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Condensate refractory inclusions from the CO3.00 chondrite Dominion Range 08006: Petrography, mineral chemistry, and isotopic compositions

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Abstract

We have found two refractory inclusions in the CO3.00 carbonaceous chondrite Dominion Range (DOM) 08006 that appear to be primary condensates from the early solar nebula. One, inclusion 56–1, contains the first four phases predicted to form by equilibrium gas-solid condensation: corundum; hibonite; grossite; and perovskite. The other, 31–2, contains nine predicted condensate phases: hibonite; grossite; perovskite; melilite; spinel; FeNi metal; diopside; forsterite; and enstatite. Except for melilite/spinel, the phases occur in the predicted sequence from core to rim of the inclusion, which has an irregular shape inconsistent with a molten stage. This inclusion preserves the most complete record of condensation in the early solar nebula that has yet been found. The physical evidence reported here supports equilibrium condensation calculations that predict the observed sequence as well as the assumptions upon which they are based, such as total pressure ($\sim 10^{-3}$ atm), bulk system composition (solar), and C—O—H proportions. All phases in both inclusions and the associated ferromagnesian silicates are ^{16}O -rich, with ^{17}O between -25 and -20% , implying that this is the original composition of the vast majority of primary condensates and that ^{16}O -poor compositions observed in many isotopically heterogeneous inclusions are largely due to subsequent isotopic exchange. While the nebula was well-mixed with respect to oxygen isotopic composition, clearly resolved anomalies in Ca and Ti isotopic compositions indicate that some isotopic heterogeneity existed early and was preserved during condensation. Inclusion 31–2 did not incorporate live ^{26}Al and has nucleosynthetic anomalies in

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APPENDIX A. SUPPLEMENTARY MATERIAL

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the heavy Ca and Ti isotopes (i.e., $\delta^{48}\text{Ca} = 4.3 \pm 1.9\%$; $\delta^{50}\text{Ti} = 8.8 \pm 2.0\%$). In contrast, inclusion 56–1 has radiogenic ^{26}Mg excesses yielding a $(^{26}\text{Al}/^{27}\text{Al})_0$ ratio of $(1.0 \pm 0.1) \times 10^{-5}$ and negative nucleosynthetic isotopic anomalies in Ca ($\delta^{48}\text{Ca} = -10.3 \pm 4.2\%$) and Ti ($\delta^{50}\text{Ti} = -4.3 \pm 2.9\%$). Thus, it represents a deviation from the mutual exclusivity relationship between ^{26}Al incorporation and large nucleosynthetic anomalies. The reservoirs in which these inclusions formed had similar O-isotopic and different Al-, Ca- and Ti-isotopic compositions, suggesting that while the CAI-forming region was well-mixed with respect to oxygen isotopic composition, clearly resolved anomalies in Ca and Ti isotopic compositions indicate that some isotopic heterogeneity existed and was preserved during condensation.

Keywords

Refractory inclusions; Corundum; Hibonite; Grossite

1. INTRODUCTION

One of the best ways to learn about the early Solar System is to study samples that formed in it. It is possible to predict what minerals should form by equilibrium condensation in a cooling gas of solar composition through thermodynamic calculations (e.g., Grossman, 1972, 2010) and to find discrete assemblages containing subsets of those phases in chondritic meteorites. After the platinum-group elements and Zr-, Sc-oxides, the most refractory minerals predicted by calculations to condense are Ca-, Al-rich oxides, and they are found in assemblages known as Ca-, Al-rich inclusions, or CAIs. Many CAIs have lost their primary condensation features because they were melted (and are now more compact and spherical), and many were altered at relatively low temperature in the nebula and/or on their parent bodies. The best recorders of high-temperature gas-solid reactions in the early Solar System are condensate refractory inclusions occurring in the least-altered, least-metamorphosed carbonaceous chondrites i.e., those of petrologic type 3.00. Such inclusions are very rare, but we have found two in a thin section of the CO3.00 chondrite Dominion Range (DOM) 08006.

The first two phases predicted by calculations (Yoneda and Grossman, 1995; Ebel and Grossman, 2000; Grossman, 2010) to condense from a gas of solar composition are corundum (Al_2O_3) and hibonite ($\text{CaAl}_{12}\text{O}_{19}$). Both of the present inclusions contain hibonite and one contains corundum. Hibonite-bearing inclusions are not extremely rare among CAI populations in certain meteorites, such as the CMs, but only ~20 corundum-bearing CAIs have been reported (e.g., Bar-Matthews et al., 1982; MacPherson et al., 1984a; Fahey, 1988; Krot et al., 2001; Simon et al., 2002; Makide et al., 2013; Needham et al., 2017; Kööp et al., 2018a). What is special about the present inclusions is that in addition to hibonite $\pm$ corundum, they contain grossite, melilite, and other phases predicted to form by equilibrium condensation from a cooling gas of solar composition, with textures and inferred crystallization sequences consistent with formation by condensation, and they occur in a type 3.00 chondrite. They represent some of the most complete records of the solar nebular equilibrium condensation sequence yet found.

Here we report the results of a multidisciplinary study, including electron petrography; major and minor element mineral chemistry; and ion probe analyses of stable and Al-Mg isotope systematics. These inclusions not only preserve valuable records of physicochemical conditions in, and isotopic properties of, the early Solar System; they provide strong evidence that equilibrium condensation calculations for a system of solar composition at a total pressure of 10^{-3} atm (e.g., Grossman, 2010) are appropriate for modeling the formation of refractory inclusions, including the precursor assemblages of ones that melted. Preliminary results were reported by Simon (2016), Simon et al. (2017), Krot et al. (2017) and K00F6öp et al. (2017).

2. ANALYTICAL METHODS

A thin section of DOM 08006 was searched with a TES-CAN LYRA3 scanning electron microscope, equipped with two Oxford Instruments X-Max-80 silicon drift detectors for energy-dispersive X-ray analysis at The University of Chicago. Inclusions were found by collection of paired backscattered electron images and Al X-ray maps. Quantitative wavelength-dispersive analyses were obtained with a Cameca SX-50 electron microprobe at the University of Notre Dame, operated at 15 kV with counting times of 10–30 s for peak and for background measurements for each analysis. Pure oxide, synthetic glass, and natural mineral standards were used. Electron probe data were reduced via the modified ZAF correction procedure PAP (Pouchou and Pichoir, 1984).

Oxygen and Al-Mg isotope systematics were investigated with a Cameca ims-1280 ion microprobe at the University of Hawai'i (UH) using the methods described in detail by Nagashima et al. (2015) and Park et al. (2017). Briefly, for oxygen, a primary Cs⁺ ion beam focused to ~1–2 μm with ~25 pA was used. Three oxygen isotopes were measured simultaneously: $^{16}\text{O}^-$ was measured on a Faraday cup (FC) and $^{17}\text{O}^-$ and $^{18}\text{O}^-$ were measured on electron multipliers. Instrumental fractionation was corrected using terrestrial standards including San Carlos olivine, augite (NMNH 164905) and Madagascar hibonite (NMNH R11608) (Thomen et al., 2016). Compositions are reported as deviations from the composition of Standard Mean Ocean Water (SMOW) in parts per thousand (‰) and as ^{17}O , deviation from the terrestrial fractionation line (e.g., Yurimoto et al., 2008; Komatsu et al., 2018), where $^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$.

