

# Agglomeratic olivine (AO) objects and Type II chondrules in ordinary chondrites: Accretion and melting of dust to form ferroan chondrules

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## Abstract

Agglomeratic olivine objects (AO objects) and possibly related chondrules in three ordinary chondrites (NWA 4910 [LL3.1], NWA 3127 [LL3.1], Sahara 98175 [LL3.5]) were studied using petrographic and microanalytical techniques to evaluate the origins of these materials. AO objects are mixtures of fine-grained ( $\leq 5\text{--}10\ \mu\text{m}$ -diameter) ferroan (Fa<sub>12–35</sub>) olivine, troilite that is often concentrated towards the periphery of objects, pyroxene, feldspathic material, relict magnesian olivine and pyroxene grains, and relict chondrules. One micro-CAI with a grossite core was also found. AO objects commonly rim chondrules. AO objects show transitional variations in texture and chemistry with Type II chondrules, ranging from AO objects that are finer grained and show no evidence of melting (AO-U objects), to weakly melted and more melted AO objects (AO-WM and AO-M objects, respectively), to fine-grained Type II chondrules (olivine grain size  $\sim 5\text{--}60\ \mu\text{m}$ ), to coarse-grained Type II chondrules (olivine grain size  $\sim 10\text{--}250\ \mu\text{m}$  across); S contents and Na/Al values are typically higher in AO objects than in Type II chondrules. The properties of AO objects and Type II chondrules are interpreted to reflect progressive heating of dust of quasi-chondritic composition, accompanied by grain coarsening during melting, partial loss of the most volatile elements (chiefly S, also Na) during evaporative melting, and back-reaction with gas, to form troilite-rimmed AO objects. Data-model comparisons suggest that progressive heating of chondritic dust to form AO objects and Type II chondrules could have occurred in a dusty environment to yield a transient, oxidizing gas of high pressure ( $\sim 10^{-3}$  bar), with gas derived from vaporized dust being much ( $>500\text{--}1000\times$  or even up to  $10^4\text{--}10^5\times$ ) more abundant than ambient solar composition gas. AO objects are protochondrules, but are themselves composed of chondrule debris of different types, suggesting that they represent one step of a chondrule recycling process that also included chondrule disaggregation and additional chemical processing. Our data appear to be compatible with the nebular shock wave model for chondrule formation.

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## 1. INTRODUCTION

Ordinary chondrites contain olivine-rich inclusions that appear to have formed primarily as aggregates of fine-grained ferrous olivine together with xenocrystic grains and rare CAIs (Weisberg and Prinz, 1994, 1996). Such

inclusions have a granular or ‘protoporphyritic’ texture (Hewins et al., 1997) and typically appear nearly opaque in petrographic thin sections using transmitted light, owing to fine grain size and high troilite content (Weisberg and Prinz, 1994, 1996). They can be ‘dark zoned’ with margins that are especially opaque in transmitted light, owing to a high concentration of peripheral sulfide (Dodd and Van Schmus, 1971). The inclusions have been termed agglomeratic chondrules (Van Schmus, 1969; Weisberg and Prinz, 1994, 1996; Connolly and Love, 1998), and they comprise  $\sim 5\%$  of the chondrule population in ordinary chondrites

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(Weisberg and Prinz, 1994) or ~2% of ordinary chondrites overall (Weisberg and Prinz, 1996). Such inclusions might be suitable precursors to chondrules (Weisberg and Prinz, 1996; Hewins, 1997; Hewins et al., 1997).

These inclusions have sizes similar to typical chondrules but differ from them in being finer-grained and in displaying more evidence for accretion than melting (Van Schmus, 1969; Weisberg and Prinz, 1996; Hewins et al., 1997). We will show that similar material is also present as fine-grained rims of obvious accretionary origin around cores composed of typical chondrules. Thus, we refer to inclusions and rims containing these materials as agglomeratic olivine objects or simply ‘AO objects’. Specifically, we define AO objects to be composed chiefly of fine-grained ( $\leq 5$ – $10 \mu\text{m}$  diameter) olivine ( $\text{Fa}_{12-35}$ ), with textures suggestive of incipient melting, that may be present as chondrule-sized inclusions or as rims around chondrules.

The overall goals of this study are to evaluate: (1) the origin of AO objects; (2) the relationship of AO objects to typical ferromagnesian chondrules; and (3) implications for the origin of chondrules.

This study involved the use of optical light microscopy (OLM), scanning electron microscopy (SEM), electron microprobe analysis (EMPA), and secondary ion mass spectrometry (SIMS) to analyze AO objects and chondrules in three weakly metamorphosed LL ordinary chondrites (NWA 4910, NWA 3127, Sahara 98175). The three chondrites span a range of low-to-moderate subtypes, including LL3.1 for NWA 4910 (also known informally as ‘Begaa’; Okazaki and Nakamura, 2005; Weisberg et al., 2009), LL3.1 for NWA 3127 (Russell et al., 2005), and LL3.5 for Sahara 98175 (Grossman, 1999). This provides an

opportunity for distinguishing primary (nebular) and secondary (metamorphic) features. Chondrules in NWA 3127 and Sahara 98175 were previously studied for trace elements (Ruzicka et al., 2008). Ours is the first study to characterize the trace element compositions of AO objects. Preliminary results were presented in abstract form (Ruzicka et al., 2010; Ruzicka and Hutson, 2011).

## 2. SAMPLES AND METHODS

Table 1 provides data concerning the materials and objects that were studied. *Electronic Annex AE-1* provides additional petrographic data. Objects of interest in the sections were identified and characterized at Portland State University (PSU), using a Leica DM2500 petrographic microscope, and backscattered electron (BSE) imaging using a JEOL JSM-35C SEM. Petrographic data were used to select areas for subsequent *in situ* chemical analyses. EMPA was used to analyze major- and minor-elements using a Cameca SX-100 electron microprobe at Oregon State University, via remote access from PSU, and trace elements were analyzed by SIMS using the modified Cameca ims-3f ion microprobe at Washington University, according to techniques described by Zinner and Crozaz (1986a). Both EMPA and SIMS analyses were obtained using ‘narrow-beam’ (1- $\mu\text{m}$ -diameter EMPA, 15–20- $\mu\text{m}$ -diameter SIMS) and ‘broad-beam’ (40–50- $\mu\text{m}$ -diameter EMPA and SIMS) conditions. As many of the objects that we studied are fine-grained (with grain diameters typically  $\leq 5$ – $10 \mu\text{m}$ ), broad-beam analyses provide estimates of local bulk compositions. Broad or ‘defocused’ beam EMPA data (DB-EMPA) for objects were obtained using a combination

Table 1

Characteristics of agglomeratic olivine (AO) objects, Type II chondrules, and ultra fine-grained matrix lumps in ordinary chondrites NWA 4910, NWA 3127, and Sahara 98175.

Type	Igneous texture?	Olivine grain diameter ( $\mu\text{m}$ ) <sup>b</sup>	Feldspathic areas, diameter ( $\mu\text{m}$ ) <sup>b</sup>	Bulk composition	Objects <sup>a</sup>
AO-U [‘unmelted’]	No	$\leq 5$	Not apparent, to $\leq 1$ –3	Often S-enriched	Beg-3, Beg-4 outer rim, Beg-6 rim, Beg-16 outer rim, Beg-16A, Beg-17X rim, NWA-11 outer rim, NWA-11A rim, NWA-11C rim, Sah98-3 rim
AO-WM [‘weakly melted’]	Variable	$\leq 5$	$\leq 1$ –3, to not apparent	Often S-enriched	Beg-1 rim, Beg-2, Beg-7, Beg-13 rim, Beg-14 rim, Beg-16 inner rim, NWA-11 inner rim, Sah98-3A rim, Sah98-4B rim, Sah98-12 core, Sah98-12 rim, Sah98-13 rim
AO-M [‘melted’]	Yes	$\leq 10$	$\leq 2$ –12 (glass)	Often S-enriched	Beg-4 inner rim, Beg-8, Beg-10 <sup>c</sup> , Beg-16 inner rim, Beg-17, Sah98-3A core
Fine II	Yes	5–60	$\leq 2$ –15 (glass)	Depleted in S and Na	Beg-6 core, Beg-13 core <sup>d</sup> , Beg-14 core, Beg-18A, NWA-11A core, NWA-21, Sah98-3 core, Sah98-4B core <sup>e</sup> , Sah98-5
Coarse II	Yes	10–250	$\leq 12$ –50 (glass)	Depleted in S and Na	Beg-1 core, Beg-4 core, Beg-5, Beg-11 (coarse object), Beg-15, Beg-16 core, Beg-17X core, NWA-6, NWA-11 core, NWA-15 core, Sah98-13 core
Ultrafine matrix lumps	No	$\leq 1$	Not obvious	Fractionated	Beg-12, Beg-17A

<sup>a</sup> Object designations: Beg = NWA 4910, also known informally as ‘Begaa’ (Okazaki and Nakamura, 2005) (PTS CML0379-A), NWA = NWA 3127 (PTS CML0248-A), Sah98 = Sahara 98175 (PTS CML0278-B). Polished thin sections (PTSs) are available at the Cascadia Meteorite Laboratory.

<sup>b</sup> Olivine predominant grain diameters, and approximate diameters of feldspathic areas, as observed in PTS.

<sup>c</sup> Pyroxene-rich object.

<sup>d</sup> Fine-grained Type I chondrule.

<sup>e</sup> Contains zoned, mostly ferroan olivine and magnesian pyroxene and appears to be transitional between Types I and II.

of traverses and targeted analyses in the objects. The composition of each DB-EMP analysis was corrected for the unequal-density-effect (Nazarov et al., 1982; Warren, 1997) using the procedure of Warren (1997). Mineral proportions were calculated for each DB-EMP analysis using a norm calculation that was tailored to minerals in ordinary chondrites. For comparison to AO and chondrule data, a version of the CWPI thermodynamic code (Petaev and Wood, 1998, 2005) was used to model equilibrium condensate compositions. All CI-normalized plots utilize the average CI chondrite data of Anders and Grevesse (1989). Plots showing elements arranged by condensation temperatures are based on the work of Lodders (2003), except that the relative order of condensation temperatures for Na and K were switched consistent with results from the CWPI code. Further details on experimental methods are given in the Appendix.

### 3. RESULTS

Textures of AO objects and possibly related chondrules are illustrated in Figs. 1–3, and petrographic and chemical data for these objects are given in Tables 1–3. Supplementary data are provided in an Electronic Annex (Appendix B) and include (1) petrographic and olivine EMPA chemical data for all 32 objects studied in detail (Table EA-1-1); (2) bulk chemical and normative compositions for objects based on DB-EMP analysis (Table EA-1-2); and (3) trace-element data (Tables EA-2-1 and EA-2-2).

#### 3.1. Petrography

The objects studied show a range of textures (Fig. 1). They can be classified as (a) AO objects (Fig. 1a), (b) fine Type II chondrules (Fig. 1b), (c) coarse Type II chondrules (Fig. 1c), and (d) ultrafine matrix lumps (Fig. 1d). Characteristics of these objects are summarized in Table 1 and are described below.

##### 3.1.1. AO objects

AO objects are composed of fine-grained ( $\leq 5\text{--}10\ \mu\text{m}$ -grain-diameter) ferrous olivine ( $\text{Fa}_{12\text{--}35}$ ), troilite, pyroxene, feldspathic material, metal, and distinctly magnesian olivine ( $\text{Fa}_{0.7\text{--}12}$ ) and pyroxene grains (Figs. 1a and 2). The magnesian grains are likely xenocrysts (relict grains) and are as identified as such both by their distinctive compositions and also by their coarser grain sizes and irregular grain shapes. Ferrous olivine grains show either no zoning or are zoned with magnesian cores. Troilite is commonly concentrated on object peripheries (Fig. 2a–f). AO objects often contain well-defined clumps of coarser material that have microporphyritic (in one case, barred olivine) textures, which appear to be relict microchondrules (Fig. 2c, e and g). AO objects can form both inclusions and rims on chondrules (Figs. 2 and 3). We categorize AO objects into three transitional stages, including (a) unmelted AO objects (AO-U), (b) weakly melted AO objects (AO-WM), and (c) melted AO objects (AO-M).

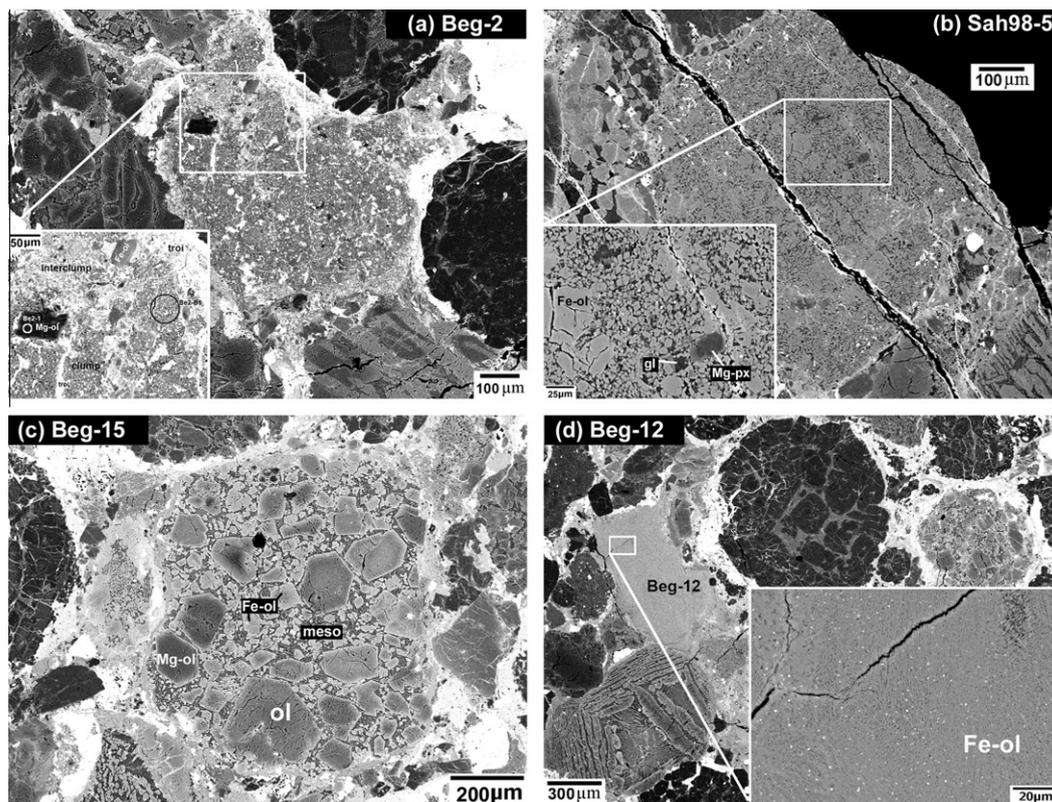


Fig. 1. BSE images showing examples of various types of objects. (a) AO object Beg-2. (b) Fine Type II chondrule Sah98-5. (c) Coarse Type II chondrule Beg-15. (d) Ultrafine matrix lump Beg-12. Circles in part a indicate SIMS analysis locations. Abbreviations: ol = olivine; troi = troilite; px = pyroxene; gl = glass; meso = mesostasis.

