

FORMATION OF CAIs: CONSTRAINTS FROM THE CALCIUM ISOTOPE COMPOSITION OF CAI (SJ101) FROM THE ALLENDE CV3 CHONDRITE. J. Farkas¹, G. Yu¹, S. Huang¹, M.I. Petaev^{1,2} and S. Jacobsen¹, ¹Department of Earth and Planetary Sciences, Harvard University, Cambridge, 021 38, MA, USA. ²Harvard-Smithsonian Center for Astrophysics (corresponding author: jfarkas@eps.harvard.edu).

Introduction: The calcium-aluminum rich inclusions (CAIs) represent the oldest objects formed in the Solar System [1], and therefore knowledge of their chemical and isotope compositions is critical for a better understanding of the origin and evolution of our Solar System and its various components, including the Earth. Previous studies on CAIs showed large mass-dependent isotope effects attributed to non-equilibrium evaporation/condensation processes [2]. Specifically, non-equilibrium evaporation of silicate melt into space leaves the residual melt isotopically heavy, as light isotopes are preferentially lost during evaporation. Alternatively, recondensation of vapors enriched in light isotopes, could in turn generate CAIs with light isotope signatures [2]. These positive and negative mass-dependent isotope anomalies in CAIs have been observed for isotope systems of elements such as Ca, Mg and Si [2-5].

Here we present new Ca isotope data from a large (~2.5x1.5 cm) CAI inclusion extracted from the Allende CV3 chondrite. Based on petrology and chemical composition this inclusion has been classified as a forsterite-bearing Type B inclusion with the Group II REE pattern, and named SJ101 [6]. We measured mass-dependent and non-mass-dependent (i.e. nucleosynthetic) Ca isotope variations in the bulk CAI, using the thermal ionization mass-spectrometry (TIMS). The results are discussed with respect to trace element and Mg and Si isotope data acquired previously from the same CAI [6]. We also present a compilation of our recent Ca isotope measurements from various objects of the Solar System including terrestrial and martian basalts, and speculate about processes responsible for the anomalous Ca isotope signatures in CAIs.

Analytical Method: Powder from the bulk CAI inclusion was dissolved in a mixture of concentrated HF-HNO₃ acid at 120 °C for 48 hours. The sample was dried down and three times treated with concentrated HNO₃ and once with 6N HCl in order to avoid the formation of CaF₂ [7]. Finally, the sample was re-dissolved in 2.5N HCl from which two aliquots have been taken - one for mass-dependent and the other for non-mass-dependent Ca isotope analysis. The former was mixed with a ⁴³Ca/⁴⁸Ca double spike prior to chromatographic clean-up on cation exchange columns filled with BioRad AG50W-X12 resin [8]. For mass spectrometry, approximately 5 µg of purified Ca was loaded on a triple-filament assembly with rhenium

ribbons. The Ca isotope abundances were measured by the IsoProbe-T TIMS instrument in a static mode using a two-sequence method. The first sequence collected masses 40 to 44 and the second 44 to 48. The mass-dependent Ca isotope variations, expressed as $\delta^{44/40}\text{Ca}$ relative to the Bulk Silicate Earth (BSE), were determined by a double spiking technique using an offline data reduction with an exponential law [8,9]; where $\delta^{44/40}\text{Ca} = [({}^{44}\text{Ca}/{}^{40}\text{Ca})_{\text{SAMPLE}}/({}^{44}\text{Ca}/{}^{40}\text{Ca})_{\text{BSE}} - 1] * 1000$. The non-mass dependent isotope effects, expressed as ϵ_{Ca} relative to BSE, were measured on unspiked sample aliquots using an online internal normalization to ⁴²Ca/⁴⁴Ca of 0.31221 [2]; where $\epsilon^{48}_{\text{Ca}} = [({}^{44}\text{Ca}/{}^{48}\text{Ca})_{\text{SAMPLE}}/({}^{44}\text{Ca}/{}^{48}\text{Ca})_{\text{BSE}} - 1] * 10000$. The long-term external reproducibility (2 σ) for $\delta^{44/40}\text{Ca}$ and $\epsilon^{48}_{\text{Ca}}$ measurements, based on repeat analysis of NIST 915a (n =27), is 0.14‰ and 1.9 ϵ -unit, respectively. Concentrations of major and trace elements (REE) in SJ101 were measured by a quadrupole ICP-MS in the solution prepared from 80 mg aliquot of the bulk sample.

Results: Our data show no detectable excess of ⁴⁸Ca (non-mass-dependent) that could arise from nucleosynthetic processes. The SJ101 yielded $\epsilon^{48}_{\text{Ca}}$ of -1.1, which falls well within the range (2 σ) of terrestrial basalts ($\epsilon^{48}_{\text{Ca}} = 0.0$; BCR1) and/or martian SNC meteorites ($\epsilon^{48}_{\text{Ca}} = 1.4$; Nakhla and Zagami), (Fig. 1A). Consequently, any deviation in $\delta^{44/40}\text{Ca}$ measured in SJ101 is due exclusively to mass-dependent isotope effects. The $\delta^{44/40}\text{Ca}$ of SJ101 yielded anomalously light value of $-4.74 \pm 0.19\text{‰}$ (Fig. 1B). The stable Ca isotope composition of martian meteorites yielded $\delta^{44/40}\text{Ca}$ of $-0.08 \pm 0.03\text{‰}$ and the estimated $\delta^{44/40}\text{Ca}$ of the Bulk Silicate Earth is $0.0 \pm 0.19\text{‰}$, based on the analysis of numerous tholeiitic basalts ($-0.05 \pm 0.13\text{‰}$) as well as mineral separates from mantle peridotites ($0.1 \pm 0.10\text{‰}$). Thus, the $\delta^{44/40}\text{Ca}$ of the studied CAI is approximately 5‰ lighter than the composition of the terrestrial planets (Fig. 1).