For Al and Mg, the measurements were done using a focused ~5 μm primary $^{16}\text{O}^-$ ion beam with a current of ~75 pA for melilite, hibonite and grossite. $^{24}\text{Mg}^+$, $^{25}\text{Mg}^+$, and $^{26}\text{Mg}^+$ were measured sequentially using a monocollector electron multiplier. $^{27}\text{Al}^+$ was measured using a multicollection FC simultaneously with $^{25}\text{Mg}^+$. The mass-resolving power was set to ~4200, sufficient to separate interfering hydrides and doubly charged $^{48}\text{Ca}^{++}$. For diopside, a ~3 nA beam focused to ~15 μm was used and all isotopes were collected simultaneously using 4 FCs. The instrumental mass-fractionation effects and relative sensitivities were corrected using synthetic melilite glass, synthetic fassaite glass and synthetic hibonite standards assumed to have terrestrial magnesium-isotope compositions [$^{25}\text{Mg}/^{24}\text{Mg} = 0.12663$, $^{26}\text{Mg}/^{24}\text{Mg} = 0.13932$ (Catanzaro et al., 1966)]. Grossite data were corrected with the hibonite standard. The contribution of radiogenic ^{26}Mg ($\delta^{26}\text{Mg}^*$) was determined using an exponential law with an exponent of 0.5128 (Davis et al., 2015) after instrumental

fractionation correction using standard-sample bracketing (Makide et al. 2009; Park et al., 2017), and $\delta^{26}\text{Mg}^* = [({}^{26}\text{Mg}/{}^{24}\text{Mg})_{\text{FRAC-corr}}^{\text{sample}} / ({}^{26}\text{Mg}/{}^{24}\text{Mg})_{\text{terrestrial}} - 1] \times 1000$.

Calcium and titanium isotopic compositions were determined with the UH Cameca ims-1280 using the same analytical conditions as those of Kööp et al. (2018b). Due to the low Ti contents of melilite and pyroxene, we only analyzed Ca isotopes in these minerals. In such cases, the following isotopes were analyzed in 60 or 120 cycles in monocollection mode: ${}^{40}\text{Ca}^+$, ${}^{42}\text{Ca}^+$, ${}^{43}\text{Ca}^+$, ${}^{87}\text{Sr}^{2+}$, ${}^{44}\text{Ca}^+$, ${}^{46}\text{Ca}^+$, ${}^{48}\text{Ti}^+$, and ${}^{48}\text{Ca}^+$. A correction for ${}^{46}\text{Ti}^+$ interferences on ${}^{46}\text{Ca}^+$ was applied using measured ${}^{48}\text{Ti}^+$ signals, assuming terrestrial isotope abundances.

Similar to Kööp et al. (2016a,b, 2018b), sample-standard bracketing was used to correct for instrumental fractionation. To correct matrix effects, different mineral standards were analyzed (i.e., Madagascar hibonite for hibonite and grossite, and Ti-rich pyroxene and melilite-composition glasses for pyroxene and melilite analyses, respectively; see Kööp et al. (2018b) for details). Any remaining fractionation is assumed to be intrinsic to the sample and was corrected using a Rayleigh law consistent with Zhang et al. (2014). Due to possible matrix effects for pyroxene (pyroxene in 31–2 is less Ti-rich than the standard) and grossite, this assumption may not be accurate for these two minerals. The ${}^{40}\text{Ca}$ – ${}^{44}\text{Ca}$ pair was used for calcium; for titanium, we report data corrected with the ${}^{46}\text{Ti}$ – ${}^{48}\text{Ti}$ as well as the ${}^{49}\text{Ti}$ – ${}^{47}\text{Ti}$ pairs to facilitate comparison with previous studies of anomalous CAIs as well as recent high precision studies. Intrinsic mass-dependent fractionation is expressed as F_{Ti} and F_{Ca} values. F_{Ti} is defined as $-\left[\Delta^{46}\text{Ti}/(\text{mass}_{\text{Ti}}^{48} - \text{mass}_{\text{Ti}}^{46})\right]$ with

$$\Delta^{46}\text{Ti} = [({}^{46}\text{Ti}/{}^{48}\text{Ti})_{\text{samples}} / ({}^{46}\text{Ti}/{}^{48}\text{Ti})_{\text{standard}} - 1] \times 1000 \text{ (analogous for the } {}^{47}\text{Ti} \text{--} {}^{49}\text{Ti}$$

normalization pair and F_{Ca}). All listed uncertainties are 2σ . Nucleosynthetic anomalies are expressed in δ -notation (e.g., for ${}^{48}\text{Ca}$:

$$\delta^{48}\text{Ca} = [({}^{48}\text{Ca}/{}^{44}\text{Ca})_{\text{samples}} / ({}^{48}\text{Ca}/{}^{44}\text{Ca})_{\text{reference}} - 1] \times 1000 \text{ for}$$

$${}^{50}\text{Ti}; \delta^{50}\text{Ti} = [({}^{50}\text{Ti}/{}^{47}\text{Ti})_{\text{samples}} / ({}^{50}\text{Ti}/{}^{47}\text{Ti})_{\text{reference}} - 1] \times 1000 \text{ (using } {}^{46}\text{Ti}/{}^{48}\text{Ti} \text{ for mass}$$

fractionation correction) or $\delta^{50}\text{Ti} = [({}^{50}\text{Ti}/{}^{47}\text{Ti})_{\text{samples}} / ({}^{50}\text{Ti}/{}^{47}\text{Ti})_{\text{reference}} - 1] \times 1000 \text{ (using } {}^{49}\text{Ti}/{}^{47}\text{Ti} \text{ for mass fractionation correction); analogous for other isotopes). All listed uncertainties are } 2\sigma$.

3. RESULTS

3.1. Petrography

Backscattered electron images of the larger of the two inclusions, 31–2, are shown in Fig. 1. The main body of the inclusion, i.e. not including the lath-shaped protuberance, is $230 \times 220 \mu\text{m}$. The inclusion has a small core of hibonite enclosed in a mantle of grossite + perovskite. This zone is enclosed in a 5–10 μm -wide band of melilite. Spinel is anhedral and is present locally between grossite and melilite, as shown in Fig. 1b. The melilite layer occurs inward of a layer of diopside that is 10–15 μm thick. FeNi metal is enclosed in diopside. Outside of the diopside layer is an unstructured region of forsterite and enstatite grains and metal. Void space occurs in the mantle and between hibonite laths in the core.