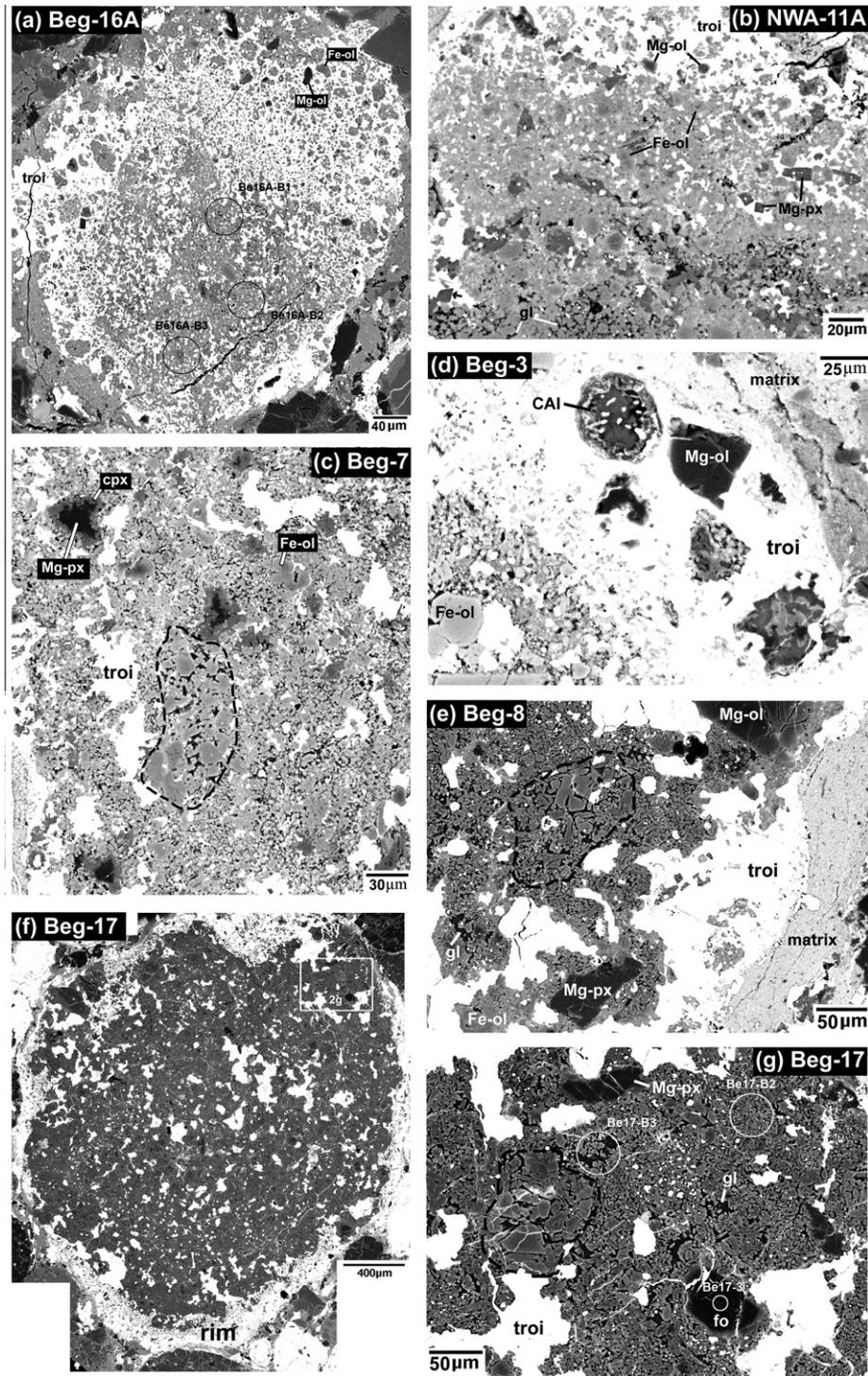


Fig. 2. BSE images of AO objects. (a) Beg-16A, a Type AO-U object containing a prominent troilite-enriched periphery composed of 'network troilite'. Circles show the locations of broad beam SIMS analyses. (b) NWA-11A, showing a thick AO-U rim between a fine Type II chondrule core (at bottom) and a troilite-enriched periphery (top). Some magnesian low-Ca pyroxene grains (Mg-px at right, arrow at lower left) have idiomorphic faces against troilite, as do Fe-ol grains (not visible in image). (c) Beg-7, an AO-WM object containing a relict chondrule (dashed line) and irregularly-shaped cores of magnesian low-Ca pyroxene (Mg-px) surrounded by coronas of augite (cpx). (d) Portion of AO-U object Beg-3, showing a CAI, forsterite clast, and other apparent fragments embedded in troilite along the edge of the object, and a portion of the interior containing fine and coarser grains (lower left). (e) Beg-8, an AO-M object showing a relict chondrule (dashed lines) and glass. (f) Beg-17 is a large AO-M object that contains a troilite-rich rim. The box shows the region magnified in part g. (g) Closer view of Beg-17 showing a relict chondrule (dashed lines), glassy mesotaxis, and the locations of SIMS analyses (circles). Abbreviations as in Fig. 1.

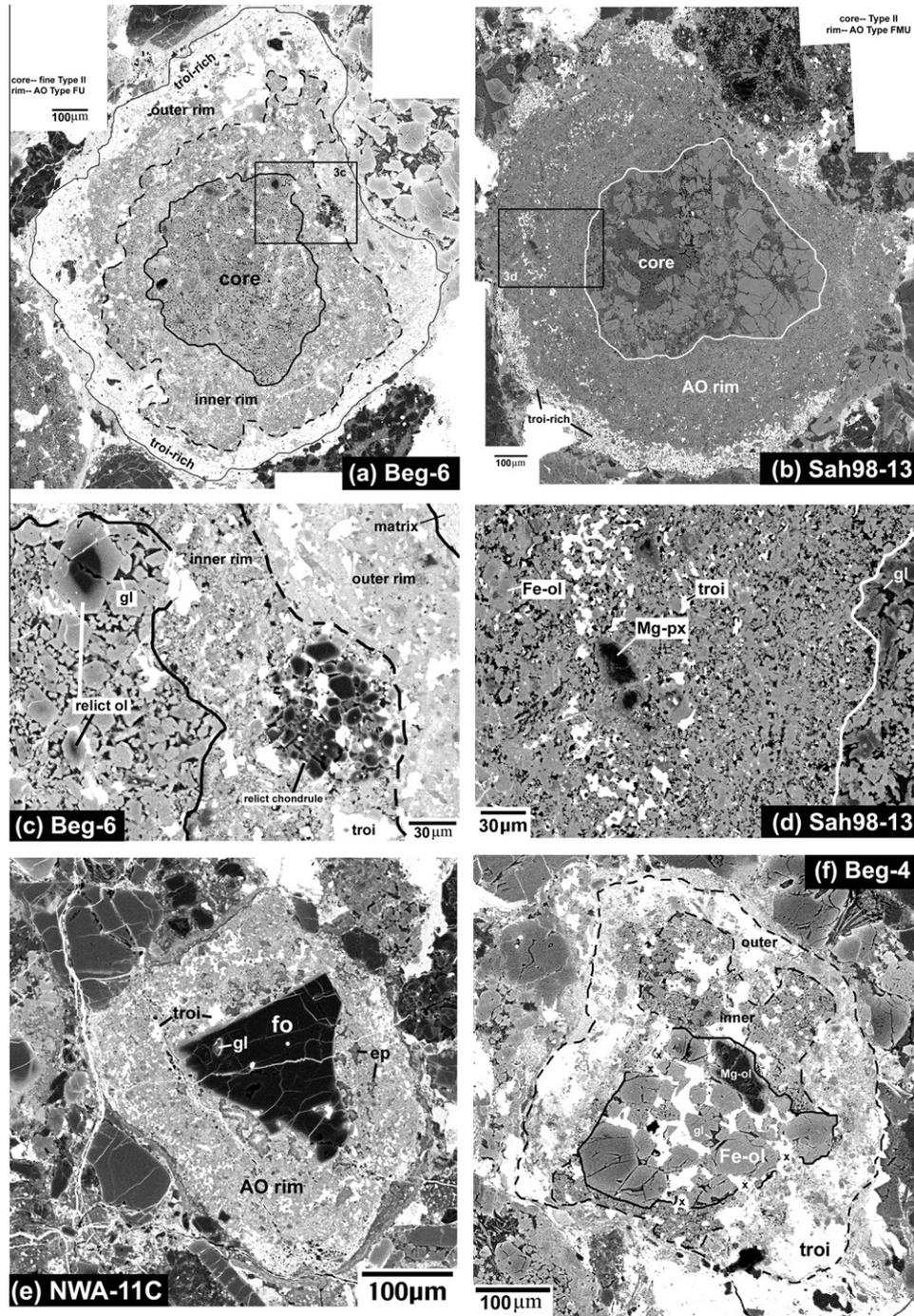


Fig. 3. BSE images of AO rimming features. (a) Beg-6 is a classic ‘dark zoned object’ that contains a fine Type II core surrounded by an inner and outer AO rim. Troilite is concentrated in the outermost portion of the outer rim. The box shows a region magnified in part c. (b) Sah98-13 contains a coarse Type II chondrule core surrounded by a thick AO rim. Troilite is concentrated in the outermost part of the rim. The box shows a region magnified in part d. (c) Close-up of Beg-6 showing the fine Type II core at left (with relict olivine grains), the inner AO-U rim which contains a relict Type I chondrule, and the outer AO-U rim that has a different texture. (d) Close-up of the AO-WM rim in Sah98-13, showing numerous feldspathic patches (dark spots), a partial concentric band of troilite, a relict grain of magnesian low-Ca pyroxene (Mg-px), and a portion of the coarse Type II core (extreme right). (e) NWA-11C contains an obvious accretionary AO-U rim that surrounds an angular forsterite grain. Glass inclusions occur in the forsterite. ep = epoxy in partially plucked areas. (f) Beg-4 has two different types of AO rims that surround a small coarse Type II chondrule core (with has a prominent relict Mg-ol grain). An outer AO-U rim largely surrounds the object; two patches of a coarser-grained inner AO-M rim are also present. Troilite has replaced mesostasis glass in the core. In a few locations (marked by x), troilite appears to cross over the edge of the core into the AO rim. Abbreviations as in Fig. 1.

Table 2  
Bulk composition and norms of AO objects and Type II chondrules.<sup>a</sup>

Type	AOs, all types <i>N</i> = 23		Fine Type II <i>N</i> = 9		Coarse Type II <sup>b</sup> <i>N</i> = 6	
	Mean (s.d.)	Range	Mean (s.d.)	Range	Mean (s.d.)	Range
<i>at.</i>						
Mg#	0.72 (0.08)	0.51–0.87	0.70 (0.08)	0.61–0.85	0.70 (0.12)	0.47–0.84
Na/Al	0.49 (0.25)	0.11–0.91	0.28 (0.14)	0.16–0.56	0.20 (0.04)	0.14–0.24
S/Al	18.5 (30.8)	0.09–122	0.44 (0.34)	0.04–1.08	0.22 (0.20)	0.06–0.60
<i>wt%</i>						
SiO <sub>2</sub>	27.2 (9.26)	7.88–42.7	36.8 (4.8)	29.3–46.9	38.9 (3.9)	32.9–45.0
Al <sub>2</sub> O <sub>3</sub>	1.69 (0.95)	0.33–4.62	2.15 (1.07)	0.86–4.57	2.55 (1.36)	1.23–4.79
Cr <sub>2</sub> O <sub>3</sub>	0.58 (0.35)	0.08–1.83	0.71 (0.23)	0.30–1.18	0.52 (0.11)	0.36–0.65
FeO	14.7 (6.5)	3.80–31.8	19.4 (5.3)	8.37–22.3	18.3 (4.8)	14.2–26.5
MnO	0.25 (0.07)	0.12–0.33	0.32 (0.06)	0.22–0.40	0.35 (0.06)	0.25–0.42
MgO	18.2 (5.4)	5.93–25.6	26.3 (4.5)	19.8–36.1	25.3 (7.7)	15.5–38.2
CaO	1.76 (1.27)	0.28–5.38	1.87 (1.09)	0.28–4.11	1.92 (1.31)	0.37–4.22
Na <sub>2</sub> O	0.45 (0.28)	0.05–1.28	0.34 (0.19)	0.17–0.60	0.33 (0.22)	0.14–0.69
Ni	1.58 (0.95)	0.16–3.55	0.85 (1.08)	0.12–3.57	1.04 (1.32)	0.05–3.37
S	9.17 (7.72)	0.25–27.2	0.58 (0.51)	0.12–1.62	0.27 (0.14)	0.07–0.46
Cl	<0.01 (0.01)	<0.01–0.03	0.01 (0.01)	<0.01–0.03	0.01 (0.01)	<0.01–0.02
Fe (troilite)	15.9 (13.4)	0.43–47.4	1.01 (0.90)	0.21–2.82	0.46 (0.24)	0.12–0.81
Fe (metal)	3.67 (2.30)	0.40–8.82	2.19 (2.68)	0.30–8.87	2.08 (2.28)	0.13–5.32
Total	95.1 (3.5)	86.4–100.8	92.5 (2.5)	88.8–96.4	92.1 (3.6)	86.2–97.6
<i>Norm (vol%)</i>						
Olivine	48.7 (17.5)	18.9–91.6	66.5 (19.0)	28.4–89.9	57.6 (19.6)	23.2–82.1
Orthopx	10.7 (11.6)	<0.01–45.6	15.4 (13.9)	1.60–43.1	25.3 (10.8)	12.1–45.0
Clinopx	5.75 (4.70)	<0.01–18.4	4.54 (3.67)	0.13–10.4	4.08 (3.33)	0.57–9.48
Plagioclase	8.82 (4.36)	1.99–20.4	9.81 (4.54)	3.00–18.7	10.2 (6.36)	3.19–21.0
Sodalite	0.03 (0.07)	<0.01–0.27	0.08 (0.10)	0.02–0.32	0.10 (0.08)	0.02–0.22
Chromite	0.66 (0.41)	0.11–2.14	0.79 (0.25)	0.33–1.29	0.57 (0.12)	0.39–0.69
Metal	2.75 (1.78)	0.27–6.77	1.61 (2.32)	0.18–7.60	1.61 (1.84)	0.08–4.2
Troilite	22.6 (20.0)	0.54–71.5	1.27 (1.10)	0.25–3.48	0.58 (0.31)	0.16–1.0

