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The first known natural occurrence of calcium monoaluminate, in a calciumaluminum-rich inclusion from the CH chondrite Northwest Africa 470

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Abstract–Natural calcium monoaluminate, $CaAl_2O_4$, has been found in a grossite-rich calciumaluminum-rich inclusion (CAI) from the CH chondrite Northwest Africa 470. The calcium monoaluminate occurs as colorless ~10 μ m subhedral grains intergrown with grossite, perovskite, and melilite. Nebular condensation is the most likely origin for the precursor materials of this CAI, but calculations suggest that dust/gas ratios substantially enhanced over solar are required to stabilize CaAl₂O₄.

INTRODUCTION

The system CaO-Al₂O₃ contains four intermediate compounds—CaAl₁₂O₁₉, CaAl₄O₇, CaAl₂O₄, and Ca₃Al₂O₆—of which only the first two have until now been found to occur in nature. An additional phase, Ca₁₂Al₁₄O₃₃ (mayenite), has been produced experimentally only in the presence of water and hence may not be a true binary compound (Nurse *et al.*, 1965; Jerebtsov and Mikhailov, 2001). All of these phases form within restricted bulk compositions at elevated temperatures, so their natural occurrences are petrogenetically informative.

Both hibonite $(CaAl_{12}O_{19})$ and grossite $(CaAl_4O_7)$ were first identified in terrestrial metamorphic rocks (Curien et al., 1956; Delbos, 1957; Gross, 1978), but their most significant natural occurrences are in calcium-aluminum-rich inclusions (CAIs) within primitive chondritic meteorites (e.g., Keil and Fuchs, 1971; Grossman, 1975; Allen et al., 1978; Weber and Bischoff, 1994; Weisberg et al., 1995; Krot et al., 2001; see review by Brearley and Jones, 1998). Hibonite is predicted by equilibrium thermodynamic calculations to condense during cooling of a hot gas of solar composition (e.g., Grossman, 1972; Yoneda and Grossman, 1995; Petaev and Wood, 1998; Ebel and Grossman, 2000). Hibonite in CAIs commonly contains clear evidence, in the form of excess ²⁶Mg, for the former presence of the short-lived radionuclide ²⁶Al ($t_{1/2} \approx 0.7$ Ma) when the crystals formed (see review by MacPherson et al., 1995, and numerous references therein). Some hibonite has also been shown to have contained the even shorter lived nuclide

 41 Ca ($t_{1/2} \approx 0.1$ Ma) at the time of formation (Srinivasan *et al.*, 1994). Hibonite-bearing CAIs therefore are believed to represent some of the very first solid matter that formed in the infant solar system at 4.56 Ga. Grossite-rich CAIs also commonly have excesses of ²⁶Mg that indicate the former presence of ²⁶Al, and hence also represent primordial solar system matter. However, grossite is rare relative to hibonite, and the reason for this is debated. Different workers have disagreed on the predicted condensation of grossite in a gas of solar composition, because the calculated results are sensitive to slight differences in the thermodynamic parameters used as input for the calculations (e.g., compare the results of Yoneda and Grossman, 1995, with those of Ebel and Grossman, 2000; see also brief historical overview in Weber et al., 1995). For "non-solar" calculations, the results are also dependent on the total assumed pressure and dust/gas ratios (e.g., Ebel and Grossman, 2000).

The phase $CaAl_2O_4$ is well known in experimental systems, but has not been found in nature until now. Here we describe the first natural occurrence of $CaAl_2O_4$, in a grossite-rich CAI from the new CH chondrite Northwest Africa (NWA) 470, and comment on its origin and rarity as a natural phase. Preliminary results were reported in Ivanova *et al.* (2001c).

ANALYTICAL PROCEDURES

A polished thin section of NWA 470, made in the Vernadsky Institute, was studied by optical microscopy, scanning electron microscopy (SEM), x-ray elemental area mapping, and electron probe microanalysis. High-resolution backscattered electron (BSE) images were obtained using a JEOL JSM-840A SEM at the Smithsonian's National Museum of Natural History (NMNH). The modal composition of the CAI was estimated by pixel counting of high-resolution/high-contrast digital BSE images, using standard commercial image processing software; the resulting area percentages were then multiplied by the relevant mineral densities to arrive at mass percentages, necessarily assuming that (a) area percentages are approximately equal to volume percentages, and (b) the area exposed in the thin section surface is representative. Mineral mass fractions were then combined with average mineral compositions to arrive at the bulk CAI composition. The estimated uncertainties in the bulk composition are approximately $\pm 5\%$ (relative) for major elements.