The smaller inclusion, 56–1, is shown in Fig. 2. It is partially rimmed and irregularly-shaped, and therefore appears to be a fragment. The inclusion is dominated by hibonite and grossite. The hibonite has inclusions of corundum (Fig. 2b). Grossite appears to have been replacing hibonite, as it occurs as extensions of hibonite laths in the locations (G1, G2) indicated in Fig. 2b. As in 31–2, grossite in 56–1 also has fine inclusions of perovskite. Also visible in Fig. 2, a thin, $\sim 2\ \mu\text{m}$ layer of melilite occurs outside of the grossite and between hibonite laths, and outside of that partial layer is a partial layer of diopside.

The distribution of phases is illustrated by false-color X-ray maps (Fig. 3). The map of 31–2 (Fig. 3a) clearly shows the continuous melilite and diopside layers outlining the highly irregular shape; the lathlike habit of grossite, and the Mg-rich accretionary mantle of enstatite and forsterite (red). The map of 56–1 (Fig. 3b) shows the thick hibonite laths, the occurrence of melilite between the laths and in a partial rim, and the thin, partial layer of diopside. The corundum in this inclusion can be clearly seen in the Al X-ray map (Fig. 3c).

3.2. Mineral chemistry

The corundum in 56–1 is near endmember Al_2O_3 , with minor element (Mg, Si, Sc, V, Cr, and Mn) oxides near or below the detection limit of the electron probe and low but measurable CaO (0.32 wt%), TiO_2 (0.21 wt%) and FeO (0.45 wt%) contents. Secondary fluorescence from the surrounding hibonite cannot be ruled out as a possible contributor to the measured abundances, especially for CaO. Hibonite in both samples has a narrow range of compositions (Table 1). Unlike corundum and grossite, in hibonite a common substitution is $\text{Ti}^{4+} + \text{Mg}^{2+}$ substituting for two Al^{3+} cations, so hibonite typically has an atomic Mg/Ti ratio ~ 1 , and this is seen in Table 1 and Fig. 4a. Fairly high Ti and Mg contents are possible in meteoritic hibonite (e.g., Simon et al., 1997), but in both of the present samples hibonite has <1.0 wt% MgO. Contents of FeO in hibonite in 56–1 are higher than those in 31–2. In many minerals, including hibonite, Mg and Fe substitute for each other, so although Mg and Ti are strongly correlated in hibonite (Fig. 4a), for hibonite with measurable FeO contents, the relationship between Mg + Fe vs. Ti cations is of interest. As shown in Fig. 4b, including Fe in the cation plot slightly improves the fit of the 31–2 analyses to the 1:1 line, but this is not the case for the 56–1 hibonite analyses, which move well off the line. This suggests that Fe did not substitute for Mg in the hibonite in 56–1.

Electron probe analyses of grossite in both inclusions are given in Table 2. As in most grossite occurrences, minor element contents are low. Two analyses of grossite in 31–2 have higher TiO_2 contents, and correspondingly lower Al_2O_3 contents, than are typical. These spots also have elevated MgO contents but their atomic Ti/Mg ratios are >1 , indicating that some of the Ti is trivalent, if hibonite-like Ti + Mg-for-Al substitution occurred.

Electron probe analyses of melilite are given in Table 3. Just one analysis ($\text{\AA}k_8$) was obtained for 56–1. Energy-dispersive analyses of other spots indicate $\text{\AA}k_{\text{ermanite}}$ contents <10 mole %. Melilite compositions in 31–2 have a surprisingly wide range, from very gehlenitic ($\text{\AA}k_3$) to fairly $\text{\AA}k_{\text{ermanitic}}$ ($\text{\AA}k_{43}$). Analysis of the narrow layer was challenging, however, and contributions from adjacent phases cannot be ruled out. The most likely contaminant would be grossite, but most analyses do not exhibit the Ca depletions that it would cause.

Pyroxene and olivine are very Mg-rich, with ~1 wt% FeO (Fs_{~1.2}, Fa_{~0.9}). Representative analyses of these phases are given in Table 4. The diopside is not aluminous and does not contain detectable levels of other minor element oxides except for FeO.

3.3. Isotopic analyses: Stable isotopes

3.3.1. Oxygen—Analyses of individual phases in both inclusions were obtained by ion microprobe and the data are presented in Table 5 and illustrated in Fig. 5. Primary, unaltered phases in refractory inclusions are typically ¹⁶O-rich (e.g., Yurimoto et al., 2008 and references therein), and the present samples are no exception, with $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values between -54‰ and -43‰ and a small range in ¹⁷O, from -25 to -20‰ , including the ferromagnesian silicates diopside, low-Ca pyroxene, and olivine. The analyses plot along the carbonaceous chondrite anhydrous mineral (CCAM) line (Fig. 5). Displacements from the CCAM line could be due to instrumental effects, including a lack of matrix-matched standards for corundum, grossite, melilite and enstatite. Corundum, hibonite and grossite have $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values -50‰ and the other phases (plus one grossite analysis) have $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values $> -50\text{‰}$. Such ¹⁶O-rich enstatite is very rare, but it has been found in amoeboid olivine aggregates (Krot et al., 2005), in the matrix of the Kakangari chondrite (Nagashima et al., 2015), and in particles from comet 81P/Wild 2 (Defouilloy et al., 2017). Such ¹⁶O-rich olivine has been found in: amoeboid olivine aggregates (Yurimoto et al., 2008; Komatsu et al., 2018); accretionary rims around CAIs (Krot et al., 2002); forsterite-bearing Type B CAIs (Bullock et al., 2012); 81P/Wild 2 comet samples (e.g., Nakashima et al., 2012), chondrules as relict grains (e.g., Yurimoto and Wasson, 2002; Schrader et al., 2018), and in chondrite matrices (e.g., Kunihiro et al., 2005). The average ¹⁷O for 31–2 is $-22.4 \pm 1.3\text{‰}$ and that for 56–1 is $-24.1 \pm 1.2\text{‰}$, similar to results for several corundum-bearing CAIs from Murchison, Murray, Adelaide and ALHA 77307 (Simon et al., 2002; Makide et al., 2013; Needham et al., 2017). The present results differ from those for inclusions from the nearly pristine CO3.1 chondrite DOM 08004, which were found to have similarly ¹⁶O-rich spinel, hibonite and Al-diopside but ¹⁶O-depleted grossite and melilite (Simon et al., 2017).