*N* = number of objects averaged and included in range; s.d. = standard deviation; Orthopyx = low-Ca pyroxene (enstatite + ferrosilite); Clinopx = high-Ca pyroxene (diopside + hedenbergite); Chromite = FeCr<sub>2</sub>O<sub>4</sub> + MgCr<sub>2</sub>O<sub>4</sub>; Metal = FeNi metal alloy. Norm adds to 100% within rounding error.

<sup>a</sup> Based on corrected defocused beam electron microprobe data. Totals are often low owing to pits and surface irregularities in the analysis volumes.

<sup>b</sup> Excludes Beg-4 and Beg-5 which have low, possibly unrepresentative, mesostasis fractions.

*AO-U objects* are composed mainly of anhedral olivine grains  $\leq 5 \mu\text{m}$  across and mostly lack feldspathic (possibly glassy) areas. Examples are Beg-16A (Fig. 2a), much of NWA-11A (Fig. 2b), and Beg-3 (Fig. 2d). All these objects contain ‘network’ troilite that compactly fills spaces between silicate grains, increasing in abundance towards the object edges. Beg-3 notably contains a layered micro-CAI, the only one found in our study, composed of a core of grossite (CaAl<sub>4</sub>O<sub>7</sub>) and perovskite (Fig. 2d).

*AO-WM objects* are composed mostly of anhedral-subhedral olivine grains  $\leq 5 \mu\text{m}$  across with a substantial proportion of feldspathic, possibly glassy domains ( $\leq 1\text{--}5 \mu\text{m}$  wide). Examples include Beg-2 (Fig. 1a) and Beg-7 (Fig. 2c). Beg-7 contains some irregularly-shaped relict magnesian low-Ca pyroxene grains that have overgrowths ( $\sim 5\text{--}10 \mu\text{m}$  wide) of augitic pyroxene (Fig. 2c). Similar high-Ca pyroxene (augite or pigeonite) overgrowths are seen in all AO object types, but they are not present in the chondrules we studied.

*AO-M objects* are slightly coarser (olivine grains  $\leq 10 \mu\text{m}$  in diameter) and show clear textural evidence for melting,

with feldspathic glassy regions up to  $\sim 2\text{--}12 \mu\text{m}$  wide occurring interstitial to euhedral-subhedral olivine and low-Ca pyroxene grains. Examples include Beg-8 (Fig. 2e) and Beg-17 (Fig. 2f and g), the latter being the largest AO object observed ( $\sim 2.5 \times 3.0 \text{ mm}$  across). Troilite in these inclusions tends to form more compact masses than the more distributed network structures in Type AO-U (compare Fig. 2f and a). Moreover, AO-M objects contain drop-formed masses of metal and troilite consistent with melting (Fig. 2g). Other objects similar to AO-M but containing more magnesian grains are present in the meteorites (e.g., Beg-9).

### 3.1.2. Type II chondrules

Type II chondrules have microporphyrritic textures and come in two textural varieties, fine Type II and coarse Type II. These chondrules contain less troilite than the AO objects described above, but like them most are dominated by ferroan olivine and contain relict magnesian olivine and low-Ca pyroxene grains.

Table 3

Representative (col. 1–5, 7–8, 10–11) and average (6, 9, 12) trace element compositions of fine-grained multi-phase areas in AO objects and Type II chondrules determined by broad beam SIMS.

Object	Relatively unfractionated <sup>1</sup>						Incompatible-element-rich <sup>2</sup>			Ca-REE-poor <sup>3</sup>		
	(1) Beg-2 AO-WM N Analysis	(2) Beg-16A AO-U 3 b	(3) Beg-17 AO-M 1 Be17-B2	(4) Sah98-5 Fine II 2 c	(5) NWA-15 Coarse II 2 d	(6) Mean (s.d.)	(7) Beg-17 AO-M 1 Be17-B3	(8) Beg-8 AO-M 2 e	(9) Mean (s.d.)	(10) Sah98-5 Fine II 1 S5-B3	(11) Sah98-12 AO-WM 3 f	(12) Mean (s.d.)
Na, mg/g	9.97	3.85	10.9	9.05	5.08	6.30 (3.60)	25.4	19.9	16.1 (6.1)	9.02	15.7	6.30 (3.60)
Mg, wt%	17.9	18.2	20.5	18.5	14.7	16.7 (3.0)	10.7	12.2	15.8 (3.3)	19.1	20.7	19.8 (1.9)
Al, wt%	1.32	0.931	1.78	1.70	1.93	1.34 (0.38)	3.72	2.16	2.24 (0.62)	1.84	1.87	1.76 (0.19)
Si, wt%	16.3	13.7	20.3	16.6	17.4	15.0 (2.4)	20.3	15.4	18.3 (2.5)	16.6	17.3	16.8 (1.6)
P, µg/g	1350	1440	478	980	1090	1090 (330)	500	1060	1020 (510)	1200	940	992 (117)
K, mg/g	1.37	0.432	1.60	1.57	0.595	0.868 (0.480)	3.51	2.47	2.30 (0.55)	1.60	1.90	1.66 (0.79)
Ca, wt%	1.12	1.27	1.32	1.42	1.53	1.14 (0.46)	1.73	1.02	1.54 (0.48)	0.525	0.238	0.350 (0.142)
Sc, µg/g	6.62	6.82	8.27	7.97	8.95	7.21 (1.56)	8.15	7.02	8.39 (0.85)	7.31	4.95	6.00 (1.29)
Ti, µg/g	601	581	744	641	896	631 (112)	1350	936	1010 (190)	466	496	513 (180)
V, µg/g	65.0	61.7	81.7	78.8	72.2	68.9 (28.3)	61.0	51.7	72.9 (16.1)	48.0	80.8	69.8 (36.8)
Cr, mg/g	3.46	3.42	3.50	3.63	3.11	3.39 (1.69)	2.82	2.26	3.51 (1.07)	2.28	3.91	3.62 (1.77)
Mn, mg/g	3.00	3.15	3.89	3.22	2.87	2.93 (0.54)	2.52	2.42	2.85 (0.37)	3.32	3.73	3.69 (0.90)
Fe, wt%	21.5	42.6	11.6	22.0	18.0	29.9 (14.9)	8.36	11.6	16.2 (6.2)	25.1	28.3	30.3 (12.0)
Co, mg/g	0.424	0.647	0.191	0.0935	0.129	0.886 (1.345)	0.508	0.290	0.329 (0.212)	0.0935	0.0868	0.113 (0.092)
Ni, mg/g	11.2	12.6	4.35	5.18	1.90	11.7 (10.9)	4.90	5.76	4.57 (3.98)	7.90	10.2	8.61 (2.81)
Rb, µg/g	6.44	1.30	n.d.	5.06	3.91	3.84 (1.93)	n.d.	6.62	6.68 (2.01)	3.83	3.64	3.76 (0.78)
Sr, µg/g	12.8	32.9	10.7	12.8	17.4	17.4 (10.1)	16.8	14.2	14.8 (6.0)	28.8	15.5	17.9 (7.1)
Y, µg/g	2.16	2.34	2.64	2.46	2.20	2.33 (0.46)	5.03	3.55	3.73 (0.92)	1.41	0.892	1.20 (0.38)
Zr, µg/g	7.29	7.68	8.34	8.46	12.7	8.35 (1.95)	17.0	11.6	11.9 (3.0)	8.89	7.11	7.58 (1.38)
Ba, µg/g	2.45	4.27	2.89	3.82	3.80	3.13 (1.37)	6.52	5.10	3.78 (1.86)	6.77	4.97	5.35 (1.26)
La, ng/g	295	296	310	270	318	289 (74)	815	535	581 (137)	212	164	189 (36)
Ce, ng/g	798	709	957	676	804	762 (168)	2020	1460	1490 (400)	516	371	450 (110)
Pr, ng/g	114	114	139	109	131	116 (27)	316	215	222 (58)	79.9	47.0	57.9 (12.6)
Nd, ng/g	531	543	653	533	598	555 (112)	1360	1010	1040 (260)	338	237	288 (62)
Sm, ng/g	163	157	193	210	200	170 (32)	415	293	311 (71)	79.5	65.2	76.7 (12.2)
Eu, ng/g	43.4	73.5	38.5	65.3	86.9	56.6 (21.3)	104	90.1	83.1 (19.6)	78.8	43.6	52.8 (14.0)
Gd, ng/g	151	181	283	264	250	217 (54)	623	424	425 (100)	128	68.7	97.5 (29.4)
Tb, ng/g	36.7	41.0	62.6	56.0	52.9	45.0 (8.3)	101	83.6	81.2 (17.1)	33.1	15.5	21.6 (6.7)
Dy, ng/g	334	287	398	370	384	340 (61)	815	600	600 (127)	191	115	154 (39)
Ho, ng/g	72.2	56.3	78.0	81.1	77.9	71.9 (17.7)	139	122	130 (27)	43.6	26.1	38.1 (13.2)
Er, ng/g	206	202	273	269	240	228 (39)	467	390	403 (70)	164	86.6	118 (33)
Tm, ng/g	26.7	27.7	44.7	40.0	37.1	34.1 (8.7)	78.4	58.4	57.7 (13.8)	25.0	11.3	18.2 (8.7)
Yb, ng/g	207	217	270	268	239	242 (40)	469	368	395 (67)	187	108	142 (50)
Lu, ng/g	37.2	37.9	74.6	44.8	44.6	41.2 (11.4)	80.2	61.6	65.0 (11.2)	37.3	20.7	26.7 (8.5)

a: Mean of analyses Be2-B1, Be2-B2, Be2-B3. b: Mean of analyses Be16A-B1, Be16A-B2, Be16A-B3. c: Mean of analyses S5-B2, S5-B4. d: Mean of analyses N15-B1, N15-B2. e: Mean of analyses Be8-B2, Be8-B3. f: Mean of analyses S12-B1, S12-B2, S12-B3. Abbreviations as in Table 2, also n.d. = not determined.

<sup>1</sup> Unfractionated pattern: individual analyses have mean lithophile element abundances of  $\sim 1.0\text{--}1.7 \times \text{CI}$  chondrites with a coefficient of variation (CV) of 19–42%.

<sup>2</sup> IE-rich pattern: individual analyses have mean abundances of  $\sim 1.8\text{--}2.8 \times \text{CI}$ , CV  $\sim 29\text{--}46\%$ .

<sup>3</sup> Ca-REE poor pattern: individual analyses have 'a W' REE pattern, CV  $> 50\%$ .

*Fine Type II chondrules* are dominated by euhedral–subhedral olivine grains (Fa<sub>12–38</sub>) that range from ~5–60 μm but are mostly <25 μm across (Fig. 1b). Glass occurs interstitial to larger olivine grains, sometimes contains pyroxene crystallites, and is present in areas ≤2–15 μm wide. Most such objects can be described as fine Type IIA or IIAB chondrules, but one object with Fa<sub>4–6</sub> olivine (the core of Beg-13) is better described as a fine Type IA chondrule, and another with magnesian pyroxene and zoned ferrous olivine (Sah98-4B, with bulk Mg# ~0.85) is better described as being transitional between fine Type II and fine Type I.

*Coarse Type II chondrules* have coarser olivine grains (10–250 μm across) and wider glassy regions (up to ~50 μm) (Fig. 1c). In the coarse Type II chondrules analyzed here, olivine grains tend to be zoned with ferrous rims and magnesian cores (range Fa<sub>6.5–31</sub>) but are dominantly ferrous (Fa<sub>>10</sub>). Beg-15 (Fig. 1c) is typical in most respects, except that it appears to contain many relict grains that did not crystallize *in situ*, as there is no correlation between olivine grain size and grain core forsterite content, a correlation that would be expected if all grains crystallized from the same parent melt.

### 3.1.3. Ultrafine matrix lumps

For comparison to AO objects and chondrules, we also studied two inclusions (Beg-12, Beg-17A) that are much finer-grained (grains ≤1 μm across). These objects lack coarser material and in BSE images appear uniform (Fig. 1d). Beg-12 (Fig. 1d) is composed primarily of ferroan olivine; Beg-17A is composed primarily of ferroan low-Ca pyroxene. Both objects have irregular shapes and contain little sulfide. We term them ultrafine matrix lumps (Table 1). These objects are relatively uncommon and were found only in NWA 4910.

