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Origin of magnetite in oxidized CV chondrites: in situ measurement of oxygen isotope compositions of Allende magnetite and olivine

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Abstract

Magnetite in the oxidized CV chondrite Allende mainly occurs as spherical nodules in porphyritic-olivine (PO) chondrules, where it is associated with Ni-rich metal and/or sulfides. To help constrain the origin of the magnetite, we measured oxygen isotopic compositions of magnetite and coexisting olivine grains in PO chondrules of Allende by an in situ ion microprobe technique. Five magnetite nodules form a relatively tight cluster in oxygen isotopic composition with $\delta^{18}O$ values ranging from -4.8 to -7.1‰ and $\delta^{17}O$ values from -2.9 to -6.3‰. Seven coexisting olivine grains have oxygen isotopic compositions from -0.9 to -6.3‰ in $\delta^{18}O$ and from -4.6 to -7.9‰ in $\delta^{17}O$.

The $\Delta^{17}O$ values of the magnetite and coexisting olivine do not overlap; they range from -0.4 to -2.6‰, and from -4.0 to -5.7‰, respectively. Thus, the magnetite is not in isotopic equilibrium with the olivine in PO chondrules, implying that it formed after the chondrule formation. The $\Delta^{17}O$ of the magnetite is somewhat more negative than estimates for the ambient solar nebula gas. We infer that the magnetite formed on the parent asteroid by oxidation of metal by H_2O which had previously experienced minor O isotope exchange with fine-grained silicates.

Keywords: magnetite; olivine; O-18/O-16; O-17/O-16; ion probe data; chondrites; meteorites

1. Introduction

Magnetite is relatively abundant in some CV chondrites but rare in others; the division of CV into oxidized and reduced CV subgroups is largely based on the modal ratio of magnetite to metal [1]. It seems probable that the magnetite formed in the oxidation process responsible for the difference between the oxidized and reduced CV chondrite subgroups.

Numerous processes have been proposed to account for the origin of magnetite in Allende and other oxidized CV chondrites, including: (1) crystallization of magnetite from cooling, oxidized chondrule melts [2,3]; (2) oxidation of chondrule metallic nodules in the nebula [4–6]; and (3) oxidation of chondrule metallic nodules in the parent asteroid [7,8].

A key issue is whether the oxidation of the magnetite (and other oxidized phases in the oxidized CV chondrites) occurred in the solar nebula or in an asteroidal setting (see Krot et al. [8] for a review on

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this subject). We have examined this problem by combining petrographic studies with analyses of the oxygen isotopic compositions of coexisting magnetite and olivine in Allende PO (porphyritic–olivine) chondrules.

Most previous O isotopic measurements of magnetite in carbonaceous chondrites were carried out using gas-source mass spectrometry applied to mineral separates from CK [9,10], CR [11], CI and ungrouped carbonaceous chondrites (Essebi and Bells; studies by Rowe et al. [12]). Hyman et al. [13] used an ion microprobe to determine the O isotopic compositions of isolated individual magnetite grains from CI chondrites; the data roughly describe a mass-dependent fractionation line with a large range in $\delta^{18}O$ (e.g., ~ 30‰ in Orgueil). Saxton et al. [14] studied one magnetite grain from LL3 Semarkona using an ion microprobe, and found that the magnetite was ~ 9‰ lighter in $\delta^{18}O$ than the bulk meteorite. Oxygen isotopic compositions of magnetite in unequilibrated chondrites fall either above (in CI, Essebi and Semarkona) or slightly below (in CR) the TF (terrestrial fractionation) line. No measurements have been reported for magnetite in CV3 chondrites.

Clayton and co-workers [9,15,16] reported that PO chondrules in Allende have O isotopic compositions on or slightly above the CCAM (carbonaceous-chondrite–anhydrous-mineral) line with $\delta^{18}O$ ranging from −2.6‰ to 2.2‰. Separated olivine grains from Allende have been measured using an ion microprobe technique by Hervig and Steele [17] and Weinbruch et al. [18]. Saxton et al. [19] measured olivine grains in Allende using an in situ ion microprobe technique. These measurements show that, when petrological information is available, more oxidized (high FeO) olivine grains or chondrules have higher (less negative) $\Delta^{17}O$ ($= \delta^{17}O - 0.52 \cdot \delta^{18}O$) values than reduced samples.

We report O isotopic compositions and petrographic observations of magnetite and coexisting olivine in PO chondrules of Allende and discuss possible origins of the magnetite.