3.3.2. Calcium and titanium—Five spot analyses were collected in CAI 31–2: two in hibonite (Ca and Ti), and one each in melilite (Ca only), grossite (Ca and Ti), and diopside (Ca only). The analyses (Table 6 and Fig. 6) show clear anomalies in the most neutron-rich isotopes of calcium and titanium. The weighted averages, weighted by the uncertainties in the individual spot analyses, are $4.2 \pm 1.6\text{‰}$ and $8.8 \pm 2.0\text{‰}$ for $\delta^{48}\text{Ca}$ and $\delta^{50}\text{Ti}$ (in ⁴⁶Ti/⁴⁸Ti normalization), respectively, and are well outside the range observed for CV CAIs (Fig. 6). No variations in $\delta^{48}\text{Ca}$ and $\delta^{50}\text{Ti}$ are resolved for different minerals in this CAI (i.e., there is no nucleosynthetic zonation). One spot analysis was collected in CAI 56–1, in hibonite. It has a clear anomaly in ⁴⁸Ca ($\delta^{48}\text{Ca} = -10.3 \pm 4.2\text{‰}$). A small negative anomaly in ⁵⁰Ti is resolved beyond 2σ in ⁴⁶Ti/⁴⁸Ti normalization, but not in ⁴⁹Ti/⁴⁷Ti normalization (Table 6). For both CAIs, effects in the lighter isotopes of these elements are either unresolved or small.

3.4. Isotopic analyses: Short-lived radionuclides

3.4.1. ^{26}Al - ^{26}Mg systematics—The Mg isotopic compositions of the Al-rich phases in both inclusions were determined by ion probe to see if excesses of ^{26}Mg due to the decay of ^{26}Al ($\delta^{26}\text{Mg}^*$) could be detected. The short-lived nuclide ^{26}Al decays to ^{26}Mg with a half-life of $(7.05 \pm 0.24) \times 10^{-5}$ yr (Norris et al., 1983; Nishiizumi, 2004). Data are reported in Table 7 and illustrated in Fig. 7. None of the analyzed phases (hibonite, grossite, melilite) in 31–2 incorporated measurable live ^{26}Al when they formed. Even grossite, with $^{27}\text{Al}/^{24}\text{Mg} > 1 \times 10^3$, has $\delta^{26}\text{Mg}^*$ within error of 0. The initial $^{26}\text{Al}/^{27}\text{Al}$ ratio [$(^{26}\text{Al}/^{27}\text{Al})_0$] of this sample is $(-2.8 \pm 8.4) \times 10^{-7}$. In contrast, the grossite and hibonite in 56–1 do have $^{27}\text{Al}/^{24}\text{Mg}$ -correlated ^{26}Mg excesses. They yield a well-defined $(^{26}\text{Al}/^{27}\text{Al})_0$ of $(1.0 \pm 0.1) \times 10^{-5}$.

4. DISCUSSION

4.1. Equilibrium condensation: Comparison of models and observations

Although it has long been known that corundum is the first major-element oxide to condense from a gas of solar composition (Grossman, 1972), thermodynamic data for other refractory aluminates have since become available, allowing calculation of a more complete condensation sequence (e.g., Grossman, 2010). As illustrated in Fig. 8, starting with a cooling gas of solar composition at a total pressure of 10^{-3} atm, Grossman (2010) found that corundum begins to form at 1730 K. It reacts with the gas to form hibonite at ~1700 K and by 1650 K, Al is almost completely condensed (i.e., the curve representing the fraction of Al condensed approaches 1.0 in Fig. 8a). As temperature falls, reactions between solids and gas yield a series of Ca-aluminates, starting with hibonite, followed by grossite and krotite (CaAl_2O_4), with increasing Ca/Al ratios. The substitution of Ti and Mg into hibonite is not accounted for in these calculations, so the stability of hibonite in natural systems could be greater than is indicated in Fig. 8. Krotite is very rare, but it has been found as the dominant phase in a rounded, oval inclusion in the CV3 chondrite NWA 1934 (Ma et al., 2011). A corundum-, hibonite-, grossite-, krotite-, spinel-, pyroxene-bearing inclusion, CAI 1344–50, was found in Adelaide (ungrouped chondrite) by Makide et al. (2013). Once melilite begins to form it consumes more Ca relative to Al, and grossite and hibonite are restabilized until spinel forms at ~1470 K. The analogous distribution of Ca is illustrated in Fig. 8b. This diagram shows that hibonite is followed not only by grossite but also by perovskite, and that melilite is followed by diopside in addition to the aluminous pyroxene components. The calculations for Mg and Fe distribution (Fig. 8c) show that FeNi metal, forsterite, and enstatite are also predicted equilibrium condensates.

The predicted condensates that are present in 31–2 are indicated with red stars in Fig. 8. They are, in order of decreasing condensation temperature: hibonite; grossite; perovskite; melilite; spinel; FeNi metal; diopside; forsterite; and enstatite. This is also the order in which they occur from innermost to outermost in 31–2 with the exception of the small amount of spinel that occurs between the melilite layer and grossite (Fig. 1b), and is therefore texturally earlier than melilite. The lathlike shapes of grossite strongly indicate formation from hibonite, as predicted by the calculations (Grossman, 2010), and the highly irregular shape of the inclusion indicates that it was never molten. Other refractory inclusions

typically either stopped reacting with the nebular gas at a high temperature and mainly contain oxides such as hibonite and spinel; continued reacting to lower temperatures at which hibonite and grossite completely reacted with the gas to form silicates; or they consist of condensate assemblages that were melted and recrystallized. These common processes did not occur in the case of 31–2. Except for corundum (and possibly krotite), the condensate phases did not completely react away as they were isolated by later phases. *This inclusion preserves the most complete record of the condensation sequence in the early solar nebula that has yet been found.*

Inclusion 56–1 also has strong textural evidence for the formation of grossite from hibonite, followed by melilite and diopside. Spinel is not present in the plane of the thin section. Equilibrium condensates found in 56–1 are indicated by the blue stars in Fig. 8. It does not contain as many phases as 31–2, but it does contain the first four, and five of the first six, phases predicted to condense.

In contrast with the present samples, there is also very clear evidence of the formation of spinel directly from hibonite in inclusions from the Murchison CM2 chondrite (MacPherson et al., 1984a; Simon et al., 2006) and ALHA 77307 CO3.0 chondrite (Han et al., 2015). MacPherson et al. (1984a) reported a Murchison inclusion with a porous core of hibonite laths and a rind of lath-shaped spinel. At the contact are laths that consist of hibonite on one end and spinel on the other. Simon et al. (2006) reported a Murchison inclusion in which the reaction went to completion, consisting almost entirely of lath-shaped spinel with no hibonite present. Both MacPherson et al. (1984a) and Simon et al. (2006) suggested that formation of melilite from hibonite was kinetically inhibited relative to spinel. In addition, Simon et al. (2006) noted that there are structural similarities between hibonite and spinel, and in an inclusion from Murchison, a close relationship with respect to crystallographic orientation of adjacent hibonite and spinel was observed with a transmission electron microscope (Han et al., 2017). Han et al. (2015) studied two hibonite-spinel inclusions from ALHA 77307 and concluded that they formed by condensation under disequilibrium conditions, possibly due to supercooling of the gas and incomplete condensation of corundum. In both Murchison and ALHA 77307, grossite-bearing inclusions are very rare, possibly because the inclusions they incorporated are not equilibrium condensates. DOM 08006, on the other hand, contains inclusions that formed by equilibrium condensation, and it is relatively rich in grossite-bearing inclusions (Simon, 2016).