Most of the analyses of individual phases reported in this work were obtained using the JEOL JXA-8900R electron microprobe at NMNH. Operating conditions were 15 KeV accelerating voltage, 15 nA beam current, and peak counting times of 20 s for major elements and 40-120 s for minor elements. Data were reduced using a proprietary ZAF correction procedure. Natural and synthetic crystalline minerals were used both as calibration standards and (in some cases) as unknowns that were analyzed at the beginning and end of every run as a check of analytical accuracy: hornblende (Ti, Si, Mg, Fe, Na, K), bytownite and anorthite (Al), synthetic wollastonite (Ca), chromite (Cr), and synthetic glass (V, Mn). Preliminary analyses reported in Ivanova et al. (2001c) were obtained using the JEOL 733 electron microprobe at the Harvard-Smithsonian Center for Astrophysics, operated at 15 KeV accelerating voltage and 20 nA beam current, using 10 s counting times, and again the data were reduced with a ZAF correction algorithm. The calibration standards used were the same as described by Petaev et al. (1994).

All analyses of all phases, collected using both the NMNH and Center for Astrophysics microprobes, showed unexpectedly high levels of FeO (about 0.4–0.8 wt%). Most or all of this is likely due to secondary x-ray fluorescence from nickel-bearing metal in close proximity to the CAI in this very metal-rich meteorite. Therefore we do not attribute significance to the measured FeO and do not report it in the tables.

SAMPLE OCCURRENCE AND DESCRIPTION

The CaAl₂O₄-bearing CAI was found in NWA 470, a new meteorite find recovered in Morocco in 1999 and recently classified as a CH chondrite (Ivanova *et al.*, 2001a). The meteorite is slightly weathered (grade W1), has weakly developed shock features (stage S1), and shows no evidence of post-accretional aqueous alteration or thermal metamorphism. NWA 470 resembles other CH (and CB) chondrites in having abundant (24 vol%) Fe-Ni metal grains with similar chemical zoning characteristics and solar Ni/Co ratios (Meibom *et al.*, 1999; Weisberg and Prinz, 1999; Petaev *et al.*, 2001, 2002), numerous small CAIs of different types, and fine-grained dark inclusions.

The CAIs and CAI fragments in NWA 470 (Ivanova *et al.*, 2001b) are mineralogically and texturally similar to those in other CH chondrites (Weber *et al.*, 1995; Krot *et al.*, 2001). Most are rounded, and they vary in size from 20 to 100 μ m with the smaller ones being most abundant. Compact grossite-bearing inclusions dominate the suite. Many of them are concentrically zoned with grossite + hibonite + perovskite ± spinel cores surrounded by melilite mantles and anorthite and Al-diopside rims. Other CAIs have porphyritic textures in which subhedral grossite crystals are embedded in a groundmass of melilite or clinopyroxene, ± minor perovskite.

One of the grossite-rich CAIs, labeled E1-005, was found to contain CaAl₂O₄ (Ivanova *et al.*, 2001c). A BSE photomicrograph of E1-005 (Fig. 1) shows that it is a fragment representing slightly more than half of what was once a spheroidal inclusion, originally ~115 μ m in diameter, with a pronounced concentrically zoned distribution of minerals. The innermost core of the CAI consists mostly of grossite, with interstitial perovskite ($\leq 3 \mu$ m) and melilite ($\leq 5 \mu$ m) grains. Surrounding this is a zone (Fig. 2) consisting mainly of CaAl₂O₄ that encloses melilite, perovskite, and minor grossite. The CaAl₂O₄-rich zone is in turn enclosed in a region consisting mostly of grossite with abundant included perovskite grains. Finally, the entire CAI is mantled by a nearly monomineralic, ~8 μ m thick rind of melilite (Fig. 3). Tiny grains of perovskite



FIG. 1. Backscattered electron image of E1-005. The innermost core of the hemispherical inclusion consists mainly of grossite (Gr) intergrown with perovskite (Pv) and melilite (Mel) that is pure gehlenite ($\underline{Akermanite_0}$); external to this is a zone rich in CaAl₂O₄ that encloses small grains of melilite, perovskite, and grossite (Grs); surrounding this is a massive zone consisting mainly of grossite that encloses perovskite, and finally the outermost zone consists exclusively of melilite that is different in composition ($\underline{Akermanite_{2-7}}$) from the small interior gehlenite grains.





FIG. 2. High-resolution backscattered electron image of the interior of E1-005, showing the textural relationship between $CaAl_2O_4$ (CA), grossite, perovskite, and melilite. Abbreviations as in Fig. 1.

FIG. 3. High-resolution backscattered electron image of the outermost part of E1-005, showing the tiny perovskite crystals that line the contact between the melilite mantle and the grossite-rich zone. Abbreviations as in Fig. 1.

