

**SUPRA-CHONDRITIC  ${}^7\text{Li}/{}^6\text{Li}$  IN THE HIBONITE-RICH FUN INCLUSION “HIDALGO” IN DAR AL GANI 027 (CO3): A HINT FOR THE FORMER PRESENCE OF BERYLLIUM-7?** M.-C. Liu<sup>1</sup>, N. Matsuda<sup>2</sup>, E. T. Dunham<sup>1</sup>, K. D. McKeegan<sup>2</sup> and K. A. McCain<sup>3</sup> <sup>1</sup>Nuclear and Chemical Sciences Division, Lawrence Livermore National Laboratory (liu88@llnl.gov), <sup>2</sup>Department of Earth, Planetary, and Space Sciences, UCLA, <sup>3</sup>Jacobs JETSII contract, NASA Johnson Space Center

**Introduction:** HIDALGO, a  $\sim 300 \times 300$   $\mu\text{m}$ , hexagonally shaped, chemically and mineralogically simple hibonite crystal residing in the matrix of the CO3 chondrite Dar al Gani 027 (DaG027), is the newest member in the FUN-hibonite family [1]. Based on the mass-dependent fractionations in O, Ca, and Ti isotopes, large negative anomalies in  $\delta^{48}\text{Ca}$  ( $= -30\%$ ) and  $\delta^{50}\text{Ti}$  ( $= -20\%$ ), and the abundances of short-lived radioisotopes of  ${}^{10}\text{Be}$ ,  ${}^{26}\text{Al}$ ,  ${}^{41}\text{Ca}$ , which have all been reported previously [1–2], we have inferred that HIDALGO evolved from a condensate that most likely formed *before*  ${}^{26}\text{Al}$  was built up and homogenized to  ${}^{26}\text{Al}/{}^{27}\text{Al} = 5.2 \times 10^{-5}$  in the solar system. This precursor also incorporated  ${}^{10}\text{Be}$  at the level of  ${}^{10}\text{Be}/{}^9\text{Be} = 7.5 \times 10^{-4}$ , possibly through local irradiation of gas and/or dust or inheritance from the molecular cloud, but the amount of  ${}^{41}\text{Ca}$  present at that time and location is uncertain. Strong heating of the precursor occurred  $\sim 0.5$  Myr after the initial condensation, leading to total melting accompanied by extensive distillation (losing Mg, Si, and other moderately volatile elements) resulting in a stoichiometrically pure hibonite crystal with strongly mass fractionated O, Ca, and Ti isotope compositions and an extreme Ce depletion relative to other REEs. Here we report the results of Li isotope analyses of HIDALGO and discuss the irradiation history of this inclusion.

**Experimental:** Lithium-beryllium measurements of HIDALGO were conducted with the UCLA ims-1290 ion microprobe by using a new analytical method reported in [3]. The in-situ production of Li and Be in HIDALGO by Galactic Cosmic Rays (GCR) irradiation of the DaG027 parent body was evaluated and corrected for by following the methods described in [4,5] with an assumed cosmic-ray exposure (CRE) age of 6.5 Myr, which corresponds to the average CRE age of CO3 chondrites in the DaG collection [6].

**Results:** The GCR-corrected  ${}^7\text{Li}/{}^6\text{Li}$  ratios measured in four spots of HIDALGO range between 20 and 49, all of which are much higher than the chondritic  ${}^7\text{Li}/{}^6\text{Li}$  value ( $= 12.02$ ; [7]). Without the GCR correction, all  ${}^7\text{Li}/{}^6\text{Li}$  ratios cluster around  $\sim 8$ , independent of Be/Li, but accounting for GCR spallation reveals a correlation of  ${}^7\text{Li}/{}^6\text{Li}$  and the  ${}^9\text{Be}/{}^6\text{Li}$  ratios. Error-weighted least-squares regression through the GCR-corrected data points yields a slope and intercept of  $(2.5 \pm 0.6) \times 10^{-4}$  and  $(-9.7 \pm 9.9)$  ( $2\sigma$ ), respectively, with a reduced  $\chi^2$  value of 7.1 (Figure

1a). Although this positive slope can be interpreted as reflecting in situ  ${}^7\text{Be}$  decay ( $t_{1/2} = 53$  days) with an abundance of  ${}^7\text{Be}/{}^9\text{Be} = 2.5 \times 10^{-4}$  at the time of Li isotopic closure in HIDALGO, whether this is a valid interpretation requires further examination given the poor goodness-of-fit. Interestingly, the  ${}^7\text{Li}/{}^6\text{Li}$  data negatively correlate with the concentrations of Li (Figure 1b).