4.2. Implications for features of the early Solar System

4.2.1. Our basic assumptions about the physicochemical conditions in the region of the solar nebula where CAIs formed are justified—The physical evidence reported here that supports the validity of the equilibrium condensation calculations of Grossman (2010) implies that the total pressure (10^{-3} atm), bulk system composition (solar), and C—O—H proportions (Allende Prieto et al., 2001, 2002) used in those calculations are fairly accurate. At a P^{tot} just one order of magnitude higher, at 10^{-2} atm, corundum has no stability field and hibonite is the first phase to condense (Yoneda and Grossman, 1995). Lower total pressure, to at least 10^{-6} bar $\pm$ modest ($\sim 100\times$) dust enrichments, cannot be ruled out, because under such conditions the predicted condensation

sequence is the same as at 10^{-3} bar, but with condensation temperatures shifted (Ebel and Grossman, 2000).

With a non-solar bulk composition at 10^{-3} bar, however, a different phase sequence would be predicted. For example, an enrichment in CI-composition dust by a factor of between $12\times$ and $13\times$ would stabilize condensation of a silicate liquid at a total pressure of 10^{-3} atm; at $100\times$ dust enrichment and the same P^{tot} , liquid becomes stable at 2200 K, replacing the aluminates and melilite (Ebel and Grossman, 2000), phases observed in many refractory inclusions.

Note that the present samples preserve equilibrium phase sequences, but not equilibrium assemblages; there were limitations on the reactivity of condensed phases with the gas. In 31–2 and 56–1, high-temperature phases have survived instead of continuing to react to form assemblages that are stable at lower temperatures. Fortunately, this was a common occurrence, otherwise refractory inclusions would be even rarer than they are, but it is unusual for condensation products to be preserved to the extent seen here. The present inclusions formed slowly enough to avoid supercooling and to largely follow the equilibrium sequence, yet they grew quickly enough for the later-formed phases to isolate and preserve earlier ones. This delicate balance may explain why such inclusions are so rare. An extreme example of phase preservation over a wide temperature range was reported by Komatsu et al. (2018), who found an amoeboid olivine aggregate in Renazzo (CR2) that contains nebular condensates that formed at temperatures as high as ~ 1800 K (Zr-, Sc-rich ultrarefractory inclusion) and as low as ~ 1150 K (silica). Calculations indicate that the object cooled at 50 K/h (Komatsu et al., 2018), which is at the upper end of the range inferred for once-molten, Type B coarse-grained CAIs (MacPherson et al., 1984b).

4.2.2. Isotopic homogeneity/heterogeneity of the early solar nebula—Based on their mineralogy and adherence to the equilibrium condensation sequence, 31–2 and 56–1 appear to have formed under similar physicochemical conditions, but their isotopic compositions indicate that they did so at different times and/or locations. They have similar oxygen isotopic compositions, yet different $(^{26}\text{Al}/^{27}\text{Al})_0$ values and different Ca and Ti isotopic compositions. Inclusion 56–1 incorporated live ^{26}Al when it formed, and 31–2 did not. Inclusion 31–2 has positive anomalies in ^{48}Ca and ^{50}Ti , and inclusion 56–1 has negative anomalies in those isotopes. This implies that the CAI-forming region of the early solar nebula was well-mixed in oxygen but not in Ca and Ti, otherwise the observed nucleosynthetic anomalies would not have been preserved.

A large spread of $(^{26}\text{Al}/^{27}\text{Al})_0$ in corundum-bearing CAIs was reported by Makide et al. (2013). Two from Adelaide show no resolvable excess of radiogenic ^{26}Mg : the inferred $(^{26}\text{Al}/^{27}\text{Al})_0$ are $(0.6 \pm 2.0) \times 10^{-6}$ and $(-0.9 \pm 1.2) \times 10^{-6}$, respectively. Slopes of the model ^{26}Al - ^{26}Mg isochrones in five corundum-bearing CAIs from Murray and Murchison are $(4.4 \pm 0.2) \times 10^{-5}$, $(3.3 \pm 0.3) \times 10^{-5}$, $(4.1 \pm 0.3) \times 10^{-5}$, $(3.9 \pm 0.4) \times 10^{-5}$, and $(4.0 \pm 2.0) \times 10^{-6}$, respectively (Makide et al., 2013). These values are lower than the canonical $(^{26}\text{Al}/^{27}\text{Al})_0$ ratio of $(5.23 \pm 0.13) \times 10^{-5}$ inferred from whole-rock magnesium isotope measurements of CV CAIs (Jacobsen et al., 2008), but are similar to the $(^{26}\text{Al}/^{27}\text{Al})_0$ ratio of $(4.1 \pm 0.2) \times 10^{-5}$ in the corundum-bearing CAI *F5* from Murray (Fahey, 1988). Of the three

corundum-bearing inclusions analyzed by Needham et al. (2017), two have radiogenic ^{26}Mg and near-canonical $(^{26}\text{Al}/^{27}\text{Al})_0$ values and one does not. The hibonite-corundum inclusion studied by Simon et al. (2002) also did not incorporate live ^{26}Al when it formed.

These results also indicate either heterogeneity in the distribution of ^{26}Al or an extended interval of corundum-hibonite-grossite condensation. Inclusion 31–2 likely formed before incorporation of ^{26}Al into the nebula, as inferred for other ^{26}Al -poor, hibonite-bearing CAIs (e.g., Simon et al., 2002; Kööp et al., 2016a). The inferred whole-rock $(^{26}\text{Al}/^{27}\text{Al})_0$ value that is needed to account for the peak metamorphic temperatures reached by the CO parent body and the ^{26}Al levels observed in chondrules is $\sim(6 \pm 2) \times 10^{-6}$ (Nagashima et al., 2018), higher than that of 31–2. These ratios may represent the $(^{26}\text{Al}/^{27}\text{Al})_0$ value at the time of accretion of CO parent asteroid through a rapid accretion of asteroid after the latest chondrule-forming event (e.g., Johansen and Klahr, 2011). If the lack of ^{26}Al in 31–2 is due to formation at a later time, after decay of ^{26}Al , it could not have been incorporated into DOM 08006. Inclusion 56–1 incorporated more live ^{26}Al than 31–2 or CO chondrules, but less than the canonical $^{26}\text{Al}/^{27}\text{Al}$ ratio, $\sim 5.2 \times 10^{-5}$ (Jacobsen et al., 2008; Larsen et al., 2011). It could have formed during the injection of ^{26}Al into the nebula (e.g., Krot et al., 2012), after most of its decay, or in a region of the nebula that did not receive the canonical proportion. Regardless, it is very unusual to find an inclusion with radiogenic ^{26}Mg and large nucleosynthetic isotopic anomalies (Clayton et al., 1988).