Discussion and Conclusions: Previous studies on the mass-dependent Ca isotope fractionation in CAIs showed a wide range of $\delta^{44/40}\text{Ca}$, from values as light as -8‰ up to +52‰ [3,10,11], where the heavy signatures are typical for FUN inclusions (i.e. HAL-type hibonites). Our data from SJ101 fall within the above range of the published $\delta^{44/40}\text{Ca}$ values, but they plot in the 'lower' more-negative end of the overall spread.

In general, the CAIs with heavy $\delta^{44/40}\text{Ca}$ signatures are interpreted as a product of non-equilibrium evaporation processes [2], as light ^{40}Ca isotope tends to escape more readily into the space during evaporation of molten silicate material, leaving the residual melt isotopically heavy. Subsequent recondensation of this isotopically light silicate vapor, derived from the previous episodes of vaporization, could in turn lead to the formation of CAIs with isotopically light $\delta^{44/40}\text{Ca}$ signatures. Thus, one way to interpret the light $\delta^{44/40}\text{Ca}$ value of SJ101 is by involving recondensation of isotopically light silicate vapor. However, the trace element and REE pattern of SJ101 (Fig. 2) as well as its close-to-solar ratios of the major elements [6] are apparently inconsistent with the above interpretation. In addition, the Mg and Si isotope composition of SJ101 [6] showed fairly limited depletions in light isotopes relative to the average chondrites (CHUR) and/or the bulk silicate Earth. Thus, it seems more plausible that the isotopically light Ca found in SJ101 is inherited from processes that involved rapid and non-equilibrium effects (*i.e.* kinetic isotope fractionation) linked to incomplete condensation of nebular gases with near-solar elemental and isotope compositions.

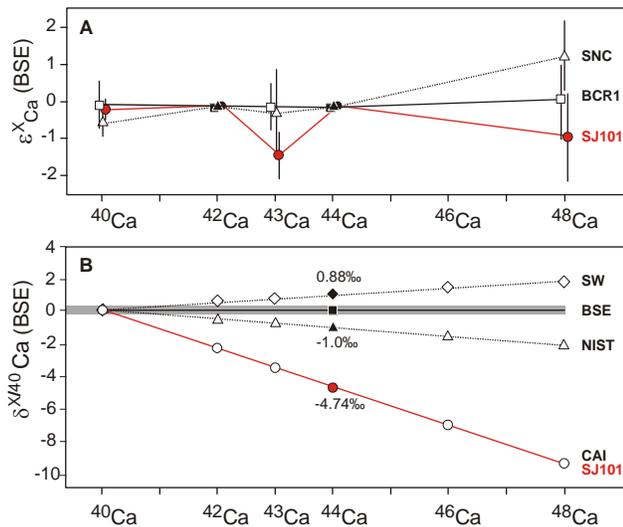


Fig. 1. (A) Non-mass-dependent Ca isotope fractionation of the CAI SJ101 (red circles), terrestrial basalt BCR1 (open squares) and martian SNC meteorites (Nakhla and Zagami, open triangles). (B) Mass-dependent Ca isotope compositions of SJ101 (circles), NIST 915 (triangles) and modern seawater SW (diamonds) normalized to the composition of the Bulk Silicate Earth (BSE, cf. gray band), the latter based on the measurements of tholeiitic basalts and mantle peridotites. Data from the SNC meteorites fell within the range of BSE. Note that the (2σ) error bars are smaller than the size of data points, (*e.g.* the error bars for $\delta^{44/40}\text{Ca}$ data are smaller than 0.2‰).

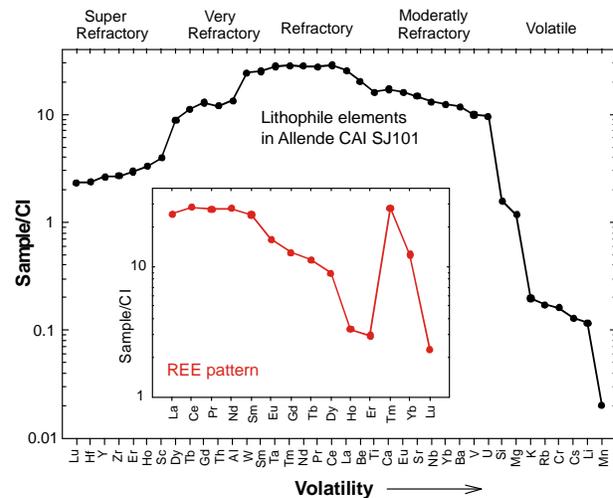


Fig. 2. Major and trace element abundances in SJ101 as a function of the elemental condensation temperatures, *i.e.* volatility [*e.g.* 12]. The inset with a red line shows the REE Group II pattern of the bulk CAI.

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