Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 196 (2017) 18–35

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

# Corundum–hibonite inclusions and the environments of high temperature processing in the early Solar System

Andrew W. Needham [a,b,*], Scott Messenger [a], Jangmi Han [b], Lindsay P. Keller [a]

[a] Robert M. Walker Laboratory for Space Science, ARES, EISD Directorate, NASA JSC, 2101 NASA Parkway, Houston, TX 77058, USA
[b] Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, TX 77058, USA

Received 27 February 2015; accepted in revised form 11 April 2016; available online 2 May 2016

---

## Abstract

Corundum-bearing Ca–Al-rich inclusions (CAIs) are a rare class of high-temperature condensates from the inner regions of the protoplanetary disk. Their mineralogy is intermediate between isolated corundum grains and CAIs where corundum has been replaced by lower-temperature phases. These inclusions sample a critical transitional period of the inner nebula where both the Sun and protoplanetary disk were rapidly evolving. We conducted O isotopic, Al–Mg chronological, petrographic, and crystallographic studies of four corundum-bearing inclusions in the Murchison CM2 and ALHA 77307 CO3.0 carbonaceous chondrites. Within each inclusion, corundum, hibonite, and spinel have indistinguishable $^{16}$O-rich compositions. The O isotopic compositions from all inclusions fall within a narrow range of $\Delta^{17}O = -22.8 \pm 3.6‰$ that matches values of most previously studied micrometer-sized corundum grains and mineralogically pristine CAIs. These data indicate that, with few exceptions, the most refractory inclusions in carbonaceous chondrites formed from the same O isotopic reservoir. One CAI from ALHA 77307, ALH-61, exhibits a continuous corundum mantle overlying a hibonite core, opposite the equilibrium condensation sequence at typical nebular pressures and dust/gas ratios. Transmission electron microscopy examination of the hibonite–corundum interface suggests that the corundum condensed on the hibonite and was itself then partially overlain with spinel. Additionally, high dust/gas ratios are interpreted from the W- and Mo-depleted composition of a refractory metal nugget within a second corundum-bearing CAI, ALH-160. Together, these observations show that the primary formation conditions of some corundum-bearing CAIs involved non-equilibrium condensation in environments with elevated dust-gas ratios.

The corundum-bearing CAIs studied here have inferred initial $^{26}Al/^{27}Al$ ratios that fall within the roughly bimodal distribution of values observed in most CAIs. ALH-160 retains no resolvable excess $^{26}$Mg while ALH-61 has a well-resolved initial $^{26}Al/^{27}Al$ ratio of $4.2 \pm 0.4 \times 10^{-5}$. The presence or absence of live $^{26}$Al at the time of CAI formation may record distinct chronology if $^{26}$Al was initially homogeneously distributed in the early Solar System. Alternatively, variations in $^{26}Al/^{27}Al$ ratios may reflect late injection and/or heterogeneous distribution of $^{26}$Al. Regardless of which model for $^{26}$Al distribution is correct, the data presented here indicate that formation of corundum-bearing CAIs was repeated during multiple heating and non-equilibrium condensation events throughout early Solar System history and within a single oxygen isotopic reservoir.

*Keywords:* Corundum; Hibonite; CAI; Chondrite; Oxygen isotopes; 26Al; Magnesium isotopes; Solar nebula; Condensation

---

## 1. INTRODUCTION

Calcium–aluminum-rich inclusions (CAIs) in primitive meteorites and comets are samples from the earliest epoch of planet formation. They record evidence of large-scale

---

* Corresponding author at: Geophysical Laboratory, Carnegie Institution for Science, 5251 Broad Branch Rd. NW, Washington, DC 20015-1305, USA.
*E-mail address:* aneedham@carnegiescience.edu (A.W. Needham).

http://dx.doi.org/10.1016/j.gca.2016.04.022
0016-7037/

mass-transport and energetic processes in the protoplanetary disk as well as the early activity of the Sun. As the oldest known Solar System materials, their ages (4567.30 ± 0.16 Ma; Connelly et al. (2012)) are often taken to represent the age of the Solar System. CAIs are composed of a suite of Ca–Al-rich minerals that are the predicted first condensates from a cooling gas of solar composition (Anders, 1968; Grossman, 1972). Moreover, CAIs are highly enriched in refractory elements and some exhibit mineral textures and rare earth element and trace element abundance patterns that are indicative of condensation processes. The implication is that some CAIs are direct samples of the first generation of solids that condensed in the solar nebula.

The O isotopic signatures of CAIs give important clues to their origins. CAIs are among the few planetary materials that have O isotopic compositions similar to the composition of the Sun (Clayton et al., 1977; McKeegan et al., 2011). Most planetary materials are depleted in $^{16}$O relative to the Sun by ~50‰. This has been the subject of intense interest for decades, but a resolution has been elusive. Recent models invoke photochemical self-shielding, either in the protoplanetary disk or in the preceding molecular cloud as an origin for the $^{16}$O-poor component (Clayton, 2002; Yurimoto and Kuramoto, 2004; Lyons and Young, 2005). The evolution of the nebular O isotopic composition is still a matter of debate but it appears that isotopically distinct regions of the nebula coexisted for a period of time (Simon et al., 2011).