These samples provide important insights into the preservation of nucleosynthetic isotopic anomalies in the nebula. In 31–2, hibonite and melilite have Ca isotopic compositions within error of each other. The condensation calculations show that Ca is not completely condensed when melilite begins to form (Fig. 8b); it incorporates Ca from the gas in addition to that in previously condensed phases, so it did not simply inherit the isotopic composition of grossite and hibonite. The fact that melilite has the same anomaly as hibonite suggests that during condensation the composition of the gas did not evolve toward a more “normal” composition, and analyses of multiple CAIs show that rather large anomalies were preserved. For example, while inclusion 31–2 is enriched in the neutron-rich isotopes of Ca and Ti (Fig. 6), two CAIs from another CO3 chondrite, DOM 08004, are strongly depleted in them. A CAI in DOM 08004, inclusion 16–1, with mineralogy and structure similar to 31–2 but with a more compact texture and rounded shape, differs from 31–2 in having large negative anomalies in ^{48}Ca and ^{50}Ti , -26.3 ± 2.9 and $-36.5 \pm 2.5\%$, respectively (Kööp et al., 2018b). For hibonite, grossite and pyroxene in inclusion 16–1, Kööp et al. (2018b) reported a $\delta^{48}\text{Ca}$ value of $-26.3 \pm 2.9\%$ and a $\delta^{50}\text{Ti}$ of $-36.5 \pm 2.5\%$; hibonite in 26–1 has $\delta^{48}\text{Ca} = -19.7 \pm 5.5\%$ and its $\delta^{50}\text{Ti}$ is $-35.4 \pm 3.2\%$.

All oxides and silicates in both inclusions have very ^{16}O -rich oxygen isotopic compositions similar to those in most CAIs from the least metamorphosed chondrites. Despite the differences in Al-Mg, Ca and Ti isotopic compositions, the environments in which 31–2 and 56–1 formed had similar O-isotopic compositions. These observations are consistent with a scenario in which the vast majority of primary, refractory condensates from the solar nebula were initially very ^{16}O -rich and that ^{16}O -poor compositions of many isotopically heterogeneous CAIs are largely due to subsequent exchange, in a ^{16}O -poor nebular reservoir

and/or during metasomatic alteration on parent asteroids (e.g., Yurimoto et al., 2008 and references therein).

5. CONCLUSIONS

1. Inclusions 31–2 and 56–1 are gas-to-solid condensates from the early solar nebula. The predicted equilibrium condensates that are present in 31–2 are, in order of decreasing condensation temperature: hibonite; grossite; perovskite; melilite; spinel; FeNi metal; diopside; forsterite; and enstatite. This is also the order in which they occur from innermost to outermost in 31–2. Its highly irregular shape indicates that it was never molten. This inclusion preserves the most complete record of condensation in the early solar nebula that has yet been found.
2. The features of these inclusions support the equilibrium condensation calculations that predict them as well as the assumptions with respect to total pressure, bulk system composition, and C—O—H proportions, upon which the calculations are based.
3. The vast majority of primary oxide and silicate nebular condensates, including forsterite and enstatite, probably were initially very ^{16}O -rich, with ^{17}O between -25 and -20% . The relatively ^{16}O -poor compositions of phases seen in many isotopically heterogeneous CAIs from metamorphosed and metasomatically altered CV and CO chondrites are likely the result of subsequent isotopic exchange, in a ^{16}O -poor nebular reservoir and/or on parent asteroids.
4. Inclusions 31–2 and 56–1 have positive and negative anomalies, respectively, in both ^{48}Ca and ^{50}Ti . This shows that nucleosynthetic isotopic heterogeneities existed early in the nebula and were preserved during condensation, despite evidence that the nebular gas in the CAI-forming region was predominantly, uniformly ^{16}O -rich.
5. Inclusion 31–2 does not contain a detectable level of radiogenic ^{26}Mg , and it probably formed before injection of ^{26}Al into the solar nebula. Inclusion 56–1 either formed during injection of ^{26}Al or in a region that received a below-canonical proportion, or after significant decay. This inclusion represents a deviation from the mutual exclusivity relationship between ^{26}Al incorporation and large nucleosynthetic anomalies.

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Fig. 1.

Backscattered electron images of inclusion 31–2. (a) View of entire inclusion. Note the interior cavities and lathlike shapes of grossite outlined by melilite. (b) Higher-magnification view of a portion of the inclusion, showing angular cavities between hibonite laths in the core, and layers of melilite and diopside wrapping around a grossite + perovskite protrusion, likely a pseudomorph of hibonite. Hib: hibonite; G: grossite; Pv: perovskite; En: enstatite; Fo: forsterite.

Fig. 2.

Backscattered electron images of inclusion 56–1. (a) View of entire inclusion. A small grain of corundum is enclosed in hibonite. Note the corroded hibonite/grossite contact. (b) Higher-magnification view. Note how grossite grains G1 and G2 appear to be extensions of remaining hibonite laths. Cor: corundum; Hib: hibonite; Mel: melilite; Pv: perovskite; Di: diopside.

Fig. 3.

(a) False-color, three-element (Mg:red; Ca:green; Al:blue), combined X-ray map of inclusion 31–2. Note the highly irregular shape of the inclusion. Note also that the mantle of enstatite (En) and forsterite (Fo) is clearly associated with the inclusion and is distinct from the relatively Mg-poor (dark) matrix. For scale see Fig. 1a. (b) False-color, three-element (Mg: red; Ca: green; Al: blue), combined X-ray map of inclusion 56–1. The melilite and diopside layers are easily seen. For scale see Fig. 2a. (c) Grayscale Al K α map of 56–1, showing inclusions of corundum in hibonite. Abbreviations as used previously except Gro: grossite; Diop: diopside.

Fig. 4.

Results of electron probe analyses of hibonite. (a) Mg vs. Ti cations per 19 oxygen anions.

(b) Mg + Fe vs. Ti cations per 19 oxygens. The fit to the 1:1 line (shown for reference) is improved for 31-2 analyses but not for 56-1.

Fig. 5.

Oxygen isotopic compositions of all phases on both inclusions. The portion of the diagram indicated by the box in (a) is shown in (b). All phases have very ^{16}O -rich compositions that plot along the carbonaceous chondrite anhydrous mineral (CCAM) line. The terrestrial fractionation (TF) line is almost off-scale, at the upper-left corner of the diagram in (b).

Fig. 6.

Calcium and titanium isotopic compositions of hibonite and grossite in 31-2 and hibonite in 56-1, showing large anomalies in ^{48}Ca and ^{50}Ti ($^{46}\text{Ti}/^{48}\text{Ti}$ normalization). Clearly resolved anomalies exist in ^{48}Ca and ^{50}Ti , but within 31-2, mineral phases show no resolved variations in these isotopes. For comparison, ranges observed for CV chondrite non-FUN CAIs are indicated by the box based on ranges of -0.11 ± 0.17 to 0.82 ± 0.44 ‰ for $\delta^{48}\text{Ca}$ (Huang et al., 2012) and -0.007 ± 0.018 to 1.371 ± 0.007 ‰ for $\delta^{50}\text{Ti}$ (Davis et al., 2018). Lines through the origin are shown for reference.