2. Analytical procedures

Chondrules containing magnetite grains larger than ~ 30 μm in diameter were selected from polished thin and thick sections. Portions of these sections having dimensions of about 5 mm and containing the chondrules were mounted in epoxy together with terrestrial magnetite and olivine standards. Chemical compositions of magnetite and olivine were determined with the UCLA automated Cameca "CAMEBAX-microbeam" electron microprobe using crystal spectrometers, counting times of 20 s, a ZAF-correction procedure, and a beam current of ~ 13 nA at 15 kV. Standards were: grossular for Si, Ca, and Al; forsterite for Mg; magnetite for Fe; spessartine for Mn; sphene for Ti; chromite for Cr; and Ni-olivine for Ni.

Two sets of O isotope measurements for magnetite (in August 1995 and February 1996) and one for olivine (in May 1996) were performed using the UCLA Cameca ims 1270 ion microprobe. Preliminary data, measured in June 1995 and published as an abstract [20], were later found to be in error due to large unreproducible instrumental mass fractionation effects; the data reported here supersede those.

A terrestrial magnetite (LP204) from the Adirondack Mountains, N.Y., whose oxygen isotope composition had been characterized by Valley and Graham [21] using both ion microprobe and conventional analyses, was used as a standard for magnetite. The LP204 magnetite is near-stoichiometric Fe_3O_4 in composition and its O-isotope composition is homogeneous at distances > 50 μm from grain boundaries [21]. A San Carlos olivine ($\delta^{18}O = +5.25$‰ [22]) was used as an olivine standard. The standards were mounted adjacent to the Allende samples and the entire mount gold (August 1995 and February 1996) or carbon (May 1996) coated to make the surface conducting.

2.1. August 1995 (magnetite)

Three magnetite grains in one PO chondrule (chondrule TS486) were measured. A ~ 0.3 nA primary Cs^+ beam was defocused to a 20–25 μm diameter spot and a field aperture inserted into the secondary ion beam to restrict the area analyzed to the central 10–15 μm. A defocused beam ("Kohler" illumination) was used to minimize the depth/diameter ratio of the crater formed by ion sputtering. Negative secondary ions were accelerated through 10 kV and detected by pulse counting with an electron multiplier. The energy slit was set to accept ions of initial kinetic energies in the range ~ 0–30 eV (i.e., no "energy filtering" was employed). Intensities were corrected for deadtime, which was determined to be 42.4 ns by measurements of the dependence of $\delta^{18}O$ on count rate for LP204 magnetite. Each analysis comprised 100 cycles, where each cycle included counts of $^{16}O^-$ (2 s), $^{17}O^-$ (10 s), $^{16}OH^-$ (1 s), and $^{18}O^-$ (5 s). A total measurement time required for each analysis was ~ 40 min. Count rates of $\sim 0.9 \times 10^6$, $\sim 4.0 \times 10^2$, and $\sim 2.1 \times 10^3$ cps were obtained for $^{16}O^-$, $^{17}O^-$, and $^{18}O^-$, respectively; similar count rates were maintained for standards and samples.

Peak intensities were measured by magnetic field switching at a mass resolving power of ~ 6500. Despite the high resolution, a correction for interference with the $^{17}O^-$ peak by the much (~ 70 ×) more intense $^{16}OH^-$ peak was required. We followed the procedure of McKeegan [23] and corrected the $^{17}O^-$ peak based on the assumption that $^{16}OH^-$ peak shape was the same as that of the $^{16}O^-$ or $^{18}O^-$ peaks. This procedure resulted in a $\Delta^{17}O$ of LP204 terrestrial magnetite of − 1‰; a minor adjustment to the tail-correction factor was made in order to make $\Delta^{17}O$ of LP204 be zero. Typical corrections were relatively large (~ 9.5‰ in $\delta^{17}O$) during this run because the peak was broadened by poor vacuum conditions. The instrumental mass fractionation (-7.9 ± 0.7‰/amu) was determined by analyzing the LP204 standard interspersed amongst the chondrule analyses, taking care to avoid cracks or grain edges of the standard magnetite. The data for each analysis were corrected to the SMOW scale by assuming a linear mass fractionation law and using the normal values $(^{18}O/^{16}O)_{SMOW} = 0.0020052$ [24] and $(^{17}O/^{16}O)_{SMOW} = 0.00038288$ [25].