Short-lived nuclide studies provide constraints on the ages and histories of CAIs and thereby the evolution of the protoplanetary disk. The Al–Mg system has been widely applied to CAIs owing to their Al-rich compositions (Bizzarro et al., 2004; Ito et al., 2006; Thrane et al., 2006). Most CAIs show evidence for the prior presence of $^{26}$Al ($t_{1/2} \sim 0.72$ Ma) (Lee et al., 1976) with initial $^{26}$Al/$^{27}$Al ratios of $\sim 5 \times 10^{-5}$ representing the 'canonical' initial ($^{26}$Al/$^{27}$Al)$_0$ for the Solar System. Some CAIs have much lower values (MacPherson et al., 1995; Makide et al., 2011; MacPherson, 2014) and there are reports of CAIs with 'supra-canonical' values up to $7 \times 10^{-5}$ (Cosarinsky et al., 2007; Young et al., 2005). Whether $^{26}$Al was uniformly distributed in the early Solar System determines whether the Al/Mg system provides meaningful chronological information, with evidence of homogeneity and heterogeneity being reported previously (Thrane et al., 2006; Larsen et al., 2011; Holst et al., 2013). Makide et al. (2011) argued that the bimodal distribution of $^{26}$Al/$^{27}$Al values of corundum grains reflects heterogeneity in $^{26}$Al early in Solar System history.

Amongst CAI minerals, corundum is the first phase predicted to form by equilibrium condensation from a cooling gas of solar composition, at ~1571–1770 K at expected nebular pressures ($10^{-6}$–$10^{-3}$ atm) (Grossman, 1972; Ebel and Grossman, 2000). Most corundum condensates are predicted to have reacted with nebular gas to form hibonite, followed at lower temperatures by grossite, perovskite, melilite, and spinel. Corundum-bearing CAIs are rare and typically also contain hibonite, ±spinel, ±perovskite, lacking lower T phases (Bar-Matthews et al., 1982; MacPherson et al., 1984; Krot et al., 2001; Simon et al., 2002; Bland et al., 2007; Liu et al., 2009; Russell and Kearsley, 2011; Makide et al., 2013). Isolated μm-sized corundum grains in meteorite matrix are more common. Such inclusions appear to represent incomplete condensation sequences and thus may be preserved nebular condensates (Bar-Matthews et al., 1982). However, corundum may also form from hibonite as an evaporative residue (MacPherson et al., 1984) so petrological constraints are required to distinguish between these origins.

Approximately 20 corundum-bearing CAIs and corundum–hibonite assemblages have been reported previously, with half of these reports containing both O and Mg isotope and petrographic data (Fahey et al., 1987; Fahey, 1988; Simon et al., 2002; Ushikubo et al., 2007; Liu et al., 2009; Makide et al., 2013). Corundum, hibonite, and spinel in these inclusions mostly show a narrow range of $\Delta^{17}$O (see Methods for definition) values near −23‰, with rarer examples ranging from $\Delta^{17}\text{O} = -12.6‰$ to −31.2‰ (Makide et al., 2009) and some preserving evidence for mass-dependent fractionation (Ushikubo et al., 2007; Liu et al., 2009). Corundum-bearing CAIs and individual corundum grains show a bimodal distribution of initial $^{26}$Al/$^{27}$Al ratios, where approximately half exhibit initial $^{26}$Al/$^{27}$Al ratios of 3–5 × $10^{-5}$, and the remainder show no resolvable $^{26}$Mg excess. Thus far, no systematic relationship between O and Al–Mg systematics has been established for corundum-bearing CAIs. It is not known whether this is due to O and/or $^{26}$Al heterogeneity in the protoplanetary disk or differences in post-formational O isotopic exchange and Al–Mg resetting events among the corundum-bearing CAIs.

In this study we present coordinated *in situ* mineralogical, O and Al–Mg isotopic measurements, and crystallographic studies of corundum-bearing CAIs. Together, these observations support the identification of preserved nebular condensates and clarify the origins of these rare objects.

## 2. METHODS AND SAMPLES

Corundum-bearing CAIs were searched for in five thin sections of the CM2 chondrite Murchison (~646 mm$^2$ total area) and one thin section of the CO3.0 chondrite ALHA 77307 (73 mm$^2$) using two field emission scanning electron microscopes (SEMs) at NASA JSC. Energy dispersive X-ray maps were obtained with a JEOL7600F SEM and cathodoluminescence (CL) images of these thin sections were obtained with a Zeiss Supra 55VP field emission SEM. Candidate corundum grains were identified as Al-rich and Si-poor regions in EDX maps or as bright regions in CL maps, where corundum usually gives the strongest signal. While it is possible to make preliminary mineral identifications by EDX mapping, this method is slow. On the other hand, while corundum cannot be definitively identified in CL maps, candidates were much more quickly identified and confirmed by follow-up SEM examination. Twenty-four candidate corundum grains identified in EDX and CL maps were examined by electron microprobe. Four of these were identified as corundum-bearing CAIs and were selected for isotopic analyses, while the remainder were determined to be hibonite grains lacking corundum.