Fig. 7. Excess ^{26}Mg ($\delta^{26}\text{Mg}^*$) as a function of $^{27}\text{Al}/^{24}\text{Mg}$. Inclusion 31-2 shows no Al-correlated $^{26}\text{Mg}^*$. Excesses are observed in 56-1 corresponding to a $(^{26}\text{Al}/^{27}\text{Al})_0$ of $(1.0 \pm 0.1) \times 10^{-5}$. Lines for $(^{26}\text{Al}/^{27}\text{Al})_0$ of 0 and 5×10^{-5} are shown for reference.

Fig. 8.

Equilibrium distribution of (a) Al, (b) Ca, and (c) Mg and Fe between vapor and condensed phases in a system of solar composition at a total pressure (P^{tot}) of 10^{-3} atm. In (a) and (b) dashed curves indicate separate components of solid solutions (ss). Stars indicate presence of phases in the present inclusions. Equilibria were calculated by Grossman (2010) using thermodynamic data for aluminates from Berman (1983) and solar abundances of oxygen and carbon relative to hydrogen from Allende Prieto et al. (2001, 2002). Abbreviations: Cor and A: corundum (Al_2O_3); Hib and CA6: hibonite ($CaO \times 6Al_2O_3$); Grss and CA2: grossite ($CaO \times 2Al_2O_3$); Kr and CA: krotite ($CaAl_2O_4$); Ge: gehlenite; Ku: kushiroite; Grsm: grossmanite; T4P: $CaTi^{4+}Al_2O_6$; Per: perovskite; Di: diopside; An: anorthite; Fo: forsterite; En: enstatite. After Grossman (2010).

Table 1

Electron microprobe analyses of hibonite.

	31-2 H1	31-2 H2	56-1 H1	56-1 H2	56-1 H3
MgO	0.82	0.95	0.73	0.76	0.84
Al ₂ O ₃	88.75	87.90	88.27	89.30	87.97
CaO	8.69	8.77	8.77	7.81	8.64
Sc ₂ O ₃	0.09	BDL	0.04	BDL	0.07
TiO ₂	1.62	2.09	1.51	1.44	1.66
V ₂ O ₃	BDL	0.05	0.04	BDL	BDL
FeO	0.10	0.12	0.38	0.62	0.66
Sum	100.08	99.90	99.75	99.98	99.86
<i>Cations per 19 oxygen anions</i>					
Mg	0.136	0.158	0.122	0.127	0.140
Al	11.689	11.613	11.683	11.757	11.647
Ca	1.040	1.053	1.055	0.935	1.040
Sc	0.004	0	0.002	0	0.003
Ti	0.136	0.176	0.128	0.121	0.141
V	0	0.002	0.002	0	0
Fe	0.009	0.012	0.036	0.058	0.062
Sum	13.020	13.014	13.030	12.998	13.033

All Ti is reported as TiO₂ and all V as V₂O₃. BDL: below detection limit (in wt%) of 0.042 for Sc₂O₃ or 0.033 for V₂O₃. Also, SiO₂ was below detection (0.012 wt%) in all analyses.

Table 2

Electron microprobe analyses of grossite.

	32-1 G1	32-1 G2	31-2 G3	31-2 G4	56-1 G1	56-1 G2
MgO	0.07	0.05	1.36	0.24	0.02	0.05
Al ₂ O ₃	77.15	76.75	72.53	75.68	75.42	75.97
CaO	22.07	22.22	22.05	22.05	22.03	22.01
Sc ₂ O ₃	0.06	BDL	BDL	BDL	BDL	BDL
TiO ₂	0.11	0.20	3.09	0.94	0.06	0.02
V ₂ O ₃	0.03	BDL	0.03	0.03	0.04	0.07
FeO	0.14	0.14	0.28	0.32	0.49	0.48
Sum	99.63	99.36	99.34	99.27	98.07	98.62
<i>Cations per 7 oxygen anions</i>						
Mg	0.005	0.003	0.089	0.016	0.001	0.003
Al	3.966	3.958	3.768	3.915	3.951	3.956
Ca	1.031	1.042	1.042	1.037	1.049	1.042
Sc	0.001	0.000	0.000	0.000	0.000	0.000
Ti	0.004	0.007	0.102	0.031	0.002	0.001
V	0.001	0.000	0.001	0.000	0.001	0.001
Fe	0.005	0.005	0.010	0.012	0.018	0.018
Sum	5.013	5.015	5.012	5.011	5.022	5.021

All Ti is reported as TiO₂ and all V as V₂O₃. BDL: below detection limit (in wt%) of 0.042 for Sc₂O₃ or 0.033 for V₂O₃. Also, SiO₂ was below detection (0.012 wt%) in all analyses.

Table 3

Electron microprobe analyses of melilite.

	56-1 MEL1	31-2 MEL1	31-2 MEL2	31-2 MEL3	31-2 MEL4	31-2 MEL5	31-2 MEL6
MgO	1.60	4.70	3.72	4.87	0.61	6.36	0.41
Al ₂ O ₃	33.74	25.02	27.37	22.97	34.40	20.33	34.63
SiO ₂	22.94	28.26	27.74	27.95	21.26	31.11	21.19
CaO	39.13	38.37	40.01	41.38	41.31	41.45	41.26
TiO ₂	0.09	0.05	0.14	0.67	0.11	0.01	0.22
FeO	0.89	0.62	0.90	0.21	0.12	0.19	0.37
Sum	98.39	97.02	99.88	98.05	97.81	99.45	98.08
<i>Cations per 7 oxygen anions</i>							
Mg	0.111	0.328	0.253	0.340	0.042	0.436	0.028
Al	1.847	1.381	1.473	1.269	1.908	1.102	1.917
Si	1.065	1.323	1.267	1.311	1.000	1.430	0.995
Ca	1.947	1.925	1.958	2.079	2.083	2.042	2.076
Ti	0.003	0.002	0.005	0.024	0.004	0.000	0.008
Fe	0.034	0.024	0.035	0.008	0.005	0.007	0.014
Sum	5.007	4.983	4.991	5.031	5.042	5.017	5.038
Åk	8.4	32.0	26.1	33.9	3.0	43.9	2.2

In all analyses, contents of Na₂O are below the detection limit of the electron microprobe, ~0.03 wt%. Åk : mole% åkermanite (Ca₂MgSi₂O₇) component, based on Mg, Al and Si cations per formula unit.

Table 4

Electron probe analyses of pyroxene and olivine associated with inclusion 31-2.