2.2. February 1996 (magnetite)

Four magnetite grains in four different porphyritic olivine chondrules (C2, C4, C6, and C9) were measured. The magnetite grain in chondrule C2 was large enough (~ 100 μm diameter) to permit the analysis of multiple spots.

Oxygen isotope measurements were performed using a defocused Cs^+ beam to sputter a ~ 25 μm diameter crater. A normally incident electron flood gun was used to compensate for possible sample charging and measurements were performed at high mass resolving power (> 6000) in order to eliminate molecular interferences. Because of improvements in the vacuum and ion optics compared to the previous measurements, peak tailing corrections due to OH^- overlap onto the $^{17}O^-$ peak required ≤ 1‰ correction in $\delta^{17}O$.

The main difference in experimental procedure compared to the August 1995 measurements is that data were collected by measuring the intense (up to $\sim 6 \times 10^7$ cps) ^{16}O peak in a Faraday cup (FC) equipped with a Keithley 642 electrometer while the ^{18}O and ^{17}O ions were counted on an electron multiplier (EM). This experimental approach has several advantages in addition to the obvious one of increasing the count rates of ^{17}O and ^{18}O by a factor of 60. The EM efficiency can be seriously degraded during oxygen isotopic measurements, due to the prolonged exposure to ^{16}O beams with intensities $> 10^6$ cps. This leads to additional uncertainty in the isotope ratios resulting from shifts in the deadtime due to changes in the EM output pulse widths. Reducing the counting rates is not an option since this would lead to intolerably long measurement times to achieve adequate precision on $\delta^{17}O$. Use of the FC permits an increase in transmission by opening the source slit, which has the additional benefit of improving reproducibility by reducing the criticality of the tuning of the secondary ion beam and the electron gun. The increased throughput allows quick data acquisition from a shallow crater; an internal precision of ~ 0.5‰ is achieved in ~ 12 min. Of course, this approach is valid only if the relative gain of the EM and FC can be held constant between analyses of the standards and unknowns. We have found that, provided count rates (of ^{18}O) do not exceed a few $\times 10^5$ per second, the EM yield is constant over the course of an analysis session (< 48 h) to within 0.2–0.3‰.

The Allende data were corrected for deadtime, EM yield, and mass fractionation (linear law) by utilizing measurements on the LP204 magnetite standard made interspersed with those of the Allende grains. The deadtime (18–20 ns) was determined from measurements of the dependence of $^{18}O/^{16}O$ on the counting rate and, because of the low count rates of ^{18}O and ^{17}O, the uncertainty in this correction has a negligible effect on determination of the

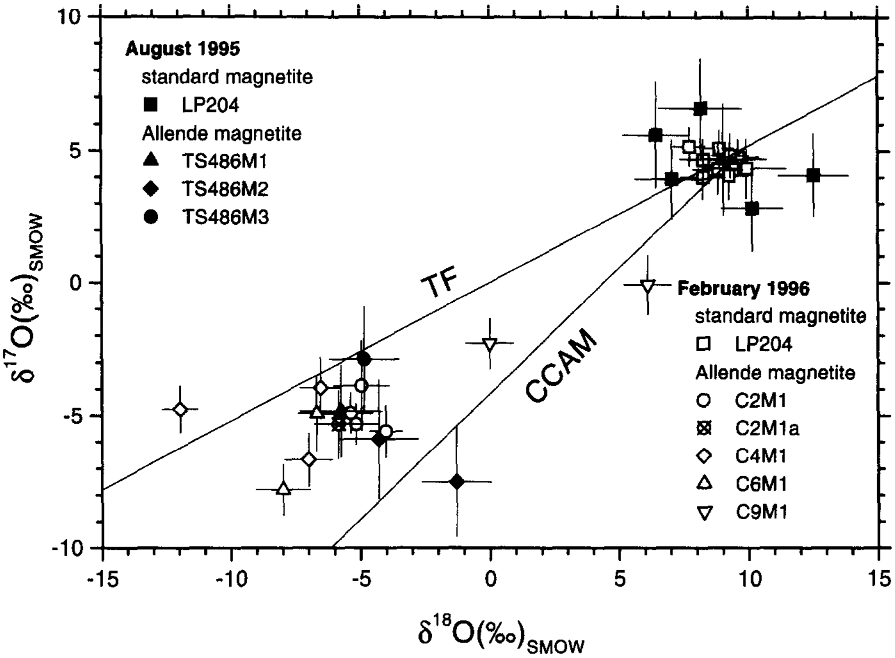

Fig. 1. Oxygen isotope measurements of the LP204 terrestrial magnetite and seven Allende magnetite grains in PO chondrules, TS486 in the August 1995 run and C2, C4, C6 and C9 in the February 1996 run. 1σ error bars are shown. Much better reproducibility in the LP204 magnetite was obtained in the second experiment. The C9M1 point may have been affected by excess amounts of mass fractionation; its sputtered crater has three large holes and a Ni–Fe metal grain. See text for details. Except C9M1 and one measurement of C4M1, the magnetite O isotope compositions in February 1996 are in good agreement with those obtained in August 1995.

