

MULTIPLE GENERATIONS OF FRACTIONATED HIBONITE-RICH CAIS SAMPLED THE SOLAR NEBULA AT DIFFERENT DEGREES OF ISOTOPIC HETEROGENEITY L. Kööp^{1,2,4}, A. M. Davis^{1,2,3,4}, P. R. Heck^{2,4}, N. T. Kita⁵, A. N. Krot⁶, P. Mane⁷, K. Nagashima⁶, D. Nakashima^{5,8}, C. Park^{6,9}, T. J. Tenner⁵, M. Wadhwa⁷, ¹Dept. of Geophysical Sciences, ²Chicago Center for Cosmochemistry, ³Enrico Fermi Institute, Univ. of Chicago, Chicago, IL, ⁴Robert A. Pritzker Center for Meteoritics and Polar Studies, Field Museum of Natural History, Chicago, IL, ⁵WiscSIMS, Dept. of Geoscience, Univ. of Wisconsin, Madison, WI, ⁶HIGP/SOEST, Univ. of Hawai'i at Mānoa, Honolulu, HI, ⁷School of Earth and Space Exploration, Arizona State Univ., Tempe, AZ, ⁸Tohoku Univ., Sendai, Japan, ⁹Korea Polar Research Institute, Incheon, Korea (E-mail: koeop@uchicago.edu)

Introduction: Calcium-aluminum-rich inclusions (CAIs) are the oldest dated objects that formed in the solar system [1]. A few of these show large mass-dependent enrichments in the heavy isotopes of some elements, attesting to a formation by melt distillation of low-temperature precursors, and are often classified as fractionated (F) CAIs ([2] and references therein). Some fractionated CAIs also have large mass-independent anomalies of nucleosynthetic origin and are classified as FUN (Fractionated and Unidentified Nuclear effects) CAIs. Other CAIs with large unidentified nuclear (UN) anomalies lack fractionation effects. While F and FUN CAIs are often not petrologically distinct from regular CAIs, UN effects are most commonly found in hibonite-rich CAIs like platy hibonite crystals (PLACs) [3].

We have studied 80 hibonite-rich CAIs separated from the Murchison meteorite for their UN characteristics [4, 5] and incorporation of ²⁶Al at their time of formation. Here, we report the mass-dependent and mass-independent isotope effects in O, Mg, Ca and Ti in 7 of these hibonite-rich CAIs that have F(UN) characteristics. We also infer their initial ²⁶Al/²⁷Al ratios [²⁶Al/²⁷Al]₀ from model and internal isochrons.

Methods: Al-Mg and O-isotope analyses were performed with the WiscSIMS Cameca ims-1280 at UW. The results for O isotopes have been previously reported [4]. For Mg isotopes, most hibonites were analyzed with a ~12 μm primary O⁻ beam and mono-EM detection [6]. Ca and Ti isotopes were analyzed with the Cameca ims-1280 at UH [7]; part of the results have been previously reported [5]. Intrinsic isotopic fractionation is expressed as F_{Ti} and F_{Ca} as defined in [3].

The major element compositions were determined by EPMA (Cameca SX-50). Trace elements (REE, Mg, Ti) were measured with the Cameca ims-6f at ASU. NIST glasses were used to obtain relative sensitivity factors and oxide interferences on the heavy REE were corrected using the ion to oxide ratios published by [8].

Results: Mineralogy and morphology: Grains 2-5-1, 2-6-6, and 2-8-7 are stubby crystals of hibonite (70 to 300 μm in size). All contain refractory metal nuggets (RMNs); those in 2-5-1 and 2-6-6 were large enough for analysis and are depleted in Mo and W. 2-2-1 and 2-8-3 are single crystals with platy morphologies. In contrast to other hibonites, their surfaces have abundant hexago-

nal pits. 1-9-1 is a platy CAI fragment consisting of a spinel and a hibonite layer. 1-10-3 is a hibonite aggregate with inclusions of corundum (<10 μm).