	31-2 DIOP1	31-2 DIOP2	31-2 EN1	31-2 OL1	31-2 OL2
MgO	18.38	18.74	42.23	55.51	54.36
SiO ₂	54.28	54.28	57.42	44.66	44.35
Al ₂ O ₃	0.34	0.23	BDL	BDL	BDL
CaO	25.93	26.18	0.08	0.17	0.19
FeO	1.05	0.74	0.76	1.16	0.73
Sum	99.99	100.17	100.49	101.50	99.63
<i>Cations per formula unit</i>					
Si	1.971	1.967	1.930	1.031	1.040
Mg	0.995	1.012	2.115	1.910	1.899
Al	0.015	0.010	0.000	0.000	0.000
Ca	1.009	1.017	0.003	0.004	0.005
Fe	0.032	0.023	0.021	0.022	0.014
Sum	4.022	4.029	4.069	2.967	2.958

In all analyses, contents of Sc₂O₃, TiO₂, V₂O₃, Cr₂O₃ and MnO are below the detection limit (BDL) of the electron microprobe, ~0.03 wt%

Table 5

Oxygen isotopic compositions of phases in inclusions 31–2 and 56–1.

Sample	Phase	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\delta^{17}\text{O}$
31–2	Hib	-52.9 ± 1.1	-50.9 ± 1.6	-23.5 ± 1.7
31–2	Hib	-51.6 ± 1.2	-50.8 ± 1.7	-23.9 ± 1.8
31–2	Gro	-53.9 ± 1.1	-50.9 ± 1.6	-22.9 ± 1.7
31–2	Gro	-47.3 ± 1.1	-44.8 ± 1.6	-20.2 ± 1.7
31–2	Mel	-44.1 ± 0.9	-43.2 ± 1.5	-20.3 ± 1.6
31–2	Mel	-45.4 ± 0.9	-45.3 ± 1.4	-21.7 ± 1.5
31–2	Diop	-45.4 ± 0.9	-45.5 ± 1.5	-21.9 ± 1.5
31–2	Diop	-45.6 ± 0.9	-46.3 ± 1.4	-22.6 ± 1.5
31–2	Diop	-44.4 ± 0.9	-47.7 ± 1.5	-24.5 ± 1.6
31–2	En	-47.3 ± 0.9	-46.0 ± 1.4	-21.4 ± 1.5
31–2	En	-47.5 ± 0.9	-47.7 ± 1.5	-23.0 ± 1.5
31–2	En	-46.1 ± 0.9	-47.2 ± 1.5	-23.2 ± 1.5
31–2	Ol	-46.0 ± 0.9	-46.4 ± 1.5	-22.5 ± 1.5
56–1	Cor	-51.1 ± 1.1	-51.7 ± 1.6	-25.2 ± 1.7
56–1	Hib	-49.7 ± 1.2	-50.0 ± 1.8	-24.2 ± 1.9
56–1	Gro	-52.1 ± 1.1	-52.1 ± 1.6	-25.1 ± 1.7
56–1	Mel	-45.7 ± 1.1	-45.9 ± 1.6	-22.1 ± 1.7
56–1	Diop	-44.5 ± 0.9	-46.9 ± 1.5	-23.8 ± 1.5

Cor: corundum; Hib: hibonite; Gro: grossite; Mel: melilite; Diop: diopside; En: enstatite; Ol: olivine. Uncertainties are 2σ .

Table 6

Isotopic compositions of Ca and Ti.

Sample	Phase	F _{Ti}	$\delta^{46}\text{Ti}$	$\delta^{48}\text{Ti}$	$\delta^{50}\text{Ti}$
31-2	Hib	0.7 ± 1.2	-3.9 ± 1.9	-0.5 ± 1.8	13.2 ± 4.1
31-2	Hib	-0.7 ± 1.8	-2.2 ± 2.9	-0.2 ± 2.7	9.8 ± 6.9
31-2	Gro	-7.3 ± 4.0	0.3 ± 8.2	0.1 ± 7.3	10.9 ± 13.9
31-2	Wtd avg	-0.2 ± 0.9	-3.3 ± 1.6	-0.4 ± 1.5	12.2 ± 3.4
56-1	Hib	2.1 ± 1.4	-2.1 ± 2.6	1.2 ± 2.3	0.5 ± 5.0
		F _{Ti}	$\delta^{47}\text{Ti}$	$\delta^{49}\text{Ti}$	$\delta^{50}\text{Ti}$
31-2	Hib	2.7 ± 0.8	2.2 ± 1.8	-1.6 ± 2.6	9.3 ± 2.6
31-2	Hib	0.6 ± 1.3	1.4 ± 2.4	-0.8 ± 2.7	7.6 ± 3.5
31-2	Gro	-7.3 ± 3.4	-0.1 ± 6.6	0.1 ± 7.4	10.7 ± 8.9
31-2	Wtd avg	1.8 ± 0.7	1.8 ± 1.4	-1.1 ± 1.8	8.8 ± 2.0
56-1	Hib	3.9 ± 0.9	0.5 ± 2.2	-2.4 ± 2.8	-4.3 ± 2.9
		F _{Ca}	$\delta^{42}\text{Ca}$	$\delta^{43}\text{Ca}$	$\delta^{48}\text{Ca}$
31-2	Mel	1.1 ± 0.4	-1.3 ± 1.7	-1.1 ± 1.8	4.8 ± 3.2
31-2	Hib	1.1 ± 0.9	-1.9 ± 2.8	-1.1 ± 3.4	2.4 ± 4.5
31-2	Hib	-0.5 ± 0.8	-1.5 ± 3.5	-0.7 ± 3.6	3.2 ± 5.0
31-2	Gro	-1.1 ± 0.9	-2.1 ± 3.7	0.0 ± 3.7	4.6 ± 5.1
31-2	Diop	1.1 ± 0.9	-2.8 ± 3.6	-0.2 ± 2.9	6.4 ± 5.1
31-2	Wtd avg	0.7 ± 0.3	-1.7 ± 1.2	-0.8 ± 1.2	4.3 ± 1.9
56-1	Hib	0.0 ± 0.8	-3.2 ± 2.8	-2.0 ± 3.4	-10.3 ± 4.2

Wtd avg: weighted average. Other abbreviations as used previously. Uncertainties are 2 σ .

Table 7

Al-Mg isotopic data for 31-2 and 56-1.

Sample	Phase	$^{27}\text{Al}/^{24}\text{Mg}$	2σ	$\delta^{26}\text{Mg}^*$	2σ
31-2	Gro	1099	111	-1.9	7.1
31-2	Hib	108	11	0.6	2.4
31-2	Mel	22	2	-0.5	3.4
31-2	Mel	72	7	-1.2	3.8
31-2	Diop	0.09	0.003	0.28	0.32
31-2	Diop	0.06	0.002	0.15	0.30
56-1	Gro	1245	125	90.7	8.4
56-1	Gro	2161	220	160.3	13.5
56-1	Hib	238	24	17.6	3.8
56-1	Hib	118	12	11.2	2.5
56-1	Hib	243	25	18.6	3.6

Phase abbreviations as in Table 4. These measurements yield $(^{26}\text{Al}/^{27}\text{Al})_0$ values of $(-2.5 \pm 8.4) \times 10^{-7}$ for 31-2 and $(1.0 \pm 0.1) \times 10^{-5}$ for 56-1.