final isotopic ratios. The $^{18}O/^{17}O$ ratio (determined solely on the EM) for the standards was used to calibrate the instrumental mass fractionation (−6.2‰/amu). With the assumption that the standard data fall on the TF line, the EM yield was determined allowing calculation of $\delta^{17}O$ and $\delta^{18}O$. Precision in both values is typically ~ 1‰ per analysis spot even after allowance for uncertainties due the EM yield and mass fractionation corrections.

The measured O isotope compositions of the standard and Allende magnetite are shown in Fig. 1 after correction for the instrumental mass fractionation and normalization to the SMOW scale. It is evident that much better reproducibility in the standard was obtained during February 1996.

2.3. May 1996 (olivine)

Seven olivine grains in three PO (chondrules C2, C4 and C6) were measured. Analytical and data reduction procedures were similar to the February

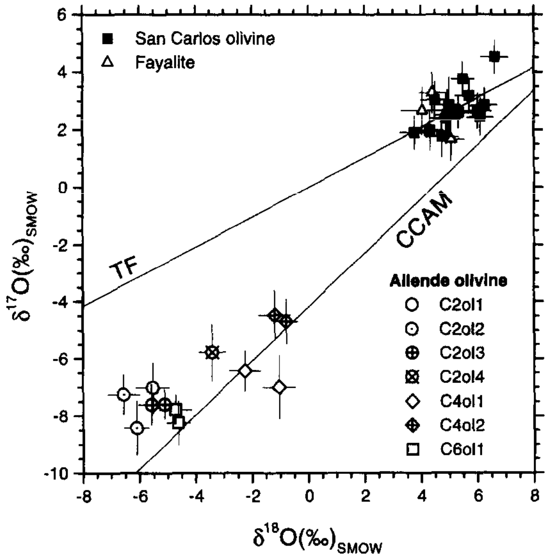

Fig. 2. Oxygen isotope measurements of a San Carlos olivine, a synthetic fayalite, and seven Allende olivine grains in PO chondrules C2, C4, and C6 in the May 1996 experiment. 1σ error bars are shown. The synthetic fayalite was used to correct for matrix effects.

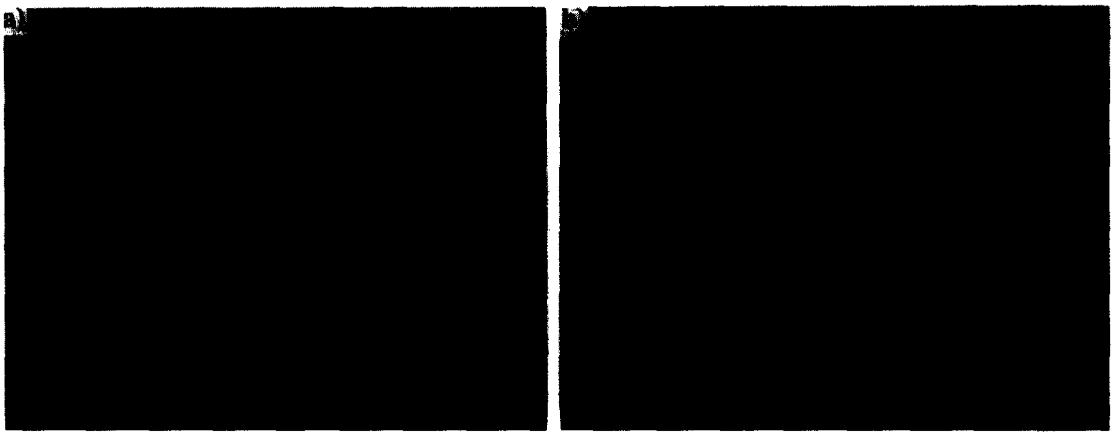

Fig. 3. SEM images of craters produced by ion probe sputtering on (a) the LP204 terrestrial magnetite and (b) the Allende magnetite TS486M3. The terrestrial magnetite shows a smooth and inclusion-free surface, while Allende magnetite has pores, cracks, and a small metallic inclusion.