> 0.00

0.00

1.00

2.99

	1	2	3	4	5	Average $(n = 5)$
		2	5			
SiO ₂	0.08	0.20	0.08	0.14	0.11	0.12
Al_2O_3	65.58	63.56	63.92	63.27	65.37	64.34
MgO	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06
CaO	35.51	35.67	35.51	35.36	35.55	35.52
TiO ₂	< 0.06	0.09	0.09	0.09	0.11	0.09
Total	101.17	99.52	99.60	98.86	101.14	100.07
		C	ations per 4 ox	cygens		
Al	2.00	1.98	1.99	1.99	2.00	1.99
Si	0.00	0.01	0.00	0.00	0.00	0.00

0.00

0.00

1.01

3.00

TABLE 1. Composition of CaAl₂O₄*.

0.00

0.00

0.99

2.99

*The following additional elements are below 3σ detection limits in CaAl ₂	O4: MnO	< 0.06 wt%, 0	$Cr_2O_3 <$
$0.05 \text{ wt\%}, V_2O_3 < 0.08 \text{ wt\%}, Na_2O < 0.03 \text{ wt\%}, K_2O < 0.02 \text{ wt\%}.$	FeO was	also measure	d in all
analyses but is deemed to be spurious. See "Analytical Procedures".			

0.00

0.00

1.01

3.00

0.00

0.00

1.01

3.00

decorate the contact between the melilite rind and the interior zone, but the melilite rind itself is notably lacking in perovskite, which is so abundant everywhere else in the CAI.

Ti

Mg

Ca

Total

The entire CAI is so small and fine grained that optical properties of the CaAl₂O₄ cannot be determined beyond the observations that it is birefringent and, when viewed in planepolarized light, colorless. The largest clear regions of CaAl₂O₄ are no larger than ~10 μ m, but the sizes of individual crystals could not be determined.

MINERAL CHEMISTRY AND BULK COMPOSITION

0.00

0.00

0.99

2.99

Representative analyses and an average composition of calcium monoaluminate from E1-005 are given in Table 1; representative analyses of grossite and melilite are given in Table 2.

The calcium monoaluminate is essentially pure, stoichiometric CaAl₂O₄ (Table 1). Attempts to analyze this phase by using corundum or spinel as calibration standards for

	1 Melilite*	2 Melilite*	3 Grossite†	4 Grossite†
SiO ₂	22.94	22.18	0.10	0.14
Al_2O_3	35.01	35.81	77.97	78.42
MgO	0.61	0.25	< 0.05	0.10
CaO	40.94	40.68	21.68	21.55
TiO ₂	0.18	0.23	0.10	0.11
Total	99.68	99.15	99.85	100.32
	(Åk 5)	(Åk 3)		

TABLE 2. Compositions of melilite and grossite.

*The following additional elements are below 3σ detection limits in melilite: MnO < 0.06 wt%, Cr₂O₃ < 0.05 wt%, V₂O₃ < 0.08 wt%, Na₂O < 0.03 wt%, K₂O < 0.02 wt%.

[†]The following additional elements are below 3σ detection limits in grossite: MnO < 0.06 wt%, Cr₂O₃ < 0.04 wt%, V₂O₃ < 0.08 wt%, Na₂O < 0.03 wt%, K₂O < 0.02 wt%.

FeO was also measured in both phases but is deemed to be spurious. See "Analytical Procedures".

aluminum gave consistently poor results, whereas the use of anorthite and bytownite resulted in Al₂O₃ determinations that are close to the theoretical value for pure CaAl₂O₄ (64.52 wt%). This finding, which is suggestive of a peak shift due to crystallographic site differences, is consistent with the results of crystal structure determinations (*e.g.*, Dougill, 1957) for synthetic CaAl₂O₄, in which the aluminum was found to be in tetrahedral coordination, not octahedral as it is in corundum and spinel (and hibonite). The absence of octahedral sites in CaAl₂O₄ may also explain the exceptionally low abundance of TiO₂ despite the fact that the bulk inclusion contains several weight percent TiO₂ (see below). The low TiO₂ in turn may account for the low MgO, as charge balance considerations require a coupled substitution.

The situation for grossite in E1-005 (Table 2) is similar to that for CaAl₂O₄. The phase is nearly pure and stoichiometric CaAl₄O₇, and again microprobe analyses made using different aluminum calibration standards are consistent with the aluminum being in tetrahedral coordination as indicated by crystal structure determinations (Goodwin and Lindop, 1970). The universal depletion of TiO₂ in grossite (see Weber and Bischoff, 1994), especially relative to coexisting hibonite, undoubtedly reflects the absence of suitable crystallographic sites for that element in this phase.