**Discussion:** The highly supra-chondritic  ${}^7\text{Li}/{}^6\text{Li}$  ratios in HIDALGO, to our knowledge, have never been found in any other meteoritic refractory inclusion. Since  ${}^7\text{Li}/{}^6\text{Li}$  inversely correlates with elemental [Li], it may be understood in the context of isotope fractionation associated with evaporation/distillation or the addition of spallogenic Li (by direct irradiation) into a solid characterized by extremely isotopically fractionated Li (low [Li] and high  ${}^7\text{Li}/{}^6\text{Li}$ , such as that in a distillation residue). Alternatively, the positive correlation between  ${}^7\text{Li}/{}^6\text{Li}$  and  ${}^9\text{Be}/{}^6\text{Li}$ , despite some apparent scatter, could originate from the in-situ decay of  ${}^7\text{Be}$ , with the initial abundance of  ${}^7\text{Be}/{}^9\text{Be} = (2.5 \pm 0.6) \times 10^{-4}$ . Below, we first demonstrate that the observed  ${}^7\text{Li}/{}^6\text{Li}$  ratios in HIDALGO are inconsistent with an evaporation origin, and then consider arguments for the in-situ decay of  ${}^7\text{Be}$  in HIDALGO.

In the context of distillation, the changes of  ${}^7\text{Li}/{}^6\text{Li}$  in a Rayleigh process can be calculated by

$$\left(\frac{{}^7\text{Li}}{{}^6\text{Li}}\right)_r = \left(\frac{{}^7\text{Li}}{{}^6\text{Li}}\right)_{ini} \times f^{(\alpha-1)}$$

$({}^7\text{Li}/{}^6\text{Li})_r$  is the ratio in the evaporation residue, and  $({}^7\text{Li}/{}^6\text{Li})_{ini}$  is the initial ratio, which is assumed to be the chondritic value. “ $f$ ” is the fraction of Li remaining in the residue; an initial [Li] = 1.46 ppm, which is the average concentration in CI chondrites [8], is used in the calculation. For the isotope fractionation factor, “ $\alpha$ ”, we adopt a value of 0.9258 ( $= \sqrt{(6/7)}$ ) as would apply to a kinetic fractionation of elemental Li during evaporation. The calculation result is plotted in Figure 2. As can be seen,  ${}^7\text{Li}/{}^6\text{Li}$  increases with decreasing Li abundances but only to about 26–28 for a residue that has [Li] comparable to that in HIDALGO (gray band), which falls far short of most values measured for this inclusion. In addition, Li is much more mobile and prone to isotope disturbance than Mg and Si; given the fact that the latter two elements were near-completely lost from the precursor material, it would be impossible for any original Li to survive a distillation

event, let alone be modified by any subsequent irradiation. This means any Li measured in HIDALGO could not have been inherited from the progenitor; rather it must have originated from post-formation processes.

One mechanism to acquire additional Li after formation is direct spallation of the inclusion by energetic charged particles, mainly protons. Spallation also co-produces  $^7\text{Be}$  and  $^{10}\text{Be}$ , as oxygen is the common target. Therefore, at the end of irradiation, the irradiated HIDALGO should have a small amount of purely spallogenic Li with an isotopic ratio of  $\sim 0.9 \pm 0.1$  [9] and live  $^7\text{Be}$  and  $^{10}\text{Be}$ . Using the model developed in [10], we calculated the Li abundance,  $^7\text{Be}/^9\text{Be}$ , and  $^{10}\text{Be}/^9\text{Be}$  produced simultaneously in a hibonite target with [Be] comparable to that of HIDALGO ( $\sim 200$  ppb). Assuming that the  $^7\text{Li}/^6\text{Li}$ - $^9\text{Be}/^6\text{Li}$  correlation originates from the decay of  $^7\text{Be}$ , we set the fluence of charged particles to produce  $^7\text{Be}/^9\text{Be} = 2 \times 10^{-4}$  because: (1) the final Li abundance includes both spallogenic ( $^7\text{Li}$  and  $^6\text{Li}$ ) and radiogenic ( $^7\text{Li}$  from the decay of  $^7\text{Be}$ ) components, and (2) the very short half-life of  $^7\text{Be}$  places a stringent constraint on the irradiation time, which in turn sets a lower limit to the flux of the charged particles. We found that the range of the required fluence would be  $(3.5\text{--}6.5) \times 10^{16} \text{ cm}^{-2}$  if  $^7\text{Be}/^9\text{Be} = 2 \times 10^{-4}$  is attained before it becomes saturated (i.e., the irradiation time is less than 1 year). The corresponding [Li] yielded within this fluence range is of order 0.037 ppb, which is remarkably consistent with the average GCR-corrected Li abundance in HIDALGO and suggests that both the observed [Li] and  $^7\text{Be}/^9\text{Be}$  in HIDALGO can be accounted for by proton irradiation of the inclusion. Moreover, the intercept of the correlation line ( $^7\text{Li}/^6\text{Li} = -9.7 \pm 9.9$ ), which represents the initial (pre-decay)  $^7\text{Li}/^6\text{Li}$  ratio of the inclusion, is marginally consistent with a very low value, such as that produced by direct irradiation. The compatibility of the calculation results with the data supports the interpretation that  $^7\text{Li}$  excesses were derived from the in-situ decay of  $^7\text{Be}$ , even though possible isotopic disturbance, which is indicated by the data scattering beyond analytical uncertainties along the correlation line, makes it difficult to ascertain the exact level of  $^7\text{Be}/^9\text{Be}$  in HIDALGO. It is worth noting that our hypothesized  $^7\text{Be}$ -making irradiation event would have only produced  $^{10}\text{Be}/^9\text{Be} \sim 5 \times 10^{-6}$ , which is negligible compared to the inferred initial  $^{10}\text{Be}$  abundance for HIDALGO.