1996 experiment for magnetite. Because inclusion-free areas in olivine are generally much larger than magnetite, a relatively large (~ 50 μm) primary beam was used. The use of higher mass resolving power (~ 7500) and better vacuum conditions obtained with the aid of a liquid N_2 cold-trap reduced peak tailing corrections due to OH^- overlap onto the $^{17}O^-$ peak to < 0.5‰ in $\delta^{17}O$.

A synthetic fayalite ($\delta^{18}O = 4.5$‰) was measured to calibrate any matrix effect in the instrumental mass discrimination due to different iron contents between the standard (Fa9) and samples (Fa0–10). The measured matrix effect in $\delta^{18}O$ was 0.054‰ per Fa mol%. Thus the maximum correction was only ~ 0.5‰.

The measured O isotope compositions of the standard and Allende olivine are shown in Fig. 2, after correction for the instrumental mass fractionation and matrix effect, and normalization to the SMOW scale. In order to test the accuracy of the correction

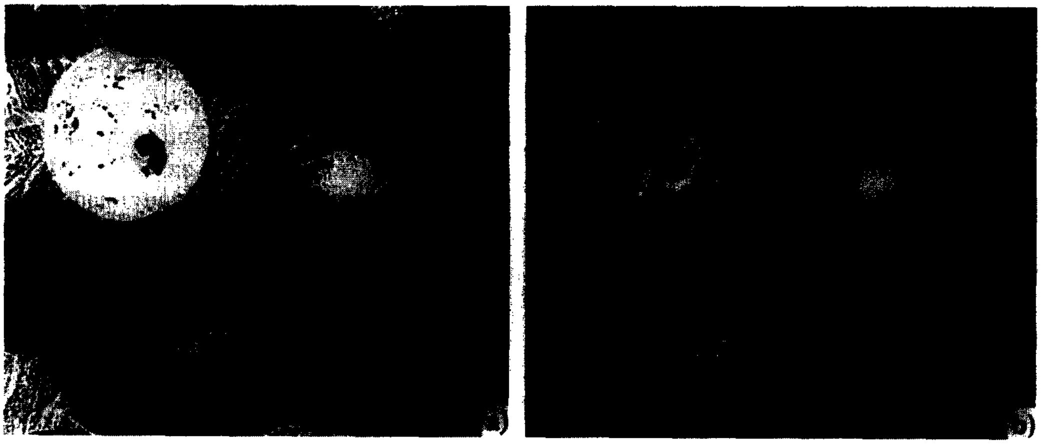

Fig. 4. (a) Back-scattered and (b) secondary electron images of Allende chondrule C2 after ion microprobe analysis showing two ion probe craters in the magnetite C2M1 and three craters in the olivines C2ol1, ol2, and ol4. A larger diameter primary beam was used for olivine. Microcracks filled with bright material (probably Fe-rich secondary minerals) are present in the crater of C2ol4.

procedures, olivine from the Eagle Station pallasite was measured ($\delta^{18}O$ was $-1.8 \pm 0.3‰$, $\delta^{17}O$ was $-6.1 \pm 0.6‰$, 1σ error). The data are consistent within 2σ error with the data given by Clayton and Mayeda [26].

Optical and secondary electron images of the samples showed that the ion probe craters in the LP204 magnetite standard are smooth with no inclusions (Fig. 3a). For the Allende magnetite nodules, although all the ion-probe craters are formed entirely within the magnetite, the surfaces show irregular roughness with small pores and cracks (Fig. 3b). These result either from structural defects or from preferential sputtering due to inclusions in the Allende magnetite. The crater of the C9M1 magnetite included Ni–Fe metal grains. Regular ion-probe craters were formed in both the standard and Allende olivine. Fig. 4 shows a back-scattered electron image (a) and a secondary electron image (b) of the Allende C2 chondrule, with two ion probe craters in magnetite C2M1, and three craters in olivines C2ol1, ol2, and ol4. The crater in C2ol4 includes cracks filled with what appears to be Fe-rich oxide or silicate.

3. Occurrence of magnetite in Allende and other carbonaceous chondrites and sample description

In unequilibrated chondrites magnetite is observed only when the meteorite is relatively oxidized. Magnetites are abundant in CI (8.5–11.1 wt%), oxidized CV (up to 13 wt%) and the two ungrouped carbonaceous chondrites Essebi (11.3 wt%) and Bells (16.1 wt%) [27,28]. Magnetite is relatively rare in CM2 or absent in CO3 and most reduced CV3 meteorites.

