THE CHEMICAL AND ISOTOPIC SIGNATURES OF THE HIBONITE-RICH FUN INCLUSION "HIDALGO" IN DAR AL GANI 027 (CO3).

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Introduction: Refractory Ca-Al-rich Inclusions (CAIs) with FUN (Fractionation with Unidentified Nuclear effects) characteristics are peculiar samples among all high-temperature components in chondritic meteorites. They are generally characterized by strong mass-dependent isotopic fractionations in several elements (e.g., O, Mg, Ca, Ti), large (~5-20‰) enrichments or depletions in neutron-rich isotopes (e.g., ^{48}Ca, ^{50}Ti, ^{54}Cr), and low inferred abundances of ^{26}Al (^{26}Al/^{27}Al < 1×10^{-5}) [1]. Understanding the origins of these features in FUN CAIs can shed light on the astrophysical environment and chemical processes that took place in the early Solar System. A large fraction (slightly less than 50%) of the ~20 FUN CAIs discovered so far are hibonite-rich (such as HAL, SHAL and DH-H1, collectively called HAL-type inclusions hereafter). According to their elemental and isotopic signatures and the results of evaporation experiments, HAL-type inclusions are thought to have formed as a distillation residue [2,3]. However, questions regarding the timing of the formation of HAL-type inclusions (or FUN inclusions in general) relative to those of regular CAIs and the decoupling between the ^{26}Al abundances and nucleosynthetic anomalies remain poorly understood. In 2021, we reported the discovery of a new HAL-type inclusion, HIDALGO (**Hi**bonite in **D**ar **al** **G**ani C**O**3) in the CO3 chondrite Dar al Gani 027 (DaG027), based on its (fractionated) oxygen isotopic compositions and low inferred ^{26}Al/^{27}Al ratio of $(1.50\pm0.02)\times10^{-5}$ [4]. Since then, more work on other short-lived and stable isotope systems and trace element abundances has been conducted. Here we report these new results and discuss the implications for the possible formation history of HIDALGO and origins of short-lived radionuclides (SLRs).

Experimental: HIDALGO is a ~300×300 μm, nearly stoichiometrically pure, single hibonite crystal, containing homogeneous CaO = 8.5% and Al_2O_3 = 91% along with trace amounts of TiO_2 = 0.2% and FeO = 0.3%. No MgO could be detected by EPMA. Measurements of HIDALGO for the SLR systems ^{10}Be-^{10}B ($t_{1/2}$ = 1.3 Myr) and ^{41}Ca-^{41}K ($t_{1/2}$ = 0.1 Myr), stable Ca-Ti isotopes, and rare earth element (REE) abundances were carried out by using the CAMECA ims-1290 ion microprobe at UCLA.

Results: Similar to oxygen, the Ca and Ti isotopic compositions in HIDALGO are also mass-dependently fractionated by 13‰/amu and 14‰/amu, respectively. HIDALGO is also characterized by large anomalies in ^{48}Ca and ^{50}Ti, with δ^{48}Ca = −31‰ (^{44}Ca/^{40}Ca-normalized) and δ^{50}Ti = −21‰ (^{46}Ti/^{48}Ti-normalized) (Fig. 1; also shown are literature Ca-Ti data for other HAL-type inclusions). Such isotopic signatures confirm the inference that HIDALGO belongs to the FUN inclusion family.

Large radiogenic ^{10}B excesses are found to correlate well with ^{9}Be/^{11}B in HIDALGO, suggesting in-situ decay of live ^{10}Be. The slope of the isochron corresponds to initial ^{10}Be/^{9}Be = $(7.96\pm0.93)\times10^{-4}$ with an intercept of ^{10}B/^{11}B = 0.2508 (χ_r^2=0.94; Fig. 2). This ratio is ~2−3 times higher than what was recorded in other FUN inclusions but comparable to that normally found in CAIs from CV3/CO3 chondrites [5]. In contrast, no resolved radiogenic ^{41}K excesses were found, even for ^{40}Ca/^{39}K ratios exceeding 3×10^{6} (Fig. 3), indicating an absence of short-lived ^{41}Ca during the final formation of HIDALGO.