### 3.1.4. Rimming structures

AO objects of different types are present as rims (discrete outer portions) around fine Type II chondrules (Fig. 3a and c), coarse Type II chondrules (Fig. 3b, d and f), and coarse, isolated olivine grains (Fig. 3e). Contacts between the rims and core objects are relatively sharp in most cases (Fig. 3). AO objects that form rims around coarser objects are sometimes layered with sulfide-rich edges (Fig. 3a, b and f). Although AO-like rims typically surround ferroan core objects, they sometimes mantle magnesian cores, including fine Type I chondrules (Beg-13), transitional fine Type I–II chondrules (Sah98-4B), and individual forsterite grains (NWA-11C, Fig. 3e). No examples were found of AO material surrounding core objects more ferroan than the rims.

Some rims have more than one AO textural type. A good example of the latter is Beg-4 (Fig. 3f). For this object, an ‘inner rim’ of Type AO-M contains glass and is present as two lobes on opposite sides of the core, whereas an ‘outer rim’ of Type AO-U surrounds the entire object except in one location. Although the contacts between the core and two rim components are fairly sharp, troilite appears to extend across the core-outer rim contact in multiple locations (marked by ‘x’ in Fig. 3f). Troilite appears to have largely replaced the glassy mesostasis of the chondrule core

(Fig. 3f). Besides Beg-4, two other objects (NWA-11 and Beg-16) show similar layered AO rims around Type II chondrules, with outer AO-U and inner AO-M rims. Two other objects (Beg-1 and Beg-17X) show textural evidence of sulfide from AO margins replacing the glassy mesostases of Type II chondrule cores.

## 3.2. Bulk chemistry

### 3.2.1. Major and minor element bulk chemistry and norms (DB-EMPA)

Table 2 presents average bulk compositions and norms for AO objects and Type II chondrules, and Table EA-1-2 and Fig. EA-1-1 in the *Electronic Appendix* provide data for individual objects. Different textural types of AO objects (Section 3.1) have similar bulk composition and norms; the same is true for fine Type II and Type II chondrules. However, AO objects (all three types) on the one hand, and Type II objects (fine and coarse) on the other, differ from one another chemically. Normative and bulk chemical data for major elements are plotted in Figs. 4 and 5.

Troilite abundance is highly variable, but on average, AO objects contain ~22 vol% normative troilite compared to ~1–2 vol% in Type II chondrules (Table 2). Most AO objects are enriched in troilite compared to bulk LL chondrites, whereas the opposite is true for Type II objects (Fig. 4a). The silicate normative mineralogy of both AO and Type II objects is highly variable but similar in terms of overall range and average composition (Fig. 4a–b, Table 2).

CI-chondrite-normalized data for average AO object and Type II chondrule bulk compositions are shown in Fig. 5. The data indicate that AO and Type II objects in these LL chondrites have compositions that are variations on a bulk LL chondrite composition. On average, AO objects are enriched in Fe, Ni, and (especially) S and slightly depleted in lithophile elements compared to LL chondrites (Fig. 5a). Although the average AO composition is low in Na compared to LL chondrites, some AO objects have a chondritic composition for all measured elements (e.g., Beg-2, Fig. EA-1-1). Both fine Type II and coarse Type II chondrules, in contrast, are clearly depleted in S and Na compared to LL chondrites and have lower S/Al and Na/Al values than AO objects (Table 2, Fig. 5b and c). Thus, AO objects are chemically like LL chondrites with additional Fe and S (troilite) and metal (Fe and Ni) components (diluting silicates and lithophile elements), whereas Type II objects are chemically like LL chondrites that are depleted in the most volatile elements (Na, S).

### 3.2.2. Trace element chemistry of multiphase areas (broad beam SIMS)

Representative and averaged trace element compositions based on SIMS analyses of multiphase fine-grained constituents in AO objects and Type II chondrules are given in Table 3 and shown in Fig. 6. *Electronic Annex EA-2* provides more complete SIMS data as well as CI-normalized plots for some representative individual analyses (Tables EA-2-1 and EA-2-2, Fig. EA-2).

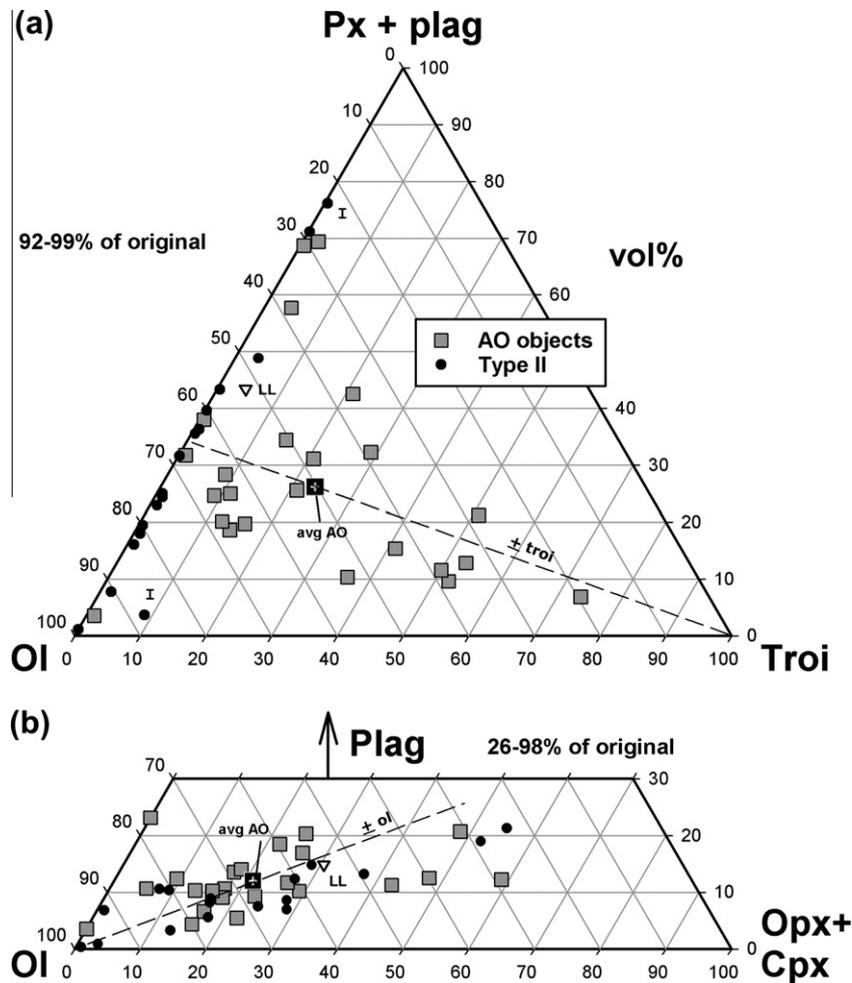


Fig. 4. Diagram illustrating the normative compositions of AO objects and Type II chondrules. The mean compositions of AO objects (this study) and LL chondrites (Jarosewich, 1990) are indicated. Abbreviations as in Fig. 1, and also plag = plagioclase; cpx = Ca-rich pyroxene; opx = low-Ca pyroxene; 'I' refers to objects better described as Type I or transitional Types I-II. (a) Ol-plag-(px + plag). A troil variation line through mean AO composition is shown for reference. The components shown represent 92-99% of the original total, with metal being the main missing component. (b) Ol-plag-(opx + cpx). An ol variation line through mean AO composition is shown for reference. The components shown represent 26-98% of the original total, with troilite being the main missing component.

Trace element compositions for fine-grained constituents display four different patterns. These can be characterized as (1) relatively unfractionated; (2) fractionated, incompatible element (IE)-enriched; (3) fractionated, Ca-REE-poor; and (4) fractionated, ultrafine lumps (Table 3, Fig. 6).

*Relatively unfractionated patterns* are most common for the fine-grained areas of AO objects (Fig. 6a). Similar patterns were also measured for fine-grained areas in some fine Type II chondrules and one coarse Type II chondrule (NWA-15). Lithophile element abundances for relatively unfractionated areas in AO and Type II objects average  $1.38 \pm 0.19 \times \text{CI}$  chondrites (mean and standard deviation, based on 31 analyses) (Fig. 6a). This is essentially identical to that of whole-rock ordinary chondrites (Kallemeyn et al., 1989; Lodders and Fegley, 1998), suggesting a chondritic overall composition.

*IE-enriched patterns* are characterized by enrichments in incompatible elements, including especially the REE, alkalis, Zr, Y, Al, and Ti (Fig. 6b). More compatible elements,

including Mg, V, Cr, Mn and Sc, are not enriched. Such patterns were obtained only for objects that contain glass in significantly large areas, namely AO-M objects and Type II chondrules, and not for AO-U or AO-WM objects. Clearly, the IE-enrichments can be explained as the result of igneous processes that resulted in a melt, which solidified as a glass analyzed by SIMS.

*Fractionated, Ca-REE-poor signatures* were obtained for some analyses of AO objects and fine Type II chondrules in Sahara 98175. These patterns are characterized by a 'W-shaped' REE pattern with relatively low abundances of REE except for a positive Eu anomaly, and large depletions in Ca and Co (Fig. 6c). A smaller depletion occurs for Y (Fig. 6c). As this pattern is seen only in Sahara 98175 (subtype 3.5) and not in the other two meteorites (subtype 3.1), it likely reflects a metamorphic effect. For this pattern, most elements that are relatively depleted (REE, Ca, Y) are known to partition in apatite, with equilibrium REE patterns for apatite being 'M' shaped (i.e., high middle REE contents with a negative Eu anomaly) (e.g., Watson and

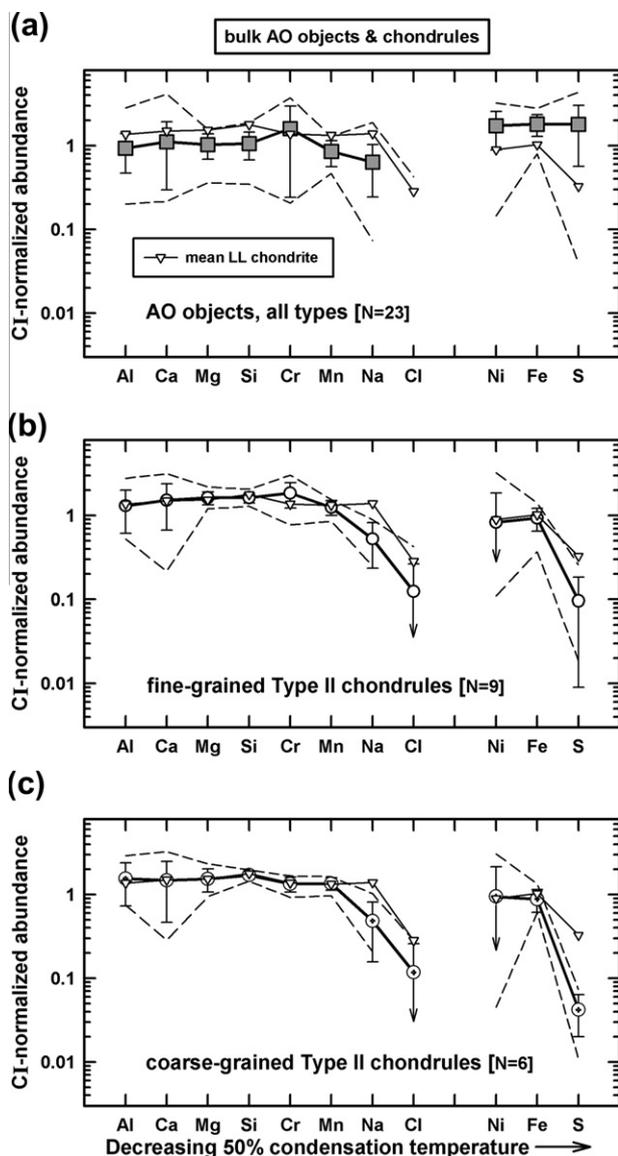


Fig. 5. CI-chondrite-normalized abundances for (a) AO objects, (b) fine Type II chondrules, and (c) coarse Type II chondrules, based on DB-EMPA data. Points show means, bars show standard deviations of the means, dashed lines indicate ranges.  $N$  = number of objects averaged. The mean LL chondrite composition is based on data from Jarosewich (1990).

Green, 1981; Fujimaki, 1986). The ‘M’ REE pattern is complementary to the ‘W’ pattern observed in the Sahara analyses. For AO objects and Type II chondrules, we suggest that metamorphic heating devitrified phosphate, which sequestered REE, Ca, Y, and possibly Co, depleting these elements elsewhere to give the observed Ca-REE-poor pattern.

The *fractionated, ultrafine lump pattern* obtained for lumps Beg-12 and Beg-17A is characterized by large fractionations, including enrichments in Mn and strong depletions in Ni, Co, and P (Fig. 6d). Moreover, Beg-12 has low abundances for Ca and Sr, and Beg-17A has low abundances of alkalis and Ba. The highly fractionated compositions of these fine matrix lumps are very different than the relatively

unfractionated compositions often obtained in AO objects and fine Type II chondrules, implying no simple genetic relationship between the lumps and the other objects.