In CI chondrites, magnetite occurs as aggregates having grain sizes ranging from < 1 μm to ~ 10 μm and framboidal, spherulitic, or plaquette morphologies [29,30]. Framboidal magnetite aggregates are also found in the matrices of Essebi, Bells [31], and Mokoia [8]. These magnetites are pure Fe_3O_4, containing $< 1\%$ of other oxides. Since these magnetites are generally associated with phyllosilicates, the consensus view is that they were formed by aqueous alteration on parent asteroids [29,31].

In contrast, the magnetite in CV3 chondrites is mostly in magnetite–metal nodules inside chondrules. This magnetite is not pure Fe_3O_4; it typically contains ~ 0.1 wt% NiO and 1–2 wt% Cr_2O_3 ([3,4], this study). It is not clear why the composition of the CV chondrule magnetite differs from that in CI chondrites, Essebi, Bells and Mokoia. Interestingly, both types of magnetite are found in Mokoia. We suggest the following scenario to explain the elevated Ni and Cr contents: the CI magnetite formed by slow oxidation that permitted Ni and Cr to diffuse to more suitable host phases, but in Allende oxidation of metal was relatively rapid, and some Ni and Cr was trapped in the growing magnetite. The Cr/Fe ratio (~ 0.015) in Allende magnetite is similar to or slightly higher than that of kamacite in chondrites (e.g., ~ 0.007 in type-2 chondrites, [32]). The increased Cr/Fe ratio and decreased Ni/Fe ratio in this magnetite compared to those of kamacite is consistent with the fact that Cr is more easily oxidized than Fe and that chromite and Fe_3O_4 form a solid solution. Nickel is less easily oxidized; much of it probably either remained in taenite or formed Ni-rich sulfides.

Magnetite in Allende is found mostly in PO chondrules as spherical nodules ([4], this study). Minor sites are Ca-, Al-rich inclusions (CAIs) [33] and matrix [4,34]. The magnetite in PO chondrules occurs with Ni-rich metal and/or Ni-rich sulfides; no kamacite has been observed. Both kamacite and Ni-rich metal are found with the magnetite in CAIs. The metal in most CV chondrites contains ≤ 50 wt% Ni, while in Allende nearly all metal grains are Ni-rich (64–71 wt% Ni, [1,3]). Several euhedral to subhedral Ni-rich metal grains are present in a relatively large magnetite-bearing nodule in a PO chondrule [3]. Nodules of magnetite + sulfides, magnetite + metal, and metal + sulfide each exhibit somewhat different textures. Ni-rich metal cores occur in many magnetite grains ([1], this study) and tiny magnetite grains are also found in Ni-rich metal.

The total abundance of magnetite in Allende is much smaller (≤ 1 wt%, [28]) than those in the other oxidized CV chondrites, and individual nodules are generally less than 50 μm in diameter. The seven magnetite grains we analyzed are in four PO chondrules found by searching sections having a total area of ~ 100 cm^2. The magnetite grains are round, with apparent diameters of about 40–100 μm. Each magnetite grain is chemically homogeneous and there

Table 1
Chemical compositions (in wt%) and petrographic characteristics of magnetites analyzed and their host chondrules

Chondrule:	TS486			C2	C4	C6
Mean Fa (mol%)	2.3			2.5	4.0	3.3
Diameter (mm)	~ 1.5			~ 1	~ 2	~ 1.5
Magnetite:	M1	M2	M3	M1	M1	M1
Diameter (mm)	~ 40	~ 40	~ 40	~ 100	~ 40	~ 50
No. of points	3	3	3	4	3	1
SiO_2	< 0.04	–	–	nm	nm	nm
TiO_2	< 0.07	< 0.04	< 0.08	< 0.1	< 0.06	0.04
Al_2O_3	0.95	0.75	0.81	0.63	0.96	0.87
Cr_2O_3	1.17	1.21	1.05	1.19	1.02	1.17
Fe_3O_4	97.3	97.4	97.3	97.0	96.5	95.5
MnO	< 0.08	< 0.1	< 0.07	< 0.08	< 0.05	0.1
NiO	0.16	0.16	0.1	nm	nm	nm
MgO	0.21	0.6	0.15	0.19	0.25	0.3
CaO	< 0.10	< 0.08	< 0.12	nm	nm	nm
Total	99.8	100.1	99.4	99.0	98.7	98.3

nm = not measured.

is no significant chemical variation among grains. Most include tiny (< 3 μm) Ni-rich metal grains. The apparent diameters of the PO chondrules having these magnetite grains vary from 1 to 2 mm. The average composition of the olivine in these PO chondrules is Fa2.3–4.0 (Tables 1 and 2). Some olivine grains show weak chemical zoning. The petrographic descriptions and chemical data for the magnetite, olivine, and host chondrules are summarized in Tables 1 and 2.