Chemical and isotopic characteristics: The results are summarized in Table 1 and Figures 1 and 2. The main observations are as follows: (1) Based on the inferred (²⁶Al/²⁷Al)₀, the hibonite-rich CAIs can be divided into three groups: ²⁶Al-free, with subcanonical ratio, and with approximately canonical ratios (Table 1). (2) All except the canonical CAIs are depleted in Mg and Ti relative to PLAC and SHIB hibonites [4]. (3) All CAIs show fractionation effects in at least one element, but never simultaneously in all four studied elements. (4) The most Mg- and Ti-rich hibonites (canonical CAIs) have the highest degrees of Ca fractionation, but lack corresponding effects in Ti, Mg and O (Fig. 2b). (5) Correlated fractionation effects in Ca and Ti are only observed in four CAIs (Fig. 2b), i.e., 1-10-3, two of the ²⁶Al-free CAIs (2-6-6, 2-5-1) and the subcanonical CAI 2-8-7. (6) Nucleosynthetic anomalies are only observed in ²⁶Al-free CAIs and are more pronounced in ⁴⁸Ca (δ⁴⁸Ca of up to 43±5‰) than in ⁵⁰Ti (Fig. 2a). (7) Most analyzed grains have Δ¹⁷O (=δ¹⁷O-0.52×δ¹⁸O) values between -23‰ and -25‰ (Fig. 1), like many FUN and normal CAIs from unmetamorphosed chondrites [e.g., 9, 10]. Only the CAI with the largest nucleosynthetic effects (²⁶Al-free CAI 2-5-1) has a distinct Δ¹⁷O of -14±1‰. (8) Only CAI 2-6-6 shows significant frac-

Table 1: Characteristics of the studied CAIs. F_{element} indicates degree of fractionation. Abbreviations: subc – subcanonical, aggr. – aggregate, cor – corundum, sp – spinel, n.a. – not analyzed, amu – atomic mass unit.

| Name | 2-5-1 | 2-6-6 | 1-9-1 | 1-10-3 | 2-8-7 | 2-8-3 | 2-2-1 |
|---|-----------------------|-------|-------|----------|-------|------------|-------|
| Classification | ²⁶ Al-free | | | | subc. | canonical | |
| ²⁶ Al/ ²⁷ Al (×10 ⁻⁵) | ~ 0 | ~ 0 | ~ 0 | n.a. | ~ 0.3 | ~ 5 | ~ 5 |
| Δ ¹⁷ O (‰) | -14 | -23 | -23 | -24 | -25 | -25 | -24 |
| F _O (‰/amu) | ~ 24 | ~ 4 | ~ 27 | ~ 3 | ~ 26 | ~ 7 | ~ 5 |
| F _{Ca} (‰/amu) | ~ 10 | ~ 5 | ~ 15 | < 5 | ~ 15 | > 15 | > 15 |
| F _{Ti} (‰/amu) | ~ 10 | < 5 | < 5 | < 5 | > 10 | ~ 0 | ~ 0 |
| F _{Mg} (‰/amu) | ~ 0 | ~ 10 | ~ 0 | n.a. | ~ 0 | ~ 0 | ~ 0 |
| MgO (wt%) | < 0.5 | < 0.5 | 0.5 | 0.5 | < 0.5 | ~ 1 | ~ 1 |
| TiO ₂ (wt%) | < 0.5 | < 0.5 | ~ 1.5 | ~ 1 | 0.5 | ~ 2 | ~ 2 |
| Morphology | stubby | platy | aggr. | stubby | platy | | |
| Additional phases | RMN | RMN | sp | cor, RMN | RMN | perovskite | |
| REE | Ce depletion | n.a. | | n.a. | low | n.a. | |

tionation in Mg isotopes. All others are indistinguishable from or slightly lighter than measured standard values.

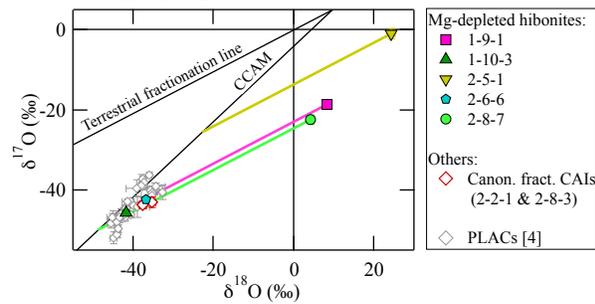


Figure 1. O isotope diagram, modified after [4].

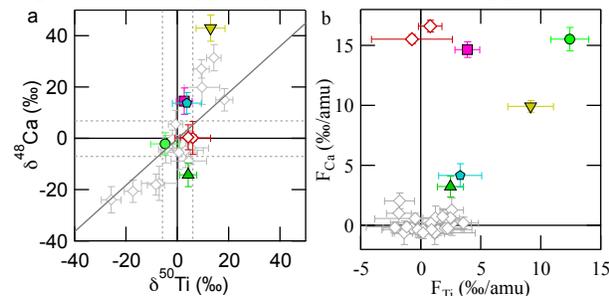


Figure 2. Ca- and Ti-isotope data for fractionated hibonite-rich CAIs, with PLAC data from [5] for comparison. a) Nucleosynthetic anomalies. b) Fractionation effects. Symbols as in Fig. 1; gray line in Fig. 2a is a fit through PLAC data.