If we accept the argument that there was once live  $^7\text{Be}$  produced by irradiation in HIDALGO, it is clear that the locale would have to be in the solar nebula as collapse times from a molecular cloud fragment to an

accretion disk are too long for the very rapid decay of  $^7\text{Be}$ . An interesting question that then arises is where in the disk this process could have taken place. From the fluence and irradiation time constrained above, a proton flux of  $\sim 1 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$  can be derived. This flux is of similar magnitude to those in the model calculations of Gounelle et al [11] and suggests that HIDALGO be irradiated at a heliocentric distance of  $\sim 0.02 \text{ AU}$ . Given the highly refractory nature of HIDALGO and the possible formation history, it is also conceivable that its precursor material (of chondritic composition in major elements) was subjected to distillation processing at this location.

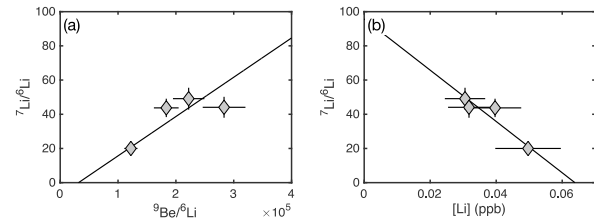


Figure 1. (a)  $^7\text{Li}/^6\text{Li}$ - $^9\text{Be}/^6\text{Li}$  correlation; (b) Negative correlation between  $^7\text{Li}/^6\text{Li}$  and [Li]

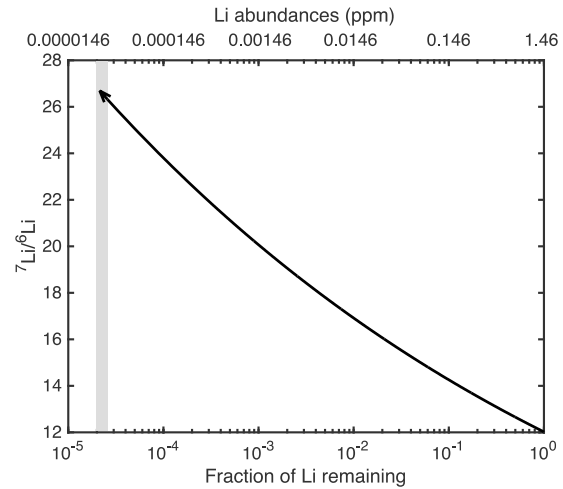


Figure 2. Lithium isotope evolution in a Rayleigh distillation process.

**References:** [1] Liu M.-C et al. (2021) *Meteoritics & Planet. Sci.*, 84, A6084. [2] Liu M.-C et al. (2023) *LPS LIV*, Abstract #1067. [3] Liu M.-C et al. (2023) *GCA* 341, 150–163. [4] Chaussidon M. et al. (2023) *GCA* 70, 224–245. [5] Desch S. J. and Ouellette N. (2006) *GCA* 70, 5426–5432. [6] Scherer P. and Schultz L. (2000), *Meteoritics & Planet. Sci* 35, 145–153 [7] Seitz H.-M. et al. (2007) *EPSL* 260, 582–596. [8] Wood B. J. et al. (2019) *Am. Mineral.* 104, 844–856. [9] Read S. M. and Viola V. E. Jr. (1984) *Atom. Data Nucl. Data Tables* 31 359–397. [10] Liu M.-C. and McKeegan K. D. (2009) *ApJ* 697, L145–L148. [11] Gounelle et al. (2001) *ApJ* 548, 1051–1070.