The melilite in the outermost mantle is very aluminum rich, with åkermanite contents only in the narrow range $Åk_{2-7}$ (Table 2). The interior grains, enclosed within CaAl₂O₄, are too small to give good quantitative results under the conditions we used for wavelength dispersive analysis. We obtained quantitative (standardized) energy-dispersive analyses using the SEM at 10 keV accelerating voltage, and thereby determined these tiny interior grains to be end-member gehlenite (Åk₀) with no detectable magnesium; there is in fact no hint of a magnesium peak visible on the spectra, unlike the spectra of



FIG. 4. Bulk chemical compositions (wt%) of E1-005 (square), grossite-rich CAIs (crosses), and types A and B CAIs (filled circles and open triangles, respectively) plotted in the systems $SiO_2-Al_2O_3-CaO$ (a) and MgO-Al_2O_3-CaO (b). Data for grossite-rich CAIs are taken from Weber and Bischoff (1994); data for type A and B CAIs are taken from Beckett (1986). The solar (CI chondrite) composition is from Anders and Grevesse (1989). The dashed line represents solar CaO/Al_2O_3.

melilite in the mantle. Repeated analyses suggest that these interior grains are indeed distinct in composition from the mantle melilite.

The tiny perovskite grains were only analyzed semiquantitatively, which served to confirm their identification.

The modal composition of the entire inclusion is (vol%): CaAl₂O₄ = 11, grossite = 54, melilite = 27, perovskite = 8. Based on this mode we calculate the bulk chemical composition of E1-005 to be: SiO₂ = 6.1 wt%, TiO₂ = 6.4 wt%, Al₂O₃ = 57.0 wt%, MgO = 0.1 wt%, CaO = 30.4 wt%.

DISCUSSION

In Fig. 4a,b we have plotted the bulk composition of E1-005 on the simple ternary oxide diagrams $CaO-Al_2O_3-SiO_2$ and

CaO-Al₂O₃-MgO, along with the bulk compositions of grossite bearing CAIs, type A CAIs, and type B CAIs. E1-005 and other grossite-bearing CAIs have systematically lower MgO and SiO₂ than do types A or B CAIs, and lower CaO/Al₂O₃ ratios relative both to the types A, B CAIs and to the solar ratio. These observations argue that high bulk Ca/Al is not the principal requirement for stabilizing CaAl₂O₄ or (as previously suggested by Weber and Bischoff, 1994) grossite. Rather, the distribution of data in Fig. 4 indicates that low SiO₂ (Fig. 4a) and low MgO (Fig. 4b) are more critical to the stability of both of these rare calcium aluminates. Supporting evidence that MgO and SiO2 diminish the stability of grossite and CaAl2O4 comes from experimentally determined crystal-melt phase equilibria. Figure 5 illustrates the liquidus relationships in the silica-poor half of the system CaO-Al₂O₃-SiO₂, which has been modified slightly from the original work to reflect the incongruent melting behavior of CaAl₂O₄ (Jerebtsov and Mikhailov, 2001). The liquidus fields of all the calcium aluminates are restricted to silica-poor compositions, with that of grossite being more restricted than that of hibonite and the field of CaAl₂O₄ is considerably more restricted than either. At SiO₂ contents greater than ~10 wt%, the field of CaAl₂O₄ is truncated by that

of gehlenite. A similar situation exists in the system CaO– Al_2O_3 -MgO (Rankin and Merwin, 1916), where elevated MgO contents stabilize spinel at the expense of CaAl₂O₄.

Also shown on Fig. 5 is the bulk composition of E1-005. It plots within the field for grossite + liquid. A melt of such composition will initially crystallize grossite, moving directly away from grossite as it does so and hitting the melilite + grossite boundary curve approximately at the grossite + melilite + $CaAl_2O_4$ invariant point, where grossite begins to react with the liquid to form melilite + CaAl₂O₄; crystallization ceases once grossite is exhausted. Thus the predicted order of appearance of phases is: grossite, followed by melilite + $CaAl_2O_4$. Although the mineralogy of E1-005 is broadly consistent with melt crystallization (with the addition of perovskite), the textures of this concentrically zoned CAI are not. Based solely upon the observed textures, if E1-005 originated as a melt droplet that crystallized from the outside inward in response to surface cooling, the order of appearance of phases was melilite, grossite + perovskite, and CaAl₂O₄. This is inconsistent with the bulk composition. Moreover, the observation that melilite is present in the mantle and in the CaAl₂O₄-rich core but absent from the intervening grossite-rich