4. Oxygen isotopic compositions

4.1. Magnetite

The O-isotopic data for the magnetite are summarized in Table 3 and Fig. 1. Among 16 measurements of the 7 magnetite nodules, 11 form a tight cluster. The two measurements of the C9M1 magnetite do not agree and are systematically heavier than the other magnetite grains. A secondary electron image of the C9M1 sputtered crater shows large pores and

Table 2
Chemical compositions (in wt%) of olivine grains analyzed for oxygen isotopes

Chondrule:	C2				C4		C6
Magnetite:	ol1	ol2	ol3	ol4	ol1	ol2	ol1
No. of points	8	3	3	2	7	4	2
SiO_2	41.98	42.12	41.96	41.89	41.68	40.78	42.62
Al_2O_3	0.19	0.27	0.19	0.20	0.18	0.10	0.26
Cr_2O_3	0.24	0.33	0.23	0.28	0.28	0.26	0.38
FeO	3.57	1.36	0.68	1.31	1.39	5.28	1.47
MnO	0.09	0.16	< 0.02	0.24	0.08	0.06	0.12
MgO	53.73	55.46	56.08	55.33	55.07	52.45	55.80
CaO	0.39	0.32	0.24	0.26	0.52	0.18	0.45
Total	100.2	100.0	99.4	99.5	99.2	99.1	101.1
Fa (mol%)	3.6	1.4	0.7	1.3	1.4	5.4	1.5

a Ni-rich metal grain. Tomeoka and Buseck [35] found phyllosilicates in some magnetite–metal nodules in chondrules of Allende. It is possible that oxygen-bearing phases previously filled the cracks and pores and that the relatively heavy O isotope compositions of the C9M1 magnetite are the result of contamination with phyllosilicates. Fractionation during the measurement related to the complex internal structure may also have played a role. Because of these uncertainties and the large difference of the C9M1 measurement from the other magnetites, we will neglect the C9M1 magnetite data in the following discussions. We also exclude the first measurement of the C4M1 magnetite grain from the average; we justify this mainly because the other two points are similar in composition and in a rough mass fractionation relationship to each other.

Table 3
Oxygen isotope compositions of Allende magnetite

Sample [a]	$\delta^{18}O \pm 1\sigma$ [b] (‰)	$\delta^{17}O \pm 1\sigma$ [b] (‰)	$\Delta^{17}O \pm 1\sigma$ (‰)
August 1995			
TS486M1_1	−5.8±1.6	−4.8±1.7	−1.8±1.9
TS486M2_1	−1.3±1.3	−7.5±2.1	−6.8±2.2
TS486M2_2	−4.3±1.5	−5.9±2.3	−3.7±2.4
mean [c] (M2)	*−2.6 ± 1.0*	*−6.7 ± 1.5*	*−5.3 ± 1.6*
TS486M3_1	−4.8±1.3	−2.9±2.0	−0.4±2.1
February 1996			
C2M1_1	−4.0±0.8	−5.6±1.1	−3.5±1.3
C2M1_2	−5.1±1.0	−5.3±0.9	−2.6±1.2
C2M1_3	−4.9±1.2	−3.8±1.7	−1.3±1.9
C2M1_4	−5.3±1.0	−4.9±0.9	−2.1±1.2
C2M1a_1 [d]	−5.8±1.0	−5.3±1.4	−2.3±1.6
mean	*−4.9 ± 0.4*	*−5.0 ± 0.5*	*−2.4 ± 0.5*
C4M1_1	−11.8±0.8	−4.7±1.0	1.4±1.2
C4M1_2	−6.9±1.0	−6.6±1.1	−3.0±1.4
C4M1_3	−6.4±0.9	−3.9±1.3	−0.6±1.4
mean [e]	*−6.7 ± 0.7*	*−5.3 ± 0.8*	*−1.8 ± 0.9*
C6M1_1	−6.6±0.9	−4.9±1.5	−1.4±1.6
C6M1_2	−7.9±1.2	−7.7±1.1	−3.6±1.4
mean	*−7.1 ± 0.7*	*−6.3 ± 0.9*	*−2.6 ± 0.9*
C9M1_1	0.0±1.0	−2.3±1.1	−2.3±1.3
C9M1_2	6.1±1.0	−0.1±1.2	−3.2±1.4