### 3.3. Mineral chemistry

#### 3.3.1. Major and minor element olivine chemistry (EMPA)

AO and Type II objects contain olivine with similar major and minor element compositions. The average Fa contents of the ferroan olivine grains (excluding magnesian relict grains) are similar: for AO objects it is  $Fa_{21.4 \pm 7.0}$  (mean and standard deviation, based on 45 analyses in 12 objects), and for Type II objects it is  $Fa_{20.3 \pm 6.6}$  (based on 129 analyses, 17 objects).  $Cr_2O_3$ , MnO, and CaO contents in olivine also show similar distributions in AO objects and Type II chondrules (Fig. 7). Olivine in both object types shows: (a) maximum chrome contents at intermediate Fa values ( $\sim Fa_{14-24}$ ) (Fig. 7a); (b) a positive correlation between MnO and Fa contents (Fig. 7b); (c) a similar scatter pattern in a CaO–Fa variation diagram (Fig. 7c); and (d) evidence for the same three chemical populations of olivine in a CaO/MnO vs. Fa plot (Fig. 7d). The populations include: (1) a low-Fa, high-CaO/MnO, low- $Cr_2O_3$  ‘refractory’ population that often forms relict grains in the ferroan objects; (2) a ‘main’ population with intermediate Fa and intermediate CaO/MnO values and relatively high  $Cr_2O_3$  contents; and (3) a ‘refractory-poor ferroan’ population with high-Fa, low-CaO/MnO, and low- $Cr_2O_3$  values (Fig. 7). In the classification scheme of Sears et al. (1992, 1995), these three populations correspond to chondrule classes (1) A1 and A2; (2) A3, A4, B1 and B2; and (3) A5 and B3, respectively. Altogether, olivine compositions obtained with EMPA suggest a close relationship between AO objects and Type II chondrules.

#### 3.3.2. Trace element mineral chemistry (SIMS)

Trace-element compositions for olivine and low-Ca pyroxene in AO and Type II objects are given in Table 4 and shown as CI-normalized abundances in Fig. 8. Analyses are limited owing to fine grain size, and those for AO objects reflect atypically coarse grains ( $>15 \mu m$  across) in the objects. In Fig. 8, elements are arranged according to volatility (50% condensation temperatures) for cooling-insensitive elements, and according to cooling-rate-sensitivity (CRS) for cooling-sensitive (CS) elements (Ruzicka et al., 2008). This acknowledges that olivine and low-Ca pyroxene which are grown from rapidly cooled (i.e.,  $2000^\circ C/h$ ) melts have elevated concentrations of CS elements that reflect disequilibrium (Kennedy et al., 1993).

Fig. 8a shows no obvious differences in the trace-element composition of olivine in different types of objects, although an isolated forsterite grain (the core object of NWA-11C, analysis N11C-1) forms a distinctive endmember enriched in refractory lithophile elements (Sc, Y, Al, Ti, Ca), depleted in volatile lithophile elements (Cr, P, Mn, Rb), and depleted in siderophile elements (Ni, Co). For all olivine analyses, there is a tendency for the abundances of CS elements (Na–La) to increase with CRS (Fig. 8a). The data imply that coarser olivine grains in AO objects, fine Type II chondrules, and coarse Type II

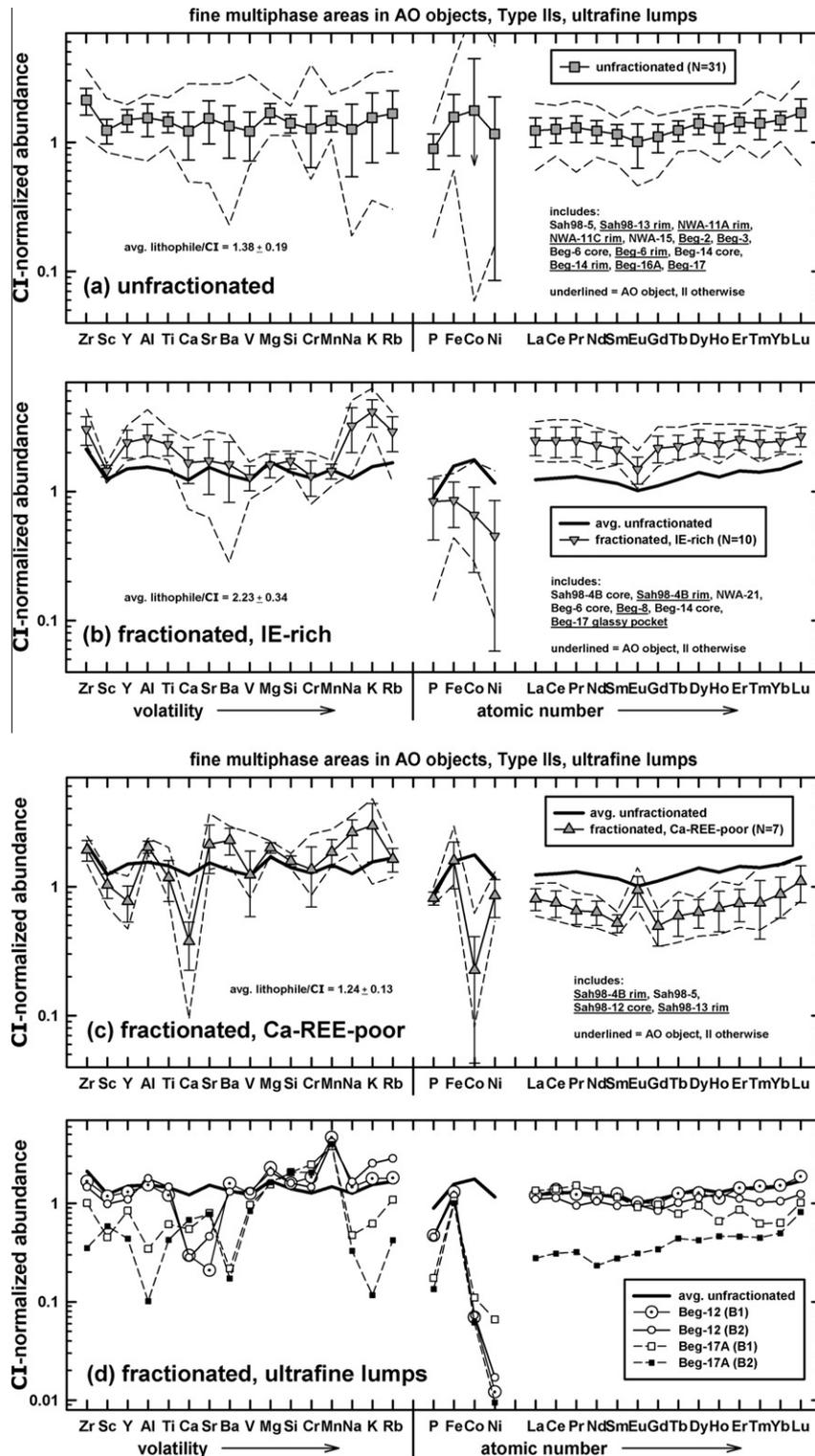


Fig. 6. CI-chondrite-normalized abundances for fine-grained multiphase areas in AO objects, Type II chondrules, and ultrafine matrix lumps, based on broad beam SIMS data. (a) Analyses of ‘unfractionated’ areas are characterized by lithophile mean abundances of  $\sim 1\text{--}1.7 \times$  CI chondrites with a coefficient of variation among different lithophile elements of 19–42%. (b) Analyses of ‘fractionated, incompatible-element-rich’ (IE-rich) areas are characterized by lithophile mean abundances of  $\sim 1.8\text{--}2.8 \times$  CI with a coefficient of variation among different lithophile elements of 29–46%. (c) Analyses of ‘fractionated, Ca-REE-poor’ areas are characterized by a ‘W’-shaped REE pattern, generally low abundances of REE, Ca, and Co, and a coefficient of variation among different lithophile elements of  $>50\%$ . (d) Analyses of ‘fractionated, ultrafine matrix lumps’ show fractionated abundances in lumps, with a coefficient of variation among lithophile elements of  $>50\%$ . Parts a–c show averaged data (points indicate means, bars indicate standard deviations, dashes indicate ranges,  $N$  = number of analyses averaged), whereas part d shows individual analyses.

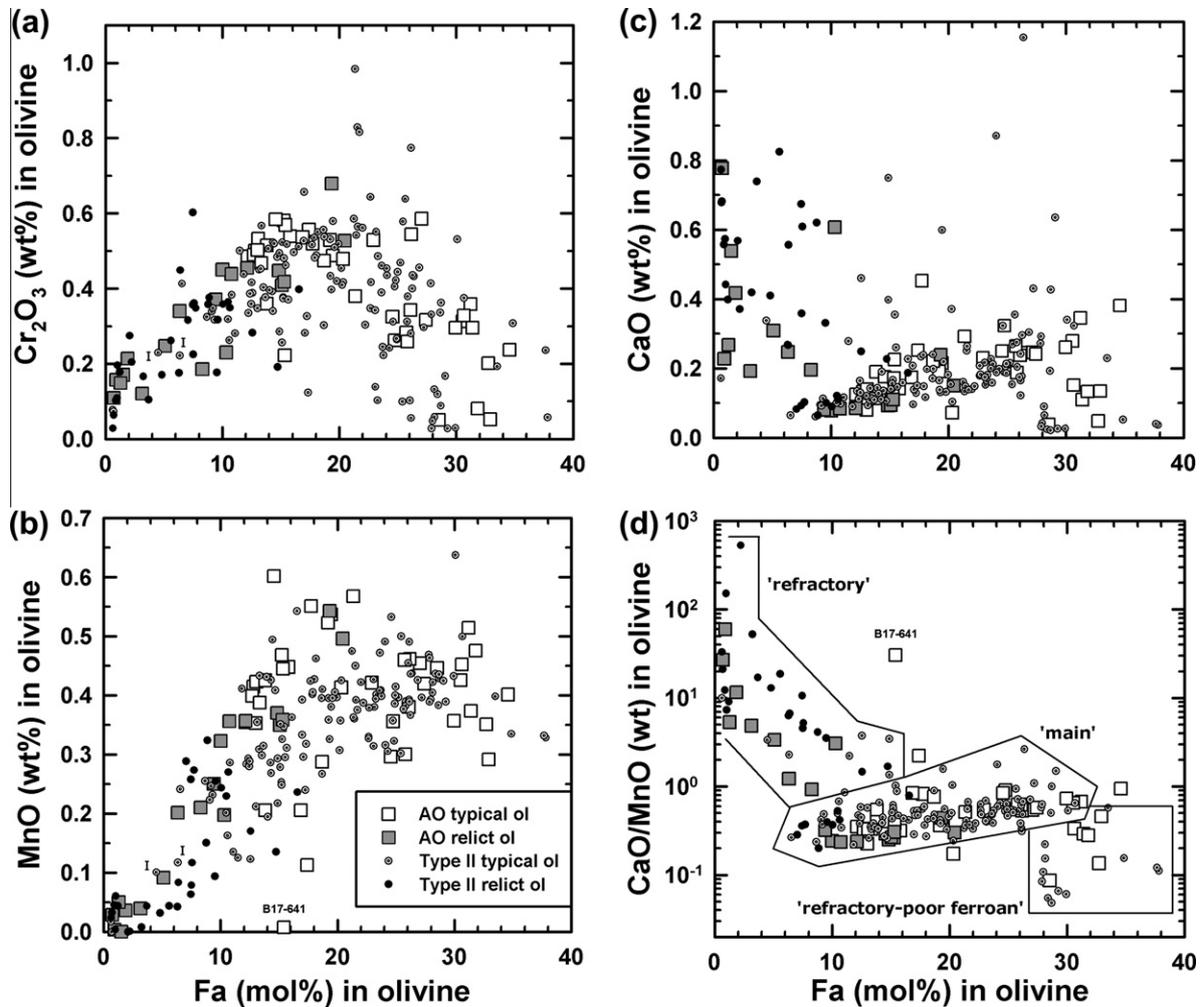


Fig. 7. Variation diagrams for minor element and Fa contents of olivine in AO objects and Type II chondrules. (a)  $\text{Cr}_2\text{O}_3$  vs. Fa, (b) MnO vs. Fa, (c) CaO vs. Fa, (d) CaO/MnO vs. Fa. Most analyses with Fa < 10 are for relict grains. 'I' refers to objects better described as Type I or transitional Types I–II. Analysis B17-641 has anomalously low MnO which may be in error.

chondrules experienced broadly similar igneous and cooling histories. Most likely, the coarser olivine grains in AO objects represent chondrule debris.

Data for low-Ca pyroxene show that relict grains in AO-U object Beg-3 and AO-M object Beg-8 have similar compositions, whereas low-Ca pyroxene in Type II chondrule Sah98-13 has higher abundances of most trace elements (Fig. 8b). CI-normalized abundances of CS elements in low-Ca pyroxene from the two AO objects generally increase with CRS, whereas this pattern is not evident in the Type II chondrule (Fig. 8b). This could indicate that an igneous signature of rapid cooling is preserved for the two AO grains from NWA 4910 (LL3.1), but not for the presumably more metamorphosed chondrule grain from Sahara 98175 (LL3.5).

#### 4. DISCUSSION

##### 4.1. Dust accretion and heating to form AO objects

Our data support the conclusions of previous researchers that AO objects represent little-melted agglomerates of

diverse components (Weisberg and Prinz, 1994, 1996). Textures suggest that AO objects contain both relict grains as well as fragments of small chondrules (Section 3.1), and mineral-chemical evidence strongly suggests that larger olivine and low-Ca pyroxene grains in AOs are chondrule debris (Section 3.3). AO objects that enclose ('rim') chondrules and coarse mineral grains (Section 3.1.4) are clearly accretionary in origin, and generally resemble previously described 'matrix-like rims' or 'dark rims' on chondrules (Ashworth, 1977; Allen et al., 1980; King and King, 1981; Metzler et al., 1992; Metzler and Bischoff, 1996). Agglomeration of AO material evidently followed previous episodes of chondrule formation and fragmentation and post-agglomeration heating episodes were of insufficient intensity to obliterate the identity of the various coarse components in AO objects.

Trace-element data suggest that the fine-grained multi-phase fraction in AO objects has a near-chondritic composition on average (Section 3.2.2). Moreover, some AO objects have essentially chondritic bulk major and minor-element compositions, although overall bulk and silicate compositions for AOs are variable (Section 3.2.1).

Table 4

Representative composition of olivine (1–7) and low-Ca pyroxene (8–10) in AO objects and chondrules determined by narrow beam SIMS.