FIG. 5. Bulk chemical composition of E1-005 (boxed cross) plotted relative to experimentally determined phase equilibrium relationships in the system $SiO_2-Al_2O_3$ —CaO. Note that the compositions of the pure phases hibonite (Hib), grossite (Gro), and $CaAl_2O_4$ (calcium monaluminate, CA) all plot outside of their own crystallization fields (+ liquid; lq) and thus melt incongruently. Accordingly, the boundary curves separating these aluminates from one another (and hibonite from corundum, Cor) are reaction curves as indicated by the double arrows. Phase relationships are from Osborne and Muan (1960) and Gentile and Foster (1963), and modified slightly (dashed curve) to take account of the incongruent melting of $CaAl_2O_4$ as demonstrated in the recent work on the CaO–Al₂O₃ join by Jerebtsov and Mikhailov (2001). Note the thermal divide on the gehlenite–grossite boundary curve (see text). For clarity, details are shown only for the fields and boundary curves of immediate relevance to this work.

zone requires that melilite ceased crystallization during the grossite interval but then reappeared once CaAl₂O₄ began crystallizing. This is inconsistent with the phase topology of Fig. 5. A melt origin is permissible, however, if the melilite mantle is interpreted as a late-stage addition (equivalent to the thin melilite rim layers observed on many CAIs in reduced CV3 chondrites such as Vigarano and Efremovka; for example, see review by Wark and Boynton, 2001). The fact that the mantle and interior differ in mineralogy (no perovskite in the mantle) and melilite composition suggests that they might indeed represent two separate events. In that case, the textures of the interior (*i.e.*, without the melilite mantle) of E1-005 become more consistent with a melt droplet origin because the sequence of crystallization then becomes grossite + perovskite followed by $CaAl_2O_4$ + perovskite + melilite. The ragged appearance of the grossite in the innermost core is consistent with its being in reaction relationship with the melt once melilite + $CaAl_2O_4$ began to crystallize; however, the fact that grossite is abundant in the very center of the CAI but deficient in the CaAl₂O₄-rich zone is less easy to understand if the CAI crystallized from the outside inward. The textures of E1-005 do not rule out the possibility of solid-state recrystallization of a Ca,Al-rich precursor. At a minimum, subsequent high-temperature processing E1-005 during the deposition of the melilite rim might have resulted in substantial modification of the original texture.

Independent of whether E1-005 ever passed through a melt stage, the main question posed by $CaAl_2O_4$ -bearing (E1-005) and grossite-bearing CAIs is why they are so rare. The essential problem revolves around producing bulk compositions that have high Ca/Al relative to hibonite but very low MgO and SiO₂. We can rule out the possibility that such bulk compositions were produced by any kind of simple igneous fractional crystallization (e.g., by ejection of interstitial melts from partially molten chondrules or CAIs-Bischoff and Keil 1983; Bischoff et al., 1989), because fractional crystallization alone cannot cross any of the several thermal divides that exist in the portion of the CaO-MgO-Al₂O₃-SiO₂ system shown in Fig. 5 (only one divide is explicitly identified in the figure). The initial melt must itself be highly CaO-Al₂O₃ rich and MgO-SiO₂ poor, which does not solve the problem. The remaining possibilities for producing such a bulk composition include either nebular condensation or evaporation, or a combination of both.

Recent studies vary significantly in their conclusions regarding the condensation of both $CaAl_2O_4$ and grossite. Primarily this is because the different studies used different sources of the thermodynamic data for the calcium aluminates (see recent review by Kuzmenko *et al.*, 1997). A secondary reason is that the various studies focused on different variables that control condensation, such as total nebular pressure (*e.g.*, Yoneda and Grossman, 1995), gas/dust ratios (Wood and Hashimoto, 1993; Ebel and Grossman, 2000), and fractional *vs.* equilibrium condensation (Petaev and Wood, 1998). The various studies can be directly compared where they report calculations for "solar" nebular condensation such as that done by Grossman (1972) (*i.e.*, $P_T 10^{-3}$ atm) complete equilibrium, and solar composition). Under these conditions, the different results for the aluminates arise entirely from the different sources of thermodynamic data used: Wood and Hashimoto (1993), Yoneda and Grossman (1995), and Petaev and Wood (1998) all found no stability field for either grossite or CaAl₂O₄; Petaev *et al.* (2002) did find a stability field for grossite but not CaAl₂O₄; and Ebel and Grossman (2000) reported stability fields for both CaAl₂O₄ and grossite, using a different thermodynamic data set (Berman, 1983; Berman and Brown, 1985) from the other studies that was chosen because it is internally consistent with the silicate melt model used in their calculations.