The REE abundances of HIDALGO are characterized by a pronounced Ce depletion (0.01×CI) in otherwise relatively uniform REE concentrations (~10×CI). This pattern resembles those in other HAL-type inclusions [2,3].

Discussion: According to the nearly pure hibonite stoichiometry and fractionated oxygen isotopes, we inferred that HIDALGO was likely of a distillation origin [2−4]. The new Ca and Ti isotope data provide further support for this explanation. The Ca and Ti mass fractionations, which are large and of almost equal magnitude, are comparable to the fractionation results derived from evaporation of chondritic starting material [3]. This suggests that HIDALGO could have formed from a precursor of chondritic composition that lost a large amount of major elements during distillation. This is consistent with the extremely low Mg abundance in HIDALGO, as this element may have been essentially completely lost. The large Ce depletion suggests that the distillation process HIDALGO experienced took place in a highly oxidizing condition.

The new data also help constrain the chronology of HIDALGO (or its precursor) formation and the origins and distributions of ^{10}Be, ^{26}Al, and ^{41}Ca in the solar nebula. The low ^{26}Al/^{27}Al ratio of $(1.50\pm0.02)\times10^{-5}$, if understood in the context of the radioactive decay of homogeneously distributed ^{26}Al in the solar nebula, would mean that the final crystallization of HIDALGO occurred ~1.3 Myr after the assumed peak formation stage of cm-sized CAIs at $^{26}Al/^{27}Al = 5.2\times10^{-5}$. The 1.3 Myr time would also allow ^{41}Ca to completely decay away (hence no ^{41}K excesses in HIDALGO), even though the true initial abundances and distributions of ^{41}Ca in the solar nebula still remain a subject of further study [6]. However, the major issue has always been the need to preserve the carriers of anomalous $\delta^{48}Ca$ and $\delta^{50}Ti$ in the nebula for >1 Myr.

Alternatively, HIDALGO could have formed when ^{26}Al was being homogenized in the solar nebula. The absence of ^{41}Ca at that time could be explained by invoking the decoupled arrival of ^{26}Al and ^{41}Ca from a massive star: ^{26}Al would have arrived in the forming solar system before ^{41}Ca due to the nature of nucleosynthesis and thus would have been subjected to earlier and more thorough mixing than ^{41}Ca [6]. This scenario could also explain why FUN inclusions carry more variable isotope anomalies in $\delta^{48}Ca$ and $\delta^{50}Ti$ compared to normal CAIs that incorporated uniformly distributed ^{26}Al.

Understanding the meaning of $^{10}Be/^{9}Be = (7.96\pm0.93)\times10^{-4}$ in HIDALGO requires discussions of the origin of ^{10}Be. One favored hypothesis is that ^{10}Be was produced in the early Solar System by charged particle irradiation of dust and/or gas (e.g., [7]), and thus would be too spatially heterogeneous to be an early solar system chronometer. Irradiation can readily produce $^{10}Be/^{9}Be$ at the level comparable to that seen in HIDALGO but in the meantime would co-produce $^{41}Ca/^{40}Ca \geq 5\times10^{-8}$ (the exact amount depends strongly on model details; e.g., [7]). The absence of fossil records of ^{41}Ca implies that the observed $^{10}Be/^{9}Be$ ratio in HIDALGO could not have resulted from irradiation of the inclusion directly, or of the gas reservoir at the time of HIDALGO formation. Rather, irradiation must have occurred to HIDALGO's precursor or to the gas ≥ 0.6 Myr before its final formation (allowing ^{41}Ca to become extinct), suggesting that the $^{10}Be/^{9}Be$ ratio in the HIDALGO-forming region could have been $\geq 1.1\times10^{-3}$. In the case of late formation of HIDALGO, an irradiation origin of ^{10}Be would mean that there existed a reservoir in the solar nebula with $^{10}Be/^{9}Be > 1.1\times10^{-3}$ when $^{26}Al/^{27}Al \geq 2.6\times10^{-5}$ (i.e., ≤ 0.7 Myr after $^{26}Al/^{27}Al = 5.2\times10^{-5}$). In contrast, if the final crystallization of HIDALGO took place early, it would require that irradiation had started 0.6 Myr before ^{26}Al homogeneity was attained. Since spallogenic ^{10}Be would be expected to vary spatially, the lower $^{10}Be/^{9}Be$ in other FUN inclusions would also be explained.