Object	Olivine							Low-Ca pyroxene		
	(1) Beg-2	(2) Beg-6 rim	(3) Beg-17	(4) NWA-11A	(5) NWA-15	(6) Sah98-13 core	(7) NWA-11C core	(8) Beg-3	(9) Beg-8	(10) Sah98-13 core
Type	AO-WM	AO-U	AO-M	Fine II	Coarse II	Coarse II	IOG <sup>b</sup>	AO-U	AO-M	Coarse II
Analysis	Be2-1	Be6-1	Be17-4	N11A-1	N15-2	S13-B5	N11C-1	Be3-1	Be8-2	S13-3
Fa, mol% <sup>a</sup>	3.1	20.3	10.0	23.1	18.0	28.1	0.6	Fs 2.9	Fs 6.3	Fs 17.5
Na, mg/g	0.151	0.0500	0.0430	0.155	0.120	0.252	0.0880	0.388	0.696	4.12
Mg, wt%	25.9	27.2	24.8	26.8	n.d.	25.7	26.2	18.2	16.9	15.3
Al, mg/g	0.485	0.347	0.230	0.309	0.476	0.321	1.60	2.39	1.96	6.87
Si, wt%	19.1	17.8	18.8	17.5	18.0	17.6	19.5	27.1	26.8	26.4
P, µg/g	449	163	65.9	441	148	72.7	38.0	94.4	124	302
K, mg/g	0.0310	0.0270	0.0180	0.0250	0.0430	0.0510	0.0687	0.0990	0.0990	0.285
Ca, mg/g	1.42	0.633	0.410	1.48	0.888	0.392	3.51	1.62	1.61	13.4
Sc, µg/g	3.08	2.93	1.13	4.77	2.91	2.30	9.22	2.88	2.07	8.43
Ti, µg/g	58.9	29.2	21.8	34.2	24.8	22.2	304	127	127	331
V, µg/g	35.0	54.0	57.2	44.1	47.9	9.82	35.8	58.1	51.3	91.6
Cr, mg/g	1.24	3.41	3.07	2.87	3.71	0.501	0.622	2.64	2.85	6.16
Mn, mg/g	0.812	4.32	2.50	3.45	2.77	4.00	0.0378	0.833	1.43	3.87
Fe, wt%	10.8	15.5	5.54	15.2	9.82	18.7	0.459	3.46	2.55	6.97
Co, mg/g	0.438	0.204	0.189	0.153	0.0820	0.0411	0.00866	0.361	0.220	0.108
Ni, mg/g	6.75	3.78	2.74	0.472	0.333	0.731	0.251	5.14	2.99	1.66
Rb, µg/g	n.d.	0.913	0.174	0.418	0.205	0.624	0.101	0.994	0.974	1.59
Sr, µg/g	3.78	0.371	0.301	0.318	0.148	0.300	0.192	1.43	0.533	2.77
Y, ng/g	243	185	65.3	91.3	83.5	50.2	485	174	366	1006
Zr, ng/g	670	356	181	154	167	621	825	569	904	3120
Ba, ng/g	597	407	682	66.2	85.5	347	103	1410	1010	663
La, ng/g	77.8	101	40.2	51.5	45.4	104	53.2	89.2	97.8	169
Ce, ng/g	80.7	88.0	34.4	61.3	19.6	64.6	24.8	118	170	449
Pr, ng/g	16.3	24.5	13.8	9.50	11.9	20.7	12.4	20.5	33.5	49.4

Abbreviations as in Table 3.

<sup>a</sup> Determined by EMPA.

<sup>b</sup> Coarse, isolated olivine grain.

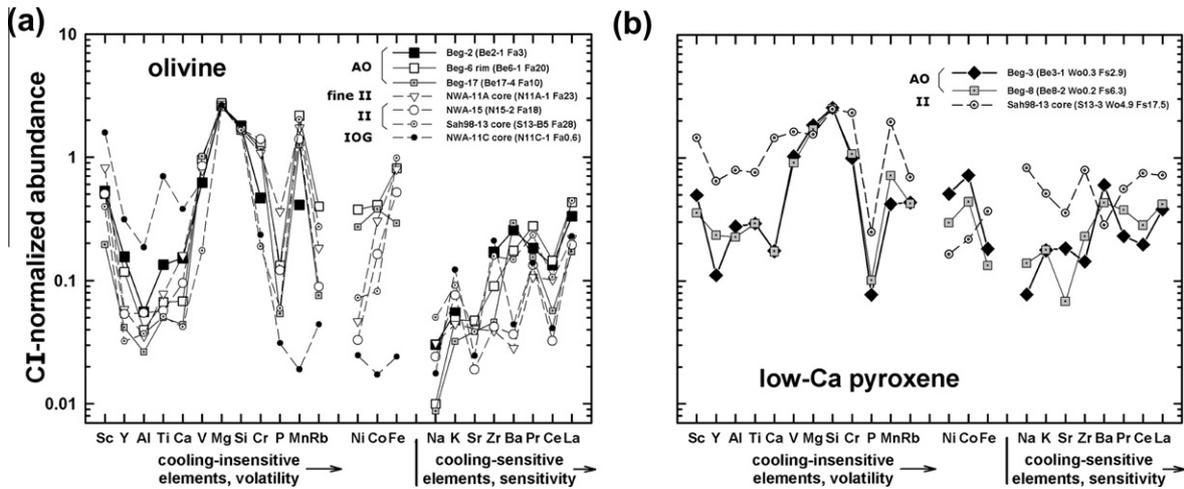


Fig. 8. CI-chondrite-normalized abundances for SIMS analyses of (a) olivine and (b) low-Ca pyroxene in AO objects, Type II chondrules, and an isolated olivine grain (IOG).

As the average AO bulk composition is enriched in S, Fe, and Ni and slightly depleted in lithophile elements compared to average LL chondrite (Section 3.2.1), AO objects can be regarded as mechanical mixtures of (a) fine silicate

dust of essentially chondritic composition, (b) variable amounts of larger mineral and lithic components (including chondrule-derived xenocrysts of olivine and pyroxene and lithic debris), and (c) additional troilite and metal.

AO objects show evidence for having been variably heated, ranging from apparently sintered (Type AO-U), to slightly melted (Type AO-WM), to more substantially melted (Type AO-M). Evidence for such a transitional heating sequence is summarized below.

- (1) AO-U objects show little evidence for silicate melting, although like other AO objects they are relatively compact. This implies that the original porosity one might expect for loosely accreted material was reduced by sintering.
- (2) AO-WM objects show textural evidence suggesting that they were weakly melted. These objects contain many discrete feldspathic areas that might be amorphous and some olivine grains with subhedral morphologies (Section 3.1.1). Idiomorphic faces for olivine are most prominent where the olivine is in contact with feldspathic areas. This implies that melting occurred in AO-WM objects but that it was largely limited to feldspathic areas.
- (3) Clinopyroxene (pigeonite, augite) overgrowths on irregularly-shaped magnesian low-Ca pyroxene relict grains are a distinctive feature found in various types of AO objects but were not observed in Type II chondrules (Section 3.1.1). As they are sometimes found in AO-U objects that were not melted appreciably and are most prominently observed in AO-WM objects that were slightly melted, such overgrowths may be coronas that formed by metamorphic reaction/growth during low degrees of melting.
- (4) AO-M objects show textural features indicative of melting, such as the presence of glass, euhedral–subhedral grain morphologies for olivine and pyroxene, and the presence of compact forms for troilite and metal, including drop-shaped masses (Section 3.1.1; see also Weisberg and Prinz, 1996). AO-M objects have textures similar to those illustrated for ‘coarse-grained’ or ‘igneous rims’ on chondrules, which may have originated by the melting of matrix-like rims (Rubin, 1984; Krot and Wasson, 1995). The observations imply that AO-M objects experienced heating sufficiently intense to partly melt all the major phases within them.
- (5) The incompatible-element-rich (IE-rich) trace element pattern found for some SIMS analyses in AO-M objects resemble those observed in Type II chondrules and suggests the existence of melt zones on a relatively large scale (i.e., a significant fraction of a ~40–50 micron broad SIMS beam) (Section 3.2.2). Conversely, the lack of IE-rich patterns for AO-U and AO-WM objects imply that melting effects in these objects, if any, were much more limited in spatial extent.
- (6) The tendency for olivine grains to be coarser in AO-M objects that were significantly melted, compared to AO-U and AO-WM objects of similar composition that were less melted, implies olivine coarsening by crystallization from a melt.

#### 4.2. Origin of troilite-rich margins in AO objects

A prominent feature of many AO objects is the concentration of troilite on the peripheries of the objects (Section 3.1.1). We infer that this reflects the late addition of S to the objects to form an S-rich melt.

A key observation is that in areas of AO objects that have the highest troilite contents, troilite forms a continuous network with embedded silicates (e.g., Fig. 2a and d). The texture cannot be explained simply by the accretion of troilite grains, as this process would not produce a continuous network of the mineral. Equilibrium condensation models for the solar nebula predict that troilite forms by reaction between metal and H<sub>2</sub>S gas (e.g., Wood and Hashimoto, 1993; Ebel and Grossman, 2000; Lodders, 2003), but there is no evidence that troilite formed by this reaction in AO objects. No remnant, corroded metal is found, even away from the edges of AO objects, and it is unlikely that network troilite formed by complete conversion of metal to troilite.

The textures of troilite-rich peripheries in AO objects are instead more consistent with troilite forming from a fluid (gas, liquid) that was easily able to penetrate between silicate grains. Some AO-U objects that show no evidence for silicate melting contain network troilite rims (Fig. 2a and d), implying that this texture was produced while silicates were solid. In some objects with Type II cores surrounded by AO rims, troilite appears to be replacing the glassy mesotases of the cores (Section 3.1.1, Fig. 3f). This could indicate replacement of silicate melt by an S-rich liquid that crystallized to troilite.

There are two viable possibilities for producing an S-rich melt on the margins of AO objects, namely by (a) direct condensation to liquid under strongly non-canonical nebular conditions, or (b) melting previously formed sulfide grains. Although sulfide melts are not explicitly predicted by condensation models (owing to a limitation of the models), such melts might be stable nebular condensates under high pressure, oxidizing conditions (Ebel and Grossman, 2000). In this case, the troilite could be a direct gas-to-liquid condensate, and the concentration on the peripheries of objects can be explained by reaction between AO objects and an S-rich gas. This scenario is supported by considering the relationship between AO objects and chondrules (Section 4.3). Iron to make troilite could have been supplied from a melt within the objects or from a vapor. Alternatively, the troilite in AO objects could reflect heating processes sufficiently intense to melt troilite that was initially present in AO objects. In this case, heating of previously assembled metal and sulfide grains could form a eutectic S-rich melt even in the presence of solid silicates. Pressures might need to be relatively high to allow a sulfide liquid to be stable (Ebel and Grossman, 2000). However, it is not obvious why melting of pre-existing grains would result in troilite concentrations at object peripheries, unless it reflects an original zonation in the objects (initially more troilite or troilite + metal towards the outside), likely reflecting late addition of S to the objects.

We note that a troilite-rich object and some chondrule rims in Bishunpur (L3.1) with network textures similar to

those of AO objects were studied by Kojima et al. (2003), who argued that troilite crystallized from S-rich shock melts, which were derived from matrix troilite and driven into chondrule rims by shock waves, which also disrupted the parent body. We consider this model highly unlikely for AO objects as (1) it does not explain why characteristic shock-produced veins, shock melt pockets, or other evidence for strong shock are entirely missing from AO objects; (2) it does not explain how concentric layering structures in AO objects could be preserved during an intense shock disturbance; (3) it does not plausibly explain why troilite should be concentrated in AO objects and not in the more voluminous chondrules; and (4) it does not plausibly explain why AO objects should be more enriched in troilite than bulk chondrites.

#### 4.3. Relationship between AO objects and Type II chondrules

Our data suggest that AO objects are transitional to Type II chondrules and that progressive heating of AO objects resulted in Type II chondrules, in a process involving both grain coarsening and evaporative melting. This supports the conclusions of various researchers that coarsening and evaporation could have been important during chondrule formation (Weisberg and Prinz, 1994, 1996; Hewins et al., 1996, 1997; Hewins, 1997).

There is a textural continuum grading from AO objects through fine and coarse Type II chondrules that extends the sequence shown within different types of AO objects. In this sequence, the textural changes include: (1) an increase in olivine grain size, (2) more prevalent euhedral and subhedral shapes for olivine grains, (3) larger areas of glassy mesostases, and (4) better development of microporphyritic textures (Section 3.1). These changes can be explained by melting and subsequent crystallization processes, which allowed fewer but coarser grains to crystallize from incomplete melts at the expense of finer-grained precursors. Experiments are consistent with this type of coarsening process and suggest that multiple heating events would be needed to make Type II chondrules from finer-grained AO object-like precursors if peak heating times were short ( $\sim 1$  min) (Hewins and Fox, 2004).

Bulk chemical data indicate that AO objects and Type II chondrules have significantly overlapping compositions, except that AO objects are usually strongly enriched in S, somewhat enriched in Fe, Ni, and have higher Na/Al values (Section 3.2). We suggest that partial loss of S and Na during evaporative heating resulted in the lower contents of these elements in Type II chondrules. The complementary S abundances for Type II chondrules (subchondritic) and AO objects (often superchondritic) (Fig. 5) can be explained by heating of dust of chondritic composition: S that was driven out of Type II chondrule melts could have been incorporated into coexisting AO objects, which were less strongly heated and therefore acted as cold traps. To account for the high Fe and Ni contents in AO objects and the textures of troilite (Section 4.2), we suggest that AO objects incorporated a metallic melt condensate that would have been enriched not only in S but also in Fe and Ni. Neither Fe nor Ni are especially volatile elements, so both

would tend to concentrate in a condensed phase such as melt.

