

Calcium isotopic composition of planetary materials. K. Misawa^{1,2} Tatsunori Yokoyama³, S. Yoneda³,
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Introduction: Calcium has six naturally occurring isotopes: ^{40}Ca , ^{42}Ca , ^{43}Ca , ^{44}Ca , ^{46}Ca and ^{48}Ca . Because of the large mass difference of the calcium isotopes ($\Delta m/m \sim 20\%$), mass fractionation effects could be occurred in nature and be applicable to nontraditional stable isotope geochemistry [1,2]. Planetary materials show calcium isotope heterogeneity at whole-rock scale (e.g. an enrichment of the most neutron-rich isotope, ^{48}Ca for ureilites, eucrites, diogenites and angrites [3] and a detectable ^{40}Ca excess in bulk samples of the Dhajala (H3.8) chondrite [4,5]).

Radiogenic ingrowth of ^{40}Ca due to decay of ^{40}K occurred and ^{40}Ca abundance varies within the solar system history. Marshall and DePaolo [6,7] demonstrated that the ^{40}K - ^{40}Ca decay system could be a useful radiogenic tracer for studies of terrestrial rocks. Shih et al. [8,9] determined ^{40}K - ^{40}Ca ages of lunar granitic rock fragments and discussed chemical characteristics of their source materials. Recently, Yokoyama et al. [10] showed the application of the ^{40}K - ^{40}Ca chronometer for old and high K/Ca materials in ordinary chondrites (OCs).

High-precision calcium isotopic data are needed [11,12] to constrain mixing processes of solar system materials and time of planetesimal formation. To better constrain the solar system calcium isotopic compositions, we have determined calcium isotopic compositions of OCs and an angrite.

Experimental: Whole-rock samples of Yamato (Y) -74442 (LL4), Peace River (L6), Leedey (L6), Shaw (L6/7), Zhaodong (L4) and D'Orbigny (angrite) were examined for calcium isotopes. Calcium was separated from other major elements using a polyethylene column filled with 1 mL cation exchange resin (BioRad AG50W-X8, 200–400 mesh) and was further purified using a quartz column filled with 200 μL Eichrom DGA resin (particle size: 50–100 μm) to remove titanium and aluminum.

The calcium isotopic data were obtained on a multi-collector thermal ionization mass spectrometer, Thermo Scientific Triton *Plus* at the National Museum of Nature and Science, equipped with nine Faraday cups. Instrumental mass fractionation was corrected using the exponential law with $^{42}\text{Ca}/^{44}\text{Ca} = 0.31221$ as the normalizing ratio [1].

Results and Discussion: After internal normalization, 26 measurements of calcium standard, NIST SRM915a yield $^{40}\text{Ca}/^{44}\text{Ca} = 47.1646 \pm 0.0044$ (2σ). Here, we report $^{40}\text{Ca}/^{44}\text{Ca}$ measurements normalized to the NIST SRM 915a

$\epsilon^{40}\text{Ca} = [(^{40}\text{Ca}/^{44}\text{Ca})_{\text{sample}}/(^{40}\text{Ca}/^{44}\text{Ca})_{\text{SRM915a}} - 1] \times 10^4$, where $(^{40}\text{Ca}/^{44}\text{Ca})_{\text{SRM915a}}$ is the SRM915a measured value of 47.1646. We plot $\epsilon^{40}\text{Ca}$ for five OCs and

an angrite with the internal uncertainties as $2\sigma_m$ (Fig. 1). The K/Ca atomic ratios of OCs vary from 0.053 to 0.071, which is comparable to the K/Ca ratio of Dhajala (H3.8) possessing an excess of ^{40}Ca (+1.7 ϵ -units) [4,5].

Hans et al. [13] reported strontium isotopic compositions of alkali-poor differentiated meteorites, and suggested that volatile loss from the angrite and eucrite parent bodies occurred within <1 Ma after formation of Ca, Al-rich inclusions. If this is the case, calcium isotopic compositions of angrite and eucrite parent bodies could be primordial, and represent isotopic compositions of early accreted materials. The OCs analyzed here (except Y-74442) have age corrected $\epsilon^{40}\text{Ca}$ values that overlap within the analytical uncertainties and are almost comparable to the measured (or age corrected [14,15]) $\epsilon^{40}\text{Ca}$ value of D'Orbigny, implying that the differences in $^{40}\text{Ca}/^{44}\text{Ca}$ between D'Orbigny and OCs are marginal. Mixing of a chondritic component with an alkali-rich component formed in the early solar nebula [16] would be lower the age corrected $\epsilon^{40}\text{Ca}$ value for Y-74442 (-1.7 ϵ -units).

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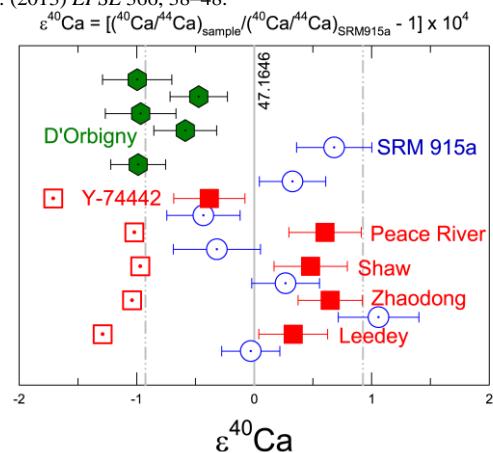


Figure 1. $^{40}\text{Ca}/^{44}\text{Ca}$ results, normalized to $^{42}\text{Ca}/^{44}\text{Ca} = 0.31221$ [1], for five OCs and an angrite (errors are $2\sigma_m$). Open squares: age (4.568 Ga) corrected for OCs. Solid line: the average value for NIST SRM 915a standard ($^{40}\text{Ca}/^{44}\text{Ca} = 47.1646$). Repeat analyses of SRM 915a show reproducibility within $\pm 0.93 \epsilon$ -units in $^{40}\text{Ca}/^{44}\text{Ca}$ when the data are corrected by the exponential law (Dashed lines are $2\sigma_p$ values of SRM 915a).