[a] _1, _2, etc., indicate successive measurements on the same spots.
[b] Standard errors include the uncertainty in the mass fractionation correction, but not in the composition of the standard.
[c] Means are weighted by the variance.
[d] C2M1a was measured on a different spot from that of C2M1.
[e] Excluding C2M4_1.

Table 4
Oxygen isotope compositions of Allende olivine

Sample [a]	$\delta^{18}O \pm 1\sigma$ [b] (‰)	$\delta^{17}O \pm 1\sigma$ [b] (‰)	$\Delta^{17}O \pm 1\sigma$ (‰)
C2ol1_1	−5.1±0.5	−7.6±0.7	−4.9±0.8
C2ol1_2	−5.6±0.5	−7.6±0.7	−4.7±0.8
mean [c]	*−5.4 ± 0.3*	*−7.6 ± 0.5*	*−4.8 ± 0.5*
C2ol2_1	−6.6±0.6	−7.3±0.7	−3.8±0.8
C2ol2_2	−6.1±0.4	−8.4±0.9	−5.2±1.0
mean	*−6.3 ± 0.3*	*−7.7 ± 0.6*	*−4.4 ± 0.6*
C2ol3_1	−5.5±0.6	−7.0±0.9	−4.1±0.9
C2ol4_1	−3.4±0.5	−5.8±1.0	−4.0±1.0
C4ol1_1	−1.0±0.6	−7.0±1.1	−6.5±1.1
C4ol1_2	−2.3±0.5	−6.4±0.7	−5.3±0.8
mean (ol1)	*−1.7 ± 0.4*	*−6.6 ± 0.6*	*−5.7 ± 0.6*
C4ol2_1	−0.8±0.4	−4.7±0.8	−4.3±0.8
C4ol2_2	−1.2±0.6	−4.5±0.9	−3.8±0.9
mean	*−0.9 ± 0.3*	*−4.6 ± 0.6*	*−4.1 ± 0.6*
C6ol1_1	−4.6±0.4	−8.2±0.8	−5.8±0.8
C6ol1_2	−4.7±0.6	−7.8±0.5	−5.3±0.6
mean	*−4.7 ± 0.3*	*−7.9 ± 0.4*	*−5.5 ± 0.5*

[a] _1 and _2 indicate successive measurements on the same spots.
[b] Standard errors include the uncertainty in the mass fractionation correction, but not in the composition of the standard.
[c] Means are weighted by the variance.

The largest magnetite grain, C2M1, was measured five times. The first three measurements are consecutive analyses on the same spot; after peak centering the first was followed immediately by the second and the cycle repeated for the third analysis. A fourth analysis on the same spot was carried out 7 h later, and the last measurement was on a new spot on the grain. Fig. 1 shows these five measurements; the circles represent measurements on the first spot and the cross-in-circle shows the analysis on the other spot. The similar compositions of these data show that we can reproduce the O isotope measurements of a small magnetite grain in silicate matrix. The similarity of data from the two spots indicates little or no internal O isotopic variation.

4.2. Olivine

The olivine O isotopic data fall on or slightly above the CCAM line (see Table 4 and Fig. 2). A similar compositional range has been measured by Saxton et al. [19] for low-FeO Allende olivine grains. Our measurements of olivine grains from the C4 PO chondrule fall within the compositional range of literature PO chondrule data [15,16], while those from chondrules C2 and C6 show more ^{16}O-enriched compositions. Apparent diameters of our PO chondrules vary from 1 to 2 mm. PO chondrules analyzed by Rubin et al. [16] have total masses between 1.75 and 11.5 mg [36], which roughly correspond to diameters between 1 and 2 mm. Therefore, there is no chondrule size bias between the two methods. The O isotopic composition of C2ol4 is about 2‰ higher in $\delta^{18}O$ relative to those of the other three olivine grains in the same chondrule. C2ol4 has narrow cracks filled with secondary minerals. If these secondary minerals are responsible for heavier O isotopic composition of C2ol4, and if most mesostasis experienced a similar alteration, this could explain the apparent difference between the O isