NON-MASS DEPENDENT CA ISOTOPIC DIFFERENCES BETWEEN METEORITES AND THE EARTH

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Introduction: Isotopic differences between meteorite parent bodies and the Earth due to non-mass dependent processes have previously been found for O isotopes, but not for the other major chemical constituents (Fe, Si, Mg, Ca). Oxygen was present in both solids and gas in the solar nebula and consequently there may have been processes to promote isotopic heterogeneity in O that would not have affected the other elements (e.g., [1]). The issue of whether there was heterogeneity in the isotopes of refractory elements has recently been raised, especially for Ba and Nd. For Mg and Ca, large isotopic variations, mostly mass-dependent but also nuclear, have been found in CAI's and chondrules, but there have been no differences reported between parent bodies or planets. The best-documented effects in early-formed solids are excesses of ^{48}Ca [2, 3].

Approach: This study reports Ca isotope data for 10 terrestrial igneous rocks and 7 meteorites. All data were obtained on unspiked samples using thermal ionization mass spectrometry, and only masses 40, 42, 43 and 44 were measured. Further measurements, some using the double spike technique, are in progress to evaluate mass-dependent fractionation and nuclear effects in the heavier isotopes.

Chemical separation. Samples were dissolved in a mixture of hydrofluoric and perchloric acids (HF-H_3ClO_4), followed by nitric acid (HNO_3), and centrifuged; no spike was added. Ca was purified on standard cation exchange columns [3, 4]. It was found that a second pass through the cation exchange resin (AG-50W-X8) reduced Al allowing for greater beam stability and intensity in samples with high Al/Ca ratios. For purposes of consistency the second column pass was used for all samples. The separated Ca was loaded in dilute HNO_3 onto Re filaments with dilute phosphoric acid (H_3PO_4) for mass spectrometric analysis.

Mass spectrometry. Calcium isotope ratios are measured with a Thermo-Finnigan Triton multi-collector mass spectrometer. The ^{39}K, ^{40}Ca, ^{42}Ca, ^{43}Ca, and ^{44}Ca beams are measured in a static cup configuration. An exponential law is used for instrumental mass discrimination correction using ^{42}Ca/^{44}Ca = 0.31221 for normalization [3]. Variations in ^{40}Ca are reported as $\varepsilon_{40/42} = (^{40}Ca/^{42}Ca_{measured}/151.023-1)*10^4$, where 151.023 ±0.008 is the ^{40}Ca/^{42}Ca value measured for terrestrial basalt standard BCR-1). The corresponding value for ^{43}Ca/^{44}Ca is 0.0648658±56. Ten measurements of BCR-1 and thirteen measurements of the SRM-915a calcium standard define the terrestrial ratios to ≤1 ε-unit. The internal precision, for a single mass spectrometer analysis is ≤0.4 ε-units. Our uncertainties are based on multiple measurements for each sample (n=2 to 6, Figure 1). Most samples yield uncertainties ≤1 ε-unit (2 s.e.), but a few did not reproduce well and have larger uncertainties.

Terrestrial materials. The 10 terrestrial rock samples include basalts from the Pacific and Atlantic mid-ocean ridges (MORB); a Hawaiian tholeiite, an island arc basalt; BCR-1; a Cenozoic crystal-rich rhyolite (the Fish Canyon Tuff) from the central San Juan Volcanic Field, CO; and a Cenozoic high silica rhyolite from the western San Juan Volcanic Field, CO. Also included are tonalite and granodiorite from the Sierra Nevada and Tertiary 2-mica granite from Arizona.

Extraterrestrial materials. Seven meteorite bulk rock samples were measured: Martian meteorite ALH84001, achondrite Angra dos Reis, enstatite chondrite Abee (EH4), and ordinary chondrites Bruderheim (L6), Paragould (LL5), and St. Severin (LL6).

Results: The terrestrial igneous rocks yield $\varepsilon_{40/42}$ values indistinguishable from zero. A two-mica granite and a high silica rhyolite show barely resolvable ^{40}Ca excesses, due to radiogenic ingrowth from ^{40}K decay in crustal source rocks. The chondritic meteorites exhibit $\varepsilon_{40/42}$ values of -2 to -10. Angra dos Reis also shows a small, although poorly resolved, ^{40}Ca deficit. ALH84001 has a slightly elevated $\varepsilon_{40/42}$ ratio, but considering the ±1 ε-unit uncertainty in the terrestrial basalts, the veracity of this apparent excess is the subject of further study. There are no variations in ^{43}Ca/^{44}Ca observed (Figure 1).

Discussion: There are previous analyses of bulk rock meteorites in the literature. Shih et al. [5] reported ^{40}Ca/^{44}Ca ratios for 4 eucrites, 2 shergottites, and lunar rocks, but found no significant differences (≤1 ε-unit) from terrestrial standards. There is a hint in their data that Shergotty has a slightly high ^{40}Ca/^{44}Ca ratio. Double-spiked samples reported in [3] showed a total variation of $\varepsilon_{40/44}$ of 37 ε-units in meteorites. These differences were interpreted as due to mass dependent fractionation. Four analyses of Abee showed a range from +10 to -28 in $\varepsilon_{40/44}$ and Guarena gave a value of -15 ±1. Other $\varepsilon_{40/44}$ results from [3] are: Haverö -7 (±1), Ibitira -2 (±2), and Norton County +9 (±1). The variations in ^{40}Ca found in [3] were larger than those measured for ^{43}Ca. Hence the results reported here are not inconsistent with these previous measurements.

With our normalization procedure, depletion in ^{40}Ca is difficult to distinguish from enrichments in ^{42}Ca and ^{43}Ca. However, if these latter nuclides are enriched, the enrichment in ^{42}Ca must be almost exactly twice that in ^{43}Ca. There are nucleosynthetic conditions in massive stars where this requirement might be met (e.g., [6]). In any case, the observed nuclear effects are indicative of either a deficit in a Ca component made during supernova explosions (explosive O-Si burning), or an enhancement in *s*-process contribution (e.g., [6]).

The Ca isotope effects might be expected to correlate with *r*-process depletions or *s*-process enrichments in heavier elements. The effects we observe in Ca for Bruderheim, Abee, and ALH84001 (Figure 2), appear to correlated with published ^{142}Nd data for a few samples where data are available [7, 8]. However the ^{40}Ca depletions are not consistent with the Nd data, since ^{142}Nd depletion should be caused by an excess of *s*-process Nd. If this correlation holds up with more data, it would tend to favor the idea that ^{142}Nd variations reflect solar nebula heterogeneity rather than radioactive decay.

Both ^{40}Ca and ^{142}Nd variations might be expected in a model of contamination of the solar nebula with material blown off from a nearby AGB star [9]. But the sense of the correlation we observe would be difficult to explain. If the ^{142}Nd enrichment for the Earth is not due to radioactive decay of ^{146}Sm, then it would remove the requirement for either a hidden low-Sm/Nd reservoir in the Earth, or for the Earth to have a non-chondritic rare earth abundance pattern [10].

Although we have not measured lunar samples, the previous results [5] suggest that there is no difference between terrestrial and lunar Ca. We are in the process of measuring additional meteorite samples. Additional measurements coupled with insights from other isotope systems (e.g., O, Nd, Ba, Sm) should expand our understanding of the magnitude and distribution of ^{40}Ca anomalies in the solar nebula, and the processes leading to the preservation of these differences in parent bodies and planets.

References:

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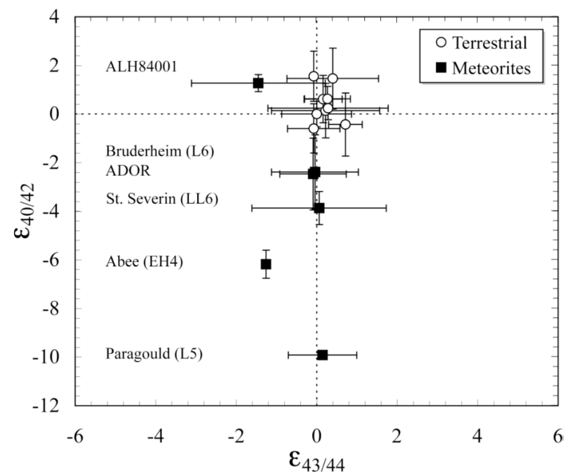

Figure 1. Measured $\varepsilon_{40/42}$ and $\varepsilon_{43/44}$ of terrestrial igneous rocks and differentiated and primitive meteorites. Uncertainties are 2 sigma. Zero is defined by the measured $^{40}Ca/^{42}Ca$ of terrestrial standards BCR-1 and SRM-915a, and has an uncertainty of about ±1 ε-unit for $\varepsilon_{40/42}$. Terrestrial rocks are indistinguishable from zero for both $^{40}Ca/^{42}Ca$ and $^{43}Ca/^{44}Ca$. Chondrites and achondrites have low $^{40}Ca/^{42}Ca$ but terrestrial values of $^{43}Ca/^{44}Ca$. Martian sample ALH84001 has slightly elevated $^{40}Ca/^{42}Ca$.

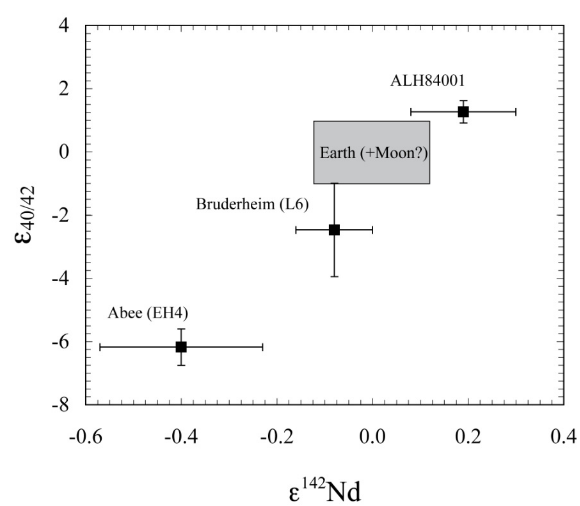

Figure 2: Correlation between ^{40}Ca and ^{142}Nd isotopic effects for two primitive chondrites, the Earth, and ALH84001. The ^{40}Ca variation is too large to be due to radioactive decay, and must reflect solar system heterogeneity. The correlation implies that the ^{142}Nd effect may also be due to heterogeneity rather than decay of ^{146}Sm. Terrestrial and chondritic Nd data from [7]. ALH84001 Nd data from [8].