#### 4.4. Formation conditions for AO objects and Type II chondrules

As the silicate solidus for chondrules is estimated as  $\sim 1300$ – $1500$  K (Connolly et al., 2006), melted AO objects (Types AO-M and AO-WM) and Type II chondrules must have been heated to peak temperatures ( $T_{\max}$ ) no less than this. Type AO-U objects were probably heated to temperatures below the silicate solidus but above the sulfide-metal eutectic ( $>1262$  K), i.e., with  $T_{\max} \sim 1260$ – $1500$  K.

To place further constraints on AO object and Type II chondrule formation conditions, we used the CWPI thermodynamic code (Petaev and Wood, 1998, 2005) to vary pressure ( $P$ ), temperature ( $T$ ), and system composition and compare model results to observations. Although objects that contain zoned or relict grains cannot be in complete equilibrium, relatively homogeneous fine-grained olivine is prevalent in most AO objects and Type II chondrules, suggesting that the fine-grained portions of these objects approached an equilibrium condition. As the fine-grained precursor material to AO objects and Type II chondrules appears to have been quasi-chondritic on average (Section 4.1), we modeled equilibrium evaporation (or sublimation) of a CI-chondrite-like (solar or ‘cosmic’) precursor under a variety of plausible nebular pressures ( $10^{-3}$ – $10^{-6}$  bar), temperatures (2500–350 K), and effective ‘dust/gas’ (D/G) ratios. The latter were calculated according to the general procedure of Wood and Hashimoto (1993), which assigns elements to different nebular fractions (gas, dust, ice, tar). Values of D/G  $>1$  ( $\times$ cosmic) represent systems enriched in vaporized dust, which is the most effective way to achieve ferroan silicates (Wood and Hashimoto, 1993; Ebel and Grossman, 2000). Although models are presented for a CI-like precursor, similar results would be obtained assuming other types of chondritic precursors such as LL chondrite.

Fig. 9 shows the bulk compositions of AO and Type II objects compared to equilibrium condensates, in terms of S/Al vs. Si/Al and S/Al vs. Na/Al diagrams, where Al represents a refractory (and relatively immobile) element. The figure shows equilibrium condensate trajectories for a cosmic composition (D/G = 1) as well as a strongly dust-dominant composition (D/G =  $10^4$ ) for two different pressures ( $10^{-6}$  and  $10^{-3}$  bar).

Variations in S/Al for AO and Type II objects are especially large, spanning three orders of magnitude (Fig. 9a). We attribute this large variation to the mobilization of S during heating. Heating will cause S/Al in condensates to fall dramatically, as S is highly volatile. Type II chondrules, which have low S/Al, could represent partly melted heating residues (condensates) produced by driving S into vapor. Conversely, objects with high S/Al (troilite-rimmed AO objects) could represent objects that reacted with the S-rich gas that was produced by evaporation (Fig. 9a).

Most Type II chondrules and some AO objects (including representatives of all types) form a cluster at low Na/Al ( $\sim 0.2$  at.) and low S/Al ( $<1$  at.) values (the ‘Type II cluster’) near one possible condensate path (Fig. 9b). These

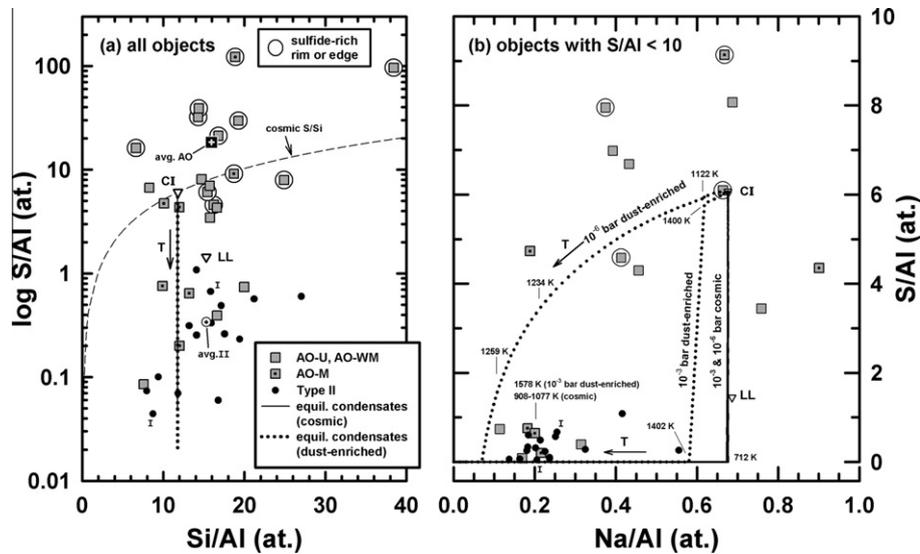


Fig. 9. Bulk compositions of AO objects and Type II chondrules compared to the compositions of equilibrium condensates in systems with overall cosmic ( $D/G = 1$ ) and dust-enriched ( $D/G = 10^4$ ) compositions (based on the CWPI thermodynamic code). (a) S/Al vs. Si/Al (all objects) and (b) S/Al vs. Na/Al (objects with S/Al < 10). ‘T’ with an arrow shows the trend of increasing temperature. ‘avg. AO’ = mean AO composition, ‘avg. II’ = mean Type II chondrule composition, ‘CI’ = mean composition of CI chondrites (Anders and Grevesse, 1989), ‘LL’ = mean composition of LL chondrites (Jarosewich, 1990), ‘I’ refers to objects better described as Type I or transitional Types I–II. Note: S/Al scale is logarithmic in part a, and linear in part b.

data are consistent with evaporation of both Na and S to form Type II chondrules and some AO objects.

Sulfur and Na vaporization depends on the heating conditions (Yu et al., 1996). For evaporating systems with cosmic composition, equilibrium models predict loss of S before Na (i.e., S is more volatile than Na), followed by Na loss, with compositions that pass through the Type II cluster (Fig. 9b). For these systems, a heating temperature of  $\sim 900$ – $1100$  K (depending on pressure) is needed to match the subchondritic S and Na contents of the Type II cluster. However, these temperatures are too low to result in silicate melting and clearly cannot account for the textures of Type II chondrules or melted AO objects.

Systems with very high D/G are more promising for allowing both evaporation and melting. The equilibrium evaporation trajectory will depend on the pressure. With  $D/G = 10^4$  and  $P = 10^{-6}$  bar, Na and S are similarly volatile and the evaporation trajectory misses the Type II cluster (Fig. 9b). For the same D/G values and  $P = 10^{-3}$  bar, however, S is more volatile than Na and the evaporation trajectory passes through the Type II cluster, with Na/Al  $\sim 0.2$  attained at a temperature of  $\sim 1580$  K (Fig. 9b). A similar situation arises for  $P = 10^{-3}$  bar at  $D/G = 10^3$  and  $10^5$ , with Na/Al  $\sim 0.2$  attained at  $T \sim 1406$  and  $\sim 1692$  K, respectively. Thus, high pressures ( $10^{-3}$  bar) and elevated D/G values can explain the characteristics of the Type II cluster. Moreover, as the solidus for chondrules is estimated to be  $\sim 1300$ – $1500$  K (Connolly et al., 2006), silicate melt would be expected for systems with elevated D/G values at  $10^{-3}$  bar. This is consistent with the results of Ebel and Grossman (2000), who included a multi-component silicate melt in thermodynamic models and found that such a melt would be stable at  $T \geq 1300$ – $1400$  K for D/G values  $\geq 500$ – $1000$  at various pressures ( $10^{-6}$ – $10^{-3}$  bar).

We therefore suggest that evaporation to form Type II and melted AO objects occurred at high  $P$  ( $\sim 10^{-3}$  bar) and D/G values ( $> 500$ – $1000$ , possibly as high as  $10^4$ – $10^5$ ), with an equilibration  $T$  of  $\sim 1410$ – $1690$  K. This  $T$  could be either the maximum temperature experienced by the objects, or a closure temperature (specifically, an Na closure temperature) during cooling. The low but non-zero contents of S in the Type II cluster presumably reflect either back-reaction with gas during cooling or incomplete removal of S during heating.

Although variations in S/Al and Na/Al can be largely explained by volatility effects, variations in Si/Al and in other major elements require a different explanation as they show no relationship to the volatile elements (Fig. 9a). The variation in Si/Al is correlated with Mg/Al (Weisberg and Prinz, 1996) but not correlated with Na/Al (Fig. EA-1-2, Electronic Annex), and we suggest that mixing of olivine, pyroxene, and feldspathic material in precursors can explain these data. Specifically, objects that have high Si/Al values are dominated by olivine, and those that have low Si/Al values are dominated by pyroxene and feldspathic glass or feldspar, suggesting that the precursors to AO and Type II objects had variable proportions of these silicates.

Formation of AO and Type II objects under oxidizing conditions is also implied by the ferroan composition of the objects. Fig. 10 shows Fa contents in olivine for a variety of D/G values at two pressures as obtained with the CWPI code. At temperatures sufficiently high to cause silicate melting ( $> 1300$  K), Fig. 10 implies that equilibrium Fa contents resembling those in AO objects and Type II chondrules can be attained only for systems with D/G values of order  $10^4$ – $10^5$ . Using a different thermodynamic code, Ebel and Grossman (2000) found that at

$10^{-3}$  bar pressure, a D/G value of 500 and 1000 would be in equilibrium with olivine with Fa contents as high as  $\sim 15$  and  $\sim 31$ , respectively, at the solidus ( $T \sim 1300$ – $1400$  K). These Fa contents are higher than predicted by the CWPI code for the same conditions, possibly owing to a different thermodynamic treatment of multicomponent melt. Nonetheless, it is apparent that to stabilize ferroan olivine at high temperature, distinctly non-cosmic, high D/G (high gas O/H) values are needed.

One alternative to avoid having high D/G values is to suppose that ferrous olivine compositions were ‘inherited’ from a pre-existing low-temperature condition which could have produced fayalitic olivine. Inheritance from low  $T$  might occur if heating events were too brief to allow equilibration at high  $T$ . Fig. 10 shows that Fa  $> 10$  can be obtained at  $T < 500$  K for a cosmic system, and at  $T < 700$  K for a D/G value of 1000. However, at such low temperatures, diffusion rates are sluggish and it seems dubious that ferroan olivine could form by any process requiring diffusional exchange in olivine (e.g., Fedkin and Grossman, 2005). Another objection to the inheritance model is that olivine grains do not show the zoning that would be expected for such a model. In systems with D/G values  $\leq 10^3$ , olivine becomes more magnesian at higher temperatures (Fig. 10; Ebel and Grossman, 2000), so partial re-equilibration during heating would result in grains with magnesian rims and ferrous cores, unlike what is found in AO objects, which have olivine grains either unzoned or zoned with magnesian cores and ferrous rims. Thus, the ferroan composition of olivine in AO objects probably was not inherited from a low  $T$  condition.

AO objects contain fine-grained ferrous grains as well as coarser magnesian relict grains. Heating in these objects would have had to occur in such a way as to equilibrate only the fine grains, and not the coarser grains. In Fig. 11, we evaluate the ability of olivine grains of different sizes (1, 10, and 100  $\mu\text{m}$  in diameter) to equilibrate during single chondrule heating events, modeled as  $\sim 1$  min in duration to peak temperatures of 1600 or 1900 K, with

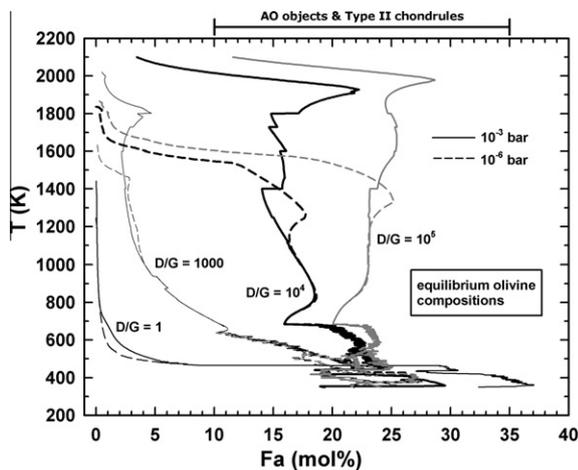


Fig. 10. Equilibrium Fa contents in olivine as a function of temperature for various dust/gas (D/G  $\times$  cosmic) ratios and pressures, as obtained with the CWPI thermodynamic code.

subsequent cooling rates of 100 or 1000 K/h. These heating and cooling conditions are representative of inferences made for chondrules (e.g., Connolly et al., 2006, and references therein), although the 1600 K temperature is considered specifically because it corresponds to a representative closure temperature as discussed above.

Fig. 11 shows that if heating occurred to a typical chondrule peak temperature of 1900 K, grains ranging from several to over 10  $\mu\text{m}$  in diameter (depending on cooling rate) should have equilibrated, whereas larger grains would not have equilibrated. Even if heating occurred to only 1600 K, grains of  $\sim 1$   $\mu\text{m}$  diameter should have equilibrated if cooling rates were rapid (1000 K/h) and grains a few  $\mu\text{m}$  across should have equilibrated if cooling rates were slower (100 K/h) (Fig. 11). Considering that heating events may have been longer than assumed or occurred more than once, diffusion constraints are consistent with fine olivine grains in AO objects ( $< 5$ – $10$   $\mu\text{m}$  across) equilibrating at  $T_{\text{max}}$ . The main conclusion to be drawn is that the fine olivine grains in AO and Type II objects reflect relatively oxidizing conditions during heating.

We do not claim that such oxidizing conditions necessarily pertained to large regions of the nebula. To the contrary, given that most of the gas appears to have been generated by vaporization of dust in dust-enriched regions, it is likely that oxidizing gas was spatially localized and transient. It may have existed only as long as the time needed for chondrule formation.

