times 10^3$ and $\delta^{43}\text{Ca}/{}^{44}\text{Ca} = \left(\frac{{}^{43}\text{Ca}^{44}\text{Ca}_{\text{measured}}/{}^{43}\text{Ca}^{44}\text{Ca}_{\text{normal}}}{0.31221} - 1\right) \times 10^3$, where 47.153 is the ⁴⁰Ca/⁴⁴Ca value and 0.31221 is the ⁴³Ca/⁴⁴Ca value assumed for “normal” bulk silicate Earth. Each sample was measured twice. All replicate measurements yielded indistinguishable values (± 0.15

‰). The measured value for standard SRM915a in this study ($\delta^{44}\text{Ca} = -1.14$ ‰) is indistinguishable from the long-term average value $\delta^{44}\text{Ca} = -1.17 \pm 0.15$ ‰, $n > 70$).

Materials. Six meteorite bulk rock samples were measured, including: enstatite chondrite Abee (EH4), ordinary chondrites Bruderheim (L6), Paragould (LL5), and St. Severin (LL6), and carbonaceous chondrites Allende (CV3) and Murchison (CM2).

Results: The chondritic meteorites exhibit $\delta^{44}\text{Ca}$ values of -0.9 to 0.0 ‰ and $\delta^{43}\text{Ca}/{}^{44}\text{Ca}$ values of -0.3 to 0.0 (Figure 1). Data lie along a trend that is consistent with that expected of mass-dependent fractionation laws and lie between terrestrial carbonate and volcanic rocks (e.g., SRM915a carbonate, this study, and mid-ocean ridge and ocean island basalts from [13]).

Discussion: Accurate spike subtraction and recovery of sample mass-dependent isotope composition assume a normal and homogenous solar calcium isotope composition. Relatively small nucleogenic differences between chondrites of up to 150 ppm have been documented [9] but would not significantly affect the spiked sample measurements (this study).

There are previous analyses of bulk rock meteorites in the literature. Double-spiked samples reported in [11, 14] showed a total $\delta^{44}\text{Ca}$ variation of ~ 3.7 ‰ in meteorites. These differences were attributed to mass-dependent fractionation. Four analyses of Abee (EH4) showed a range from +1.0 to -2.8 ‰ in $\delta^{44}\text{Ca}$, Orgueil (C11) yielded a value of $+0.3 \pm 0.1$ ‰, and Guarena (H6) gave a value of -1.5 ± 0.1 ‰. The measurements in our study yielded smaller (e.g., < 1 ‰) and more reproducible effects (e.g., Abee replicates = $+0.01$ and -0.02 ‰ in $\delta^{44}\text{Ca}$). The variations in $\delta^{44}\text{Ca}$ found in [11] were larger than those measured for $\delta^{43}\text{Ca}/{}^{44}\text{Ca}$. Hence, the results reported here are consistent, but more precise than the previous measurements.

Similar to silicon isotopes it can be seen in a calcium three-isotope plot (shown in Figure 1) that all of the chondrite data plot on the same mass-dependent fractionation line [6], suggesting that initially a single homogeneous calcium isotopic reservoir existed in the inner Solar System. Unlike silicon, calcium in chondrites shows a range with the greatest amount of heavy isotope enrichment in enstatite chondrites, followed by ordinary chondrites, then carbonaceous chondrites. An increase in $\delta^{44}\text{Ca}$ from carbonaceous chondrites to terrestrial rocks might be due to mass dependent evaporative losses during accretion (Figure 1).

The current calcium isotopic database for planetary materials and terrestrial igneous rock is incomplete; notably it is unclear whether planetary differentiation, particularly production of crust, can generate calcium isotope fractionation as is debated for the ~ 0.2 ‰ variation in iron isotopes among terrestrial rocks and planetary objects [1-5]. For similar reasons, it is unclear if higher pressure processes like core-formation could also cause calcium fractionation and thus change the calcium composition of silicate mantles (cf. reported for silicon isotopes [6]). It is clear, however, that the variation among the undifferentiated chondrites is due to a mass-dependent process unrelated to planetary differentiation.