In spite of the differences in the various calculations, some general trends emerge in comparing their results with respect to grossite and CaAl₂O₄. In particular, the studies of Wood and Hashimoto (1993) and Ebel and Grossman (2000) both demonstrate that enhanced dust/gas ratios increase the stability of grossite at the expense of hibonite even where (in the work by Wood and Hashimoto) grossite is not stable under "solar" conditions. Ebel and Grossman (2000) also found that enhanced dust/gas ratios increase the stabilities both of CaAl₂O₄ and a melt condensate that is very close in bulk chemistry to that of E1-005. Yoneda and Grossman (1995) showed that high nebular gas pressure (10^{-2} atm) also stabilizes not only grossite and CaAl₂O₄ but also Ca-Al-rich melt.

We used the condensation with partial isolation (CWPI) code of Petaev and Wood (1998) to explore fractional condensation (incomplete back reaction of condensing phases), and found that fractional condensation alone in the absence of any dust/gas enrichment did not result in condensation of grossite or CaAl₂O₄. Enhanced dust/gas ratios do, however, stabilize grossite and CaAl₂O₄ during fractional condensation just as they do for equilibrium condensation. For example, at dust/gas = 100 and an "isolation degree" (a complex fractionation factor; see Petaev and Wood, 1998) of 1%, the assemblage of CaAl₂O₄, grossite, perovskite, and minor Ca₂SiO₄ is stable in the temperature interval of 1873–1867 K. Interestingly, the calculated bulk condensation trajectory also (similar to that of Ebel and Grossman, 2000) passes through the bulk composition of E1-005.

We also explored condensation under more radical (and *ad hoc*) departures from canonical solar conditions, and found that enriching the gas in Ca significantly increases the stability of grossite and CaAl₂O₄. With dust/gas = 1, CaAl₂O₄ can condense only from nebular gases enriched in Ca by a factor of 5 or more compared to a system of solar composition, and even then only traces of CaAl₂O₄ coexist with hibonite, grossite, and perovskite. At Ca = 10× solar, hibonite condensation at 1710 K is followed by grossite at 1662 K, perovskite at 1654 K, and CaAl₂O₄ at 1626 K. At 1610 K, the stable mineral assemblage is CaAl₂O₄ (48 wt%), grossite (46 wt%), and perovskite (6 wt%). Even at such elevated Ca abundances,

however, once gehlenitic melilite appears at 1600 K it becomes the dominant condensate (with perovskite) below 1596 K.

It is well known experimentally that melt evaporation can produce refractory CAI-like residues (*e.g.*, Hashimoto, 1983). Ulyanov *et al.* (1990) produced evaporation residues consisting mainly of different Ca aluminates, by evaporating about 86– 95 wt% of basaltic starting materials in a vacuum some of which have bulk compositions similar to that of E1-005. The main caveat here is that, although the isotopic composition of E1-005 itself has yet to be measured, grossite-bearing CAIs were analyzed by Weber *et al.* (1995), who found no systematic massdependent enrichment in heavy magnesium isotopes as might be expected if the CAIs owed their essential refractory compositions or severe magnesium depletions primarily to melt evaporation.

We therefore consider it more likely that E1-005 and similar CAIs owe their refractory character to condensation. Why then are CaAl₂O₄- and grossite-rich CAIs so rare? We suggest that such objects might be sensitive indicators of local, and apparently uncommon, elevated dust/gas ratios in the solar nebula, since all of the calculations share in common the fact that elevated dust/gas ratios enhance the stability of grossite and/or CaAl₂O₄.

SUMMARY

The first natural occurrence of $CaAl_2O_4$ has been found in a grossite-rich CAI from the CH chondrite NWA 470. The precursor most likely formed by condensation, and calculations by a diversity of investigators suggest that the condensation of $CaAl_2O_4$ from a nebular system requires enrichment in dust relative to gas. The presence of this rare phase, and perhaps grossite as well, may (with proper experimental calibration) serve as a local "dustometer" of solar nebular condensation. Subsequent to formation of the precursor, the CAI may have experienced melting or, at a minimum, significant solid-state recrystallization. The monomineralic melilite outer mantle formed in a subsequent event.

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REFERENCES

ALLEN J. M., GROSSMAN L., DAVIS A. M. AND HUTCHEON I. D. (1978) Mineralogy, textures, and mode of formation of a hibonite-bearing Allende inclusion. *Proc. Lunar Planet. Sci. Conf.* 9th, 1209–1233.