#### 4.5. Processing of dust to make chondrules

Fig. 12 schematically illustrates our model for how dust was processed in the early solar system. AO objects were

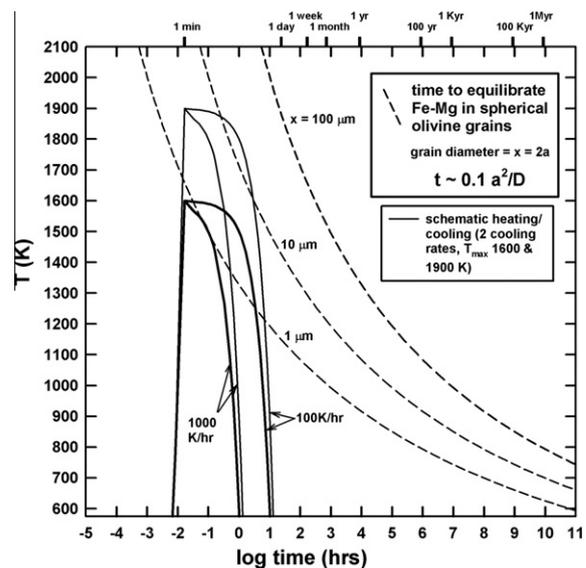


Fig. 11. Time needed to equilibrate Fe-Mg in spherical olivine grains of different diameters (1, 10, 100  $\mu\text{m}$ ) (dashed lines) based on the diffusion data of Chakraborty (1997), compared to schematic heating-cooling paths for chondrules which assume a short ( $\sim 1$  min) duration of heating to two peak temperatures (1600 K, 1900 K) and two different cooling rates (100 K/h, 1000 K/h).

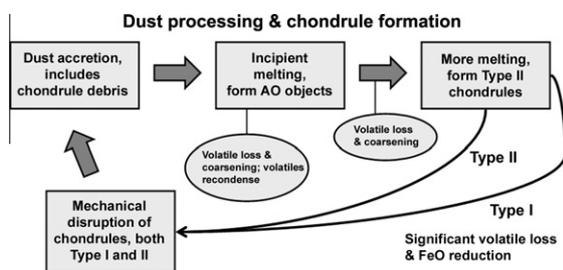


Fig. 12. Model of dust processing and chondrule formation.

formed by dust accretion and subsequent heating, and Type II chondrules were made by progressive heating of AO objects. Heating involved grain coarsening and volatile (S, Na) loss, with volatiles substantially recondensing as AO object dust. An important constituent of the accreted dust for AO objects was chondrule debris, including material derived both from ferroan (Type II) and magnesian (Type I) chondrules. Thus, mechanical disruption of chondrules must have preceded the formation of AO dust clumps. Type II chondrules could have been intensely heated and transformed into Type I chondrules by significant volatile loss and FeO reduction (Huang et al., 1996; Cohen et al., 2004; Ruzicka et al., 2008).

AO material may have played an important role in recycling Type I chondrules into Type II chondrules. Conversion of Type I to Type II chondrules would require the addition of volatiles; one possibility is exchange between gas and Type I chondrules while they were partially molten (Ruzicka et al., 2008). The present work suggests another possibility: volatiles may have been added by the accretion of volatile-rich fine-grained constituents to Type I chondrule fragments to form AO objects, and by subsequent melting of this assemblage to create Type II chondrules. In this case, Type I chondrules are converted to Type II after partial disaggregation and passing through an AO object stage.

The high gas pressures ( $10^{-3}$  bar) inferred for ferroan AO objects and Type II chondrules are plausible for the nebula, if much gas was locally derived by the evaporation of dust. However, the Type II and AO objects we studied show clearly that evaporation effects were limited only to the most volatile elements, not to major elements such as Mg and Si (Section 4.4). Thus, one needs to invoke substantially more heating and attendant vaporization of dust elsewhere in the system to create the high pressure gas. Dust processing and chondrule formation therefore must have occurred in such a way as to allow variable particle heating in the same general location of the nebula, ranging from vaporization, to melting, to annealing.

#### 4.6. Chondrule formation by nebular shock waves?

The nebular shock wave model has emerged as the favored and best-constrained mechanism for forming chondrules (e.g., Hood and Horányi, 1991, 1993; Boss, 1996, 2005; Connolly and Love, 1998; Jones et al., 2000; Iida et al., 2001; Desch and Connolly, 2002; Miura et al., 2002; Ciesla, 2005; Desch et al., 2005; Connolly et al.,

2006; Miura and Nakamoto, 2005). This model is compatible with our observations, as explained below.

- (1) *Heating by nebular shock waves can explain the transformation of unmelted fine dust into coarser melted objects.* With this mechanism grains less  $<10 \mu\text{m}$  across are predicted either to not melt (for slow-moving shocks) or to vaporize (for fast-moving shocks), unlike coarser particles that melt (Miura and Nakamoto, 2005). This implies that fine-grained AO material ( $<10 \mu\text{m}$  across) prior to its agglomeration into inclusions or rims could have been annealed, or that it could have condensed from vaporized gas, but that it would not have melted. However, once the dust accreted to form an agglomerate (AO object), it could have melted. This agrees with our observations.
- (2) *The shock wave model can explain accretionary structures.* As particles of different sizes will accelerate differently in shocked gas, one can expect the accretion of fine-grained material onto coarser objects, as the latter run into the former (Connolly and Love, 1998). The fine-grained material would be less heated, so objects with coarse-grained cores surrounded by fine-grained (AO-like) rims could be explained.
- (3) *Nebular shock waves can explain a high pressure nebular formation environment.* Transient high pressures of  $\sim 10^{-3}$  bar can be generated during passage of a shock wave, or up to two orders of magnitude higher pressure than canonical ambient nebular gas (Connolly and Love, 1998; Desch and Connolly, 2002). A high pressure origin matches the conditions of evaporative melting proposed here (Section 4.5), and makes chemical-isotopic exchange between chondrule liquids and surrounding gas likely (Miura et al., 2002). Such back-reaction is suggested to account for textures and the Na and S contents in AO objects and chondrules. However, a two orders of magnitude increase in pressure implies a maximum D/G value of 100, which is too low for ferroan chondrules. A larger increase in pressure and a larger D/G is needed.
- (4) *The shock wave model can explain variable heating effects occurring in proximal materials.* Our data suggest that the chondrule-forming mechanism must have allowed variable heating of different constituents, with these constituents sufficiently proximal to allow interactions between annealed, melted, and vaporized material (Section 4.5). Differential heating by particle size is one aspect of shock wave heating consistent with the observations.
- (5) *Complementary chemical and textural features between chondrules and AO objects for some elements are consistent with the variable heating of chondritic dust.* Previous researchers have noted an apparent chemical relationship between chondrules and matrix or matrix-like rims and suggested that heating could have driven volatiles from chondrule precursors into a gas phase, which condensed as fine, matrix-like

particles (e.g., Kong et al., 1999; Kong and Palme, 1999; Bland et al., 2005; Hezel and Palme, 2010). Metal may have been expelled from chondrules and mixed with fine-grained dust (Grossman and Wasson, 1987; Lauretta and Buseck, 2003; Bland et al., 2005). Our data are consistent with the partial removal of S, Fe, and Ni from chondrules and their incorporation into AO object dust, and with the partial removal of Na from AO object dust during heating to make chondrules.

- (6) *The shock wave model can explain the presence of apparent chondrule fragments in AO objects.* Fragmentation of objects potentially can occur in shock waves (Connolly and Love, 1998) and ram pressure might also limit the ability of larger melt drops to form (Susa and Nakamoto, 2002). Thus, the same process potentially can produce both chondrule debris within, and the heating of, AO objects.

## 5. CONCLUSION

- (1) AO objects in ordinary chondrites formed by the accretion of dust followed by variable heating. AO object dust included chondrule debris and on average had a composition similar to whole-rock ordinary chondrites. Some objects were largely sintered, others were partly melted.
- (2) There is good evidence that ferroan AO objects are protochondrules, and that they were melted to form Type II chondrules.
- (3) Progressive heating during chondrule formation resulted in grain coarsening and evaporative melting. Coarsening occurred by crystallization from incomplete melts. Sulfur, Na, and a Fe + Ni (metal) component were partly lost during heating.
- (4) In AO objects, troilite formed by crystallization from a melt, mostly likely in the form of a metallic melt condensate.
- (5) The ferroan compositions of fine-grained olivine in AO objects reflect oxidizing conditions during heating, and the bulk compositions and textures of Type II chondrules imply that heating occurred at relatively high pressures ( $\sim 10^{-3}$  bar) in an oxidizing gas. These oxidizing, high pressure conditions probably reflect transient conditions created by the evaporation of dust in regions with dust/gas ratios  $> 500$ – $1000$  and possibly up to  $10^4$ – $10^5 \times$  cosmic. The fine-grained fraction of Type II chondrules approached equilibration at a temperature of  $\sim 1410$ – $1690$  K.
- (6) Fine-grained matrix-like materials in chondrites did not all form in the same way; two matrix lumps had a different origin than AO objects.
- (7) The trace-element bulk compositions of fine-grained materials in AO objects and Type II chondrules are sensitive recorders of melting and metamorphic processes. Metamorphism in subtype 3.5 materials resulted in the formation of phosphate that caused local elemental re-distribution.
- (8) The data are compatible with the nebular shock wave model for chondrule formation.

## ACKNOWLEDGMENTS

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## APPENDIX A. DETAILS ON EXPERIMENTAL CONDITIONS AND METHODS

*Electron microprobe:* Major and minor elements were analyzed using an electron microprobe at Oregon State University in wavelength-dispersive mode. Operating conditions included a 15 KeV accelerating voltage and a beam current of 50 nA. Well-characterized minerals and glasses were used as standards, and data were reduced using the nominal Cameca PAP procedure (Pouchou and Pichoir, 1985). Nominal criteria for accepting analyses included totals between 97 and 102 wt%; cations/4O for olivine ranging from 2.95 to 3.05 (most analyses had 2.98–3.02); and cations/6O for pyroxene ranging from 3.93 to 4.07 (most analyses had 4.00–4.03).

*Norm calculation:* ‘Defocused’ beam EMPA data (DB-EMPA) were obtained to estimate mineral proportions in analysis areas using a norm calculation. The calculation assumes as possible normative minerals the phases that are found in AO objects. These include: olivine, low-Ca pyroxene or orthopyroxene (the sum of normative enstatite + ferrosilite), clinopyroxene (diopside + hedenbergite), plagioclase (albite + anorthite), metal [with assumed 28 wt% Ni, equivalent to the average composition of metal in LL chondrites (Jarosewich, 1990)], chromite, and troilite. All chlorine was assumed to be present in the form of sodalite, but the actual siting of Cl was not determined in most cases. All Fe remaining after assignment to troilite and metal was partitioned in olivine and pyroxene according to apparent Mg#. The following mineral densities ( $\rho$ , all in  $\text{g}/\text{cm}^3$  and based on Gaines et al., 1997) were assumed to convert weight to volume fractions for mineral phases:

$\rho_{\text{forsterite}} = 3.24,$	$\rho_{\text{fayalite}} = 4.39,$	$\rho_{\text{diopside}} = 3.28,$
$\rho_{\text{hedenbergite}} = 3.65,$	$\rho_{\text{enstatite}} = 3.20,$	$\rho_{\text{ferrosilite}} = 4.00,$
$\rho_{\text{anorthite}} = 2.76,$	$\rho_{\text{albite}} = 2.62,$	$\rho_{\text{Fe-metal}} = 7.97,$
$\rho_{\text{Ni-metal}} = 8.14,$	$\rho_{\text{chromite}} = 5.06,$	$\rho_{\text{sodalite}} = 2.30,$
		$\rho_{\text{troilite}} = 4.84.$

*Corrected DB-EMPA data:* Apparent initial mineral proportions implied by the norm were used together with measured or assumed phase compositions and mineral densities to estimate correction factors based on the unequal-density effect (Warren, 1997). The effect of the correction is to adjust the wt% concentration of elements sited in high-density phases (e.g., Fe in metal and troilite) upwards and the concentration of elements sited in low-density phases (e.g., Na and Al in feldspar) downwards. The

corrected ('true') norm was then recalculated for each analysis.

*Ion microprobe:* SIMS was used to analyze trace elements at Washington University. All analyses were made using an O<sup>-</sup> primary beam and energy filtering at low mass resolution to remove complex molecular interferences. The resulting mass spectrum was deconvolved in the mass ranges K–Ca–Sc–Ti and Rb–Sr–Y–Zr to remove simple molecular interferences that are not eliminated with energy filtering (Alexander, 1994; Hsu, 1995). Sensitivity factors for the REE are from Zinner and Crozaz (1986b), and those for other elements are from Hsu (1995) and are listed in Table 1 of Floss et al. (1998). For mixed phases, average sensitivity factors are used for Mg, Fe and Ca, and average (non-plagioclase) sensitivity factors are assumed for the REE. Absolute concentrations were determined by normalizing ion signal concentrations to concentrations determined by electron microprobe analysis, using Si as the normalizing element. Each SIMS analysis was evaluated to take into account the possibility of analyzing off the desired target area. Apparent concentrations derived by SIMS were compared to concentrations obtained by EMPA for the same elements at the same or nearby location. If values agreed substantially, the analysis was accepted as is. If the values did not substantially agree, the analysis was rejected.

*Thermodynamic modeling:* For comparison to AO data, we used a version of the CWPI thermodynamic code (Petaev and Wood, 1998, 2005), developed and kindly provided by Mikhail Petaev, to model condensate compositions in a 20-element system (H, He, C, N, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni). For all runs, isobaric conditions and complete equilibrium (no isolation of condensates) were assumed so as to minimize the number of free parameters. Investigated system compositions included 'cosmic', based on the average composition of CI chondrites (Anders and Grevesse, 1989), and 'dust-enriched' systems (e.g., Wood and Hashimoto, 1993; Ebel and Grossman, 2000). In runs of given pressure and system composition, temperature was varied in 2 K intervals.

## APPENDIX B. SUPPLEMENTARY DATA

Supplementary data (Electronic Annex 1 file) associated with this article can be found, in the online version, at doi:10.1016/j.gca.2011.10.020.

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