There are general similarities and differences between the measured calcium isotopic compositions of chondrites and their respective $\epsilon^{54}\text{Cr}/^{52}\text{Cr}$ and $\Delta^{17}\text{O}$ values. For example, while members of each chondrite group display similar $\delta^{44}\text{Ca}$ compositions, isotopic differences exist between groups. Despite some variability of oxygen isotopes among enstatite chondrites [15], our $\delta^{44}\text{Ca}$ measurements of Abee (EH4) contribute to the evidence that enstatites and the Earth and Moon may have shared a common reservoir. Furthermore, like chromium and oxygen, the calcium data indicate that there are at least two reservoirs in the solar system from which planetary materials are derived.

Summary: Chondrites exhibit a range of calcium isotopic signatures that appear to represent evaporative loss during accretion. The different chondrites and/or their precursor materials formed from regions with different calcium or, alternatively, from the same reservoir that experienced a range of physiochemical conditions. The increasing $\delta^{44}\text{Ca}$ from carbonaceous to ordinary to enstatite chondrites corresponds with their decreasing abundance of moderately volatile elements and is consistent with increasing degree of evaporative loss. Hence these results may be due to the heliocentric distance and/or height of their formation within the protoplanetary disk. Notably the terrestrial volcanic rocks and Abee appear to represent a high $\delta^{44}\text{Ca}$ end-member rather than an intermediate isotopic mixture of chondrite parent bodies (cf. [7]) (Figure 2).

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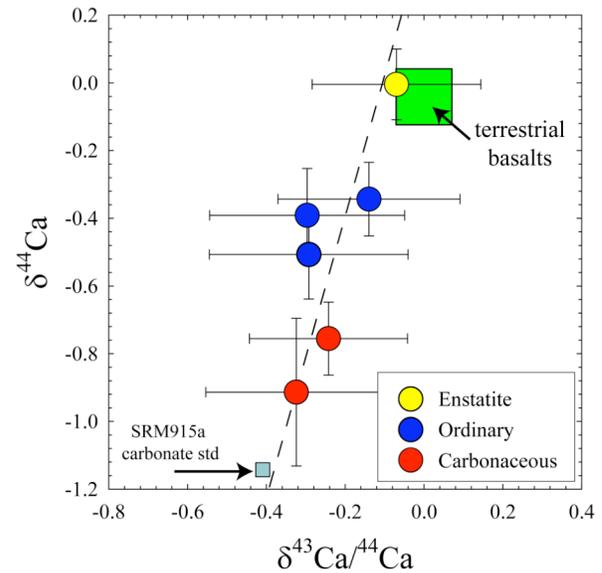


Figure 1. Measured $\delta^{44}\text{Ca}$ and $\delta^{43}\text{Ca}/^{44}\text{Ca}$ of chondritic meteorites that lie along a mass-dependent fractionation line (dashed line). Uncertainties are 2σ . Zero is "normal" calcium [10] as defined by measured terrestrial igneous rocks.

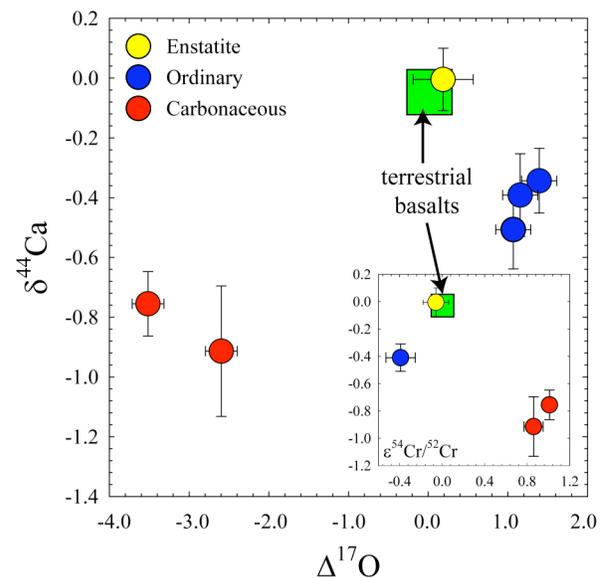


Figure 2: Plot of $\delta^{44}\text{Ca}$ versus $\Delta^{17}\text{O}$ for different chondrites that shows distinct isotopic signatures between groups. Inset is $\delta^{44}\text{Ca}$ versus $\epsilon^{54}\text{Cr}/^{52}\text{Cr}$ that also shows differences between groups. Oxygen data come from [15-17] and chromium data from [7].