- ANDERS E. AND GREVESSE N. (1989) Abundances of the elements: Meteoritic and solar. Geochim. Cosmochim. Acta 53, 197–214.
- BECKETT J. R. (1986) The origin of calcium-, aluminum-rich inclusions from carbonaceous chondrites: An experimental study. Ph.D. dissertation, University of Chicago, Chicago, Illinois, USA. 373 pp.
- BERMAN R. G. (1983) A thermodynamic model for multicomponent melts, with application to the system CaO-MgO-Al₂O₃-SiO₂.
 Ph.D. dissertation, Univ. British Columbia, Vancouver, British Columbia, Canada. 178 pp.
- BERMAN R. G. AND BROWN T. H. (1985) Heat capacity of minerals in the system Na₂O-K₂O-CaO-MgO-FeO-Fe₂O₃-Al₂O₃-SiO₂-TiO₂-H₂O-CO₂. Contrib. Mineral. Petrol. 89, 168-183.
- BISCHOFF A. AND KEIL K. (1983) Ca-Al-rich chondrules and inclusions in ordinary chondrites. *Nature* 303, 588-592.
- BISCHOFF A., PALME H. AND SPETTEL B. (1989) Al-rich chondrules from the Ybbsitz H4-chondrite—Evidence for formation by collision and splashing. *Earth Planet. Sci. Lett.* 93, 170–180.
- BREARLEY A. J. AND JONES R. H. (1998) Chondritic meteorites. In Planetary Materials (ed. J. J. Papike), pp. 3–01 to 3–398. Rev. Mineral. 36, Mineral. Soc. Am., Washington D.C., USA.
- CURIEN H., GUILLEMIN C., ORCEL J. AND STERNBERG M. (1956) La hibonite, nouvelle espèce minérale. *Compt. Rend. Acad. Sci.* 242, 2845–2847.
- DELBOS L. (1957) New occurrences of hibonite in metamorphic rocks. Compt. Rend. Acad. Sci. 244, 1, 214–215.
- DOUGILL M. W. (1957) Crystal structure of calcium monoaluminate. Nature 180, 292–293.
- EBEL D. S. AND GROSSMAN L. (2000) Condensation in dust-enriched systems. *Geochim. Cosmochim. Acta* 64, 339–366.
- GENTILE A. L. AND FOSTER W. R. (1963) Calcium hexaluminate and its stability relations in the system CaO-Al₂O₃-SiO₂. J. Am. Ceram. Soc. 46, 74-76.
- GOODWIN D. W. AND LINDOP A. J. (1970) The crystal structure of CaO.2Al₂O₃. Acta Cryst. B26, 1230–1235.
- GROSS S. (1977) The mineralogy of the Hatrurim formation, Israel. Geol. Surv. Isr. Bull. 70, 1–80.
- GROSSMAN L. (1972) Condensation in the primitive solar nebular. Geochim. Cosmochim. Acta 36, 597–619.
- GROSSMAN L. (1975) Petrography and mineral chemistry of Ca-rich inclusions in the Allende meteorite. *Geochim. Cosmochim. Acta* 39, 433–454.
- HASHIMOTO A. (1983) Evaporation metamorphism in the early solar nebula—Evaporation experiments on the melt FeO-MgO-SiO₂-CaO-Al₂O₃ and chemical fractionations of primitive materials. *Geochem. J.* 17, 111–145.
- IVANOVA M. A., PETAEV M. I., CLAYTON R. N., MAYEDA T. K., HUTCHEON I. D., PHINNEY D., NAZAROV M. A., TAYLOR L. A. AND WOOD J. A. (2001a) NWA 470, a new CH chondrite from the Moroccan Sahara (abstract). *Lunar Planet. Sci.* 32, #1817, Lunar and Planetary Institute, Houston, Texas, USA (CD-ROM).
- IVANOVA M. A., PETAEV M. I., NAZAROV M. A., TAYLOR L. A. AND WOOD J. A. (2001b) Refractory inclusions from the new CH, NWA 470 (abstract). *Lunar Planet. Sci.* 32, #1392, Lunar and Planetary Institute, Houston, Texas, USA (CD-ROM).
- IVANOVA M. A., PETAEV M. I., NAZAROV M. A., TAYLOR L. A., MACPHERSON G. J. AND WOOD J. A. (2001c) The first known occurrence of CaAl₂O₄ in a CAI from the new CH chondrite NWA 470 (abstract). *Lunar Planet. Sci.* 32, #1957, Lunar and Planetary Institute, Houston, Texas, USA (CD-ROM).
- JEREBTSOV D. A. AND MIKHAILOV G. G. (2001) Phase diagram of CaO-Al₂O₃ system. *Ceramics Intl.* **27**, 25-28.
- KEIL K. AND FUCHS L. H. (1971) Hibonite [Ca₂(Al,Ti)₂₄ O₃₈] from the Leoville and Allende chondritic meteorites. *Earth Planet. Sci. Lett.* 12, 184–190.