Another possible source for ^{10}Be is the Sun's parental molecular cloud. Inheritance would lead to a homogeneous distribution of ^{10}Be in the solar system and allow it to be used for chronometry (e.g., [5]). If the low $^{26}Al/^{27}Al$ in HIDALGO resulted from late formation, the $^{10}Be/^{9}Be$ ratio in the HIDALGO-forming reservoir when $^{26}Al/^{27}Al = 5.2\times10^{-5}$ should be 1.6×10^{-3}, much higher than the value recorded by >80% of the normal CV3/CO3-chondrite CAIs [5]. This suggests that either HIDALGO's precursor (or forming reservoir) had incorporated extra ^{10}Be through additional irradiation prior to the final formation of HIDALGO (see above), or the ^{10}Be homogeneity is an incorrect assumption. If HIDALGO was an early-formed inclusion, the fact that it and normal CV3/CO3 CAIs have the same $^{10}Be/^{9}Be$ but different $^{26}Al/^{27}Al$ may imply fast mixing of ^{26}Al. However, the $^{10}Be/^{9}Be$ ratios found in other FUN CAIs cannot be understood chronologically and thus require other interpretations.

References: [1] Wasserburg et al. 1977, *GRL*, **4**, 299 [2] Ireland et al. 1992, *GCA*, **56**, 2503 [3] Floss et al. 1996, *GCA*, **60**, 1975 [4] Liu et al. (2021) *Met. Soc. Meeting,* #6084 (abstr.). [5] Dunham et al. 2021, *GCA*, **324**, 194 [6] Liu 2017, *GCA*, **201**, 123 [7] Gounelle et al. 2001 *ApJ*, **548**, 1051

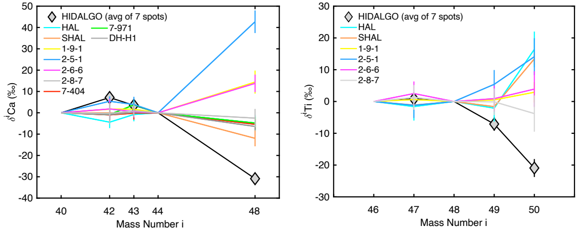

Fig. 1. Ca and Ti isotopic compositions of HIDALGO.

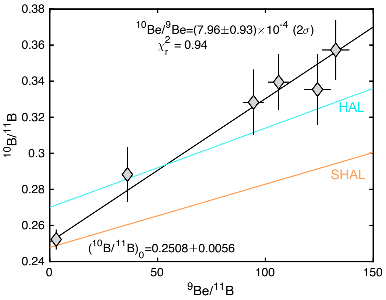

Fig. 2. The ^{10}Be-^{10}B isochron of HIDALGO.

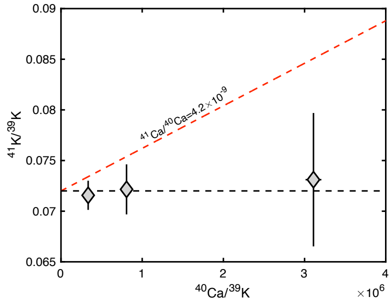

Fig. 3. The K isotopic compositions of HIDALGO. $^{41}Ca/^{40}Ca = 4.2\times10^{-9}$ [6] is shown for reference.