Discussion: The fractionated CAIs 2-2-1 and 2-8-3 have particularly enigmatic isotopic compositions (high fractionation in Ca, yet not in O, Mg and Ti, \sim canonical ($^{26}\text{Al}/^{27}\text{Al}_0$)). Their identical morphological, chemical and isotopic characteristics suggest that they may have been liberated from the same CAI, possibly during acid treatment.

A general feature of the studied CAIs is that fractionation effects can be observed in all analyzed elements, yet never simultaneously in the same CAI. This could be a result of complicated condensation and evaporation histories or of reintroduction of isotopically normal Mg and/or Ti after CAI crystallization.

Most fractionated hibonites studied here lack fractionation in Mg. This has been observed in previous studies and attributed to quantitative Mg evaporation, followed by Mg surface contamination [11]. However, as Mg and Ti contents are generally coupled in the hibonites studied here, most prominently in the Mg- and Ti-rich canonical CAIs, we argue against contamination, but favor late-stage reintroduction of normal Mg (and possibly also Ti) to explain the lack of Mg fractionation effects. Indicators that reintroduction of Mg also resulted in addition of isotopically normal Ti include (1) the lack of fractionation effects in Ti in the CAIs that show high degrees of Ca fractionation (2-8-3, 2-2-1 and less pro-

nounced in 1-9-1) and (2) the steep distribution of $\delta^{48}\text{Ca}$ vs. $\delta^{50}\text{Ti}$ compared to PLACs (Fig. 2a), which could indicate dilution of ^{50}Ti anomalies in the Ti-poor fractionated CAIs. Alternatively, isotopically normal Mg could have entered the hibonite lattice without Ti, possibly facilitated by an overabundance of Ti^{4+} (and vacancies) relative to Mg^{2+} in the hibonite lattice, as hinted at by our SIMS analyses. Enhanced Ti may be a result of crystallization in a melt with high Ti/Mg due to preferential evaporation of the more volatile Mg. That the excess Ti is present as Ti^{3+} is unlikely, given that Ce depletions in hibonite (Table 1) and W and Mo depletions in RMNs indicate formation under oxidizing conditions.

The mass-independent effects suggest that the samples record at least three different stages of solar nebular history. The range of resolvable anomalies in ^{48}Ca and ^{50}Ti indicates that the ^{26}Al -free fractionated CAIs formed early in a heterogeneous nebula, that was evolving towards a uniform $\Delta^{17}\text{O}$ of $\sim -24\%$ prior to the arrival of ^{26}Al . The subcanonical CAI may have formed during admixture of ^{26}Al (although formation after significant ^{26}Al decay cannot be excluded), in a nebula characterized by a $\Delta^{17}\text{O}$ of $\sim -24\%$, in which nucleosynthetic anomalies had been homogenized to a level of $< \sim 5\%$. Finally, the canonical hibonites formed around the same time as normal CAIs. Whether or not the subcanonical level indicates early or late formation, the approximately constant $\Delta^{17}\text{O}$ value indicates that the oxygen isotopic evolution of the CAI-forming region appears to have stagnated for a significant amount of time.

Conclusions: The lack of Mg and Ti isotopic fractionation in some hibonites with high Ca fractionation suggests that late-stage reintroduction of Mg and Ti may have diluted isotopic effects in these elements. As Ca abundance is fixed by mineral chemistry, this element likely provides a more robust record of the original mass-dependent and -independent isotope effects in hibonite. The variable nucleosynthetic anomalies and levels of ^{26}Al incorporation suggest that these CAIs represent at least three different isotopic populations and sample different evolutionary stages of the nebula. This further implies that conditions favorable for melt distillation existed over a significant period of nebula history.

References: [1] Amelin Y. et al. (2002) *Science*, 297, 1678–1683. [2] MacPherson G. J. (2014) *Treatise on Geochemistry*, 2nd Ed. [3] Ireland T. (1990) *GCA*, 54, 3219–3237. [4] Kööp L. et al. (2014) *LPS*, 45, 2508. [5] Kööp L. et al. (2014) *MAPS*, 49, #5384. [6] Ushikubo T. et al. (2013) *GCA*, 109, 280–295. [7] Park C. et al. (2014) *LPS*, 45, #2656. [8] Fahey A. J. et al. (1987) *GCA*, 51, 329–350. [9] Krot A. N. et al. (2010) *ApJ*, 713, 1159–1166. [10] Makide K. et al. (2009) *GCA*, 73, 5018–5050. [11] Ireland T. et al. (1992) *GCA*, 56, 2503–2520.