- KROT A. N., MCKEEGAN K. D., RUSSEL S. S., MEIBOM A., WEISBERG M. K., ZIPFEL J., KROT T. V., FAGAN T. J. AND KEIL K. (2001) Refractory calcium-aluminum-rich inclusions and aluminumdiopside-rich chondrules in the metal-rich chondrites Hammadah al Hamra 237 and Queen Alexandra Range 94411. *Meteorit. Planet. Sci.* 36, 1189–1216.
- KUZMENKO V. V., USPENSKAYA I. A. AND RUDNYI E. B. (1997) Simultaneous assessment of thermodynamic functions of calcium aluminates. *Bull. Soc. Chim. Belg.* 106, 235–243.
- MACPHERSON G. J., DAVIS A. M. AND ZINNER E. K. (1995) 26-Aluminum in the early solar system: A reappraisal. *Meteoritics* 30, 365–386.
- MEIBOM A., PETAEV M. I., KROT A. N., WOOD J. A. AND KEIL K. (1999) Primitive Fe,Ni metal grains in CH carbonaceous chondrites formed by condensation from a gas of solar composition. J. Geophys. Res. 104, 22 053-22 059.
- NURSE R. W., WELCH J. H. AND MAJUMDAR A. J. (1965) The CaO-Al₂O₃ system in a moisture free atmosphere. *Trans. British Ceramic Soc.* 64, 409–418.
- OSBORNE E. F. AND MUAN A. (1960) Phase Equilibrium Diagrams Of Oxide Systems. The System CaO-Al₂O₃-SiO₂. American Ceramic Society and the Edward Orton Jr. Ceramic Foundation, Columbus, Ohio, USA. Plate I.
- PETAEV M. I. AND WOOD J. A. (1998) The condensation with partial isolation (CWPI) model of condensation in the solar nebular. *Meteorit. Planet. Sci.* 33, 1123–1137.
- PETAEV M. I., BARSUKOVA L. D., LIPSCHUTZ M. E., WANG M-S., ARISKIN A. A., CLAYTON R. N. AND MAYEDA T. K. (1994) The Divnoe meteorite: Petrology, chemistry, oxygen isotopes and origin. *Meteoritics* 29, 182–199.
- PETAEV M. I., MEIBOM A., KROT A. N., WOOD J. A. AND KEIL K. (2001) The condensation origin of zoned metal grains in Queen Alexandra Range 94411: Implications for the formation of the Bencubbin-like chondrites. *Meteorit. Planet. Sci.* 36, 93–106.

- PETAEV M. I., WOOD J. A., MEIBOM A., KROT A. N. AND KEIL K. (2002) The ZONMET thermodynamic and kinetic model of metal condensation. *Geochim. Cosmochim. Acta* (in press).
- RANKIN G. A. AND MERWIN H. W. (1916) The ternary system CaO-Al₂O₃-MgO. J. Am. Chem. Soc. 38, 568–588.
- SRINIVASAN G., ULYANOV A. A. AND GOSWAMI J. N. (1994) ⁴¹Ca in the early solar system. Astrophys. J. Lett. 431, L67–L70.
- ULYANOV A. A., KONONKOVA N. N., YAKOVLEV O. I. AND KOROVKIN M. A. (1990) About the calcium aluminates in refractory inclusions of the Efremovka meteorite (in Russian). *Meteoritika* 49, 92–104.
- WARK D. A. AND BOYNTON W. V. (2001) The formation of rims on calcium-aluminum-rich inclusions: Step I—Flash heating. *Meteorit. Planet. Sci.* 36, 1135–1166.
- WEBER D. AND BISCHOFF A. (1994) The occurrence of grossite (CaAl₄O₇) in chondrites. *Geochim Cosmochim. Acta* 58, 3855–3877.
- WEBER D., ZINNER E. AND BISCHOFF A. (1995) Trace element abundances and magnesium, calcium, and titanium isotopic compositions of grossite-containing inclusions from the carbonaceous chondrite Acfer 182. Geochim. Cosmochim. Acta 59, 803-823.
- WEISBERG M. K. AND PRINZ M. (1999) Zoned metal in the CR clan chondrites. Proc. NIPR Symp. Antarct. Meteorites 30, 189–190.
- WEISBERG M. K., PRINZ M., CLAYTON R. N., MAYEDA T. K., GRADY M. M. AND PILLINGER C. T. (1995) The CR chondrite clan. Proc. NIPR Symp. Antarct. Meteorites 8, 11–32.
- WOOD J. A. AND HASHIMOTO A. (1993) Mineral equilibrium in fractionated nebular systems. Geochim. Cosmochim. Acta 57, 2377–2388.
- YONEDA S. AND GROSSMAN L. (1995) Condensation of CaO-MgO-Al₂O₃-SiO₂ liquids from cosmic gases. *Geochim. Cosmochim. Acta* **59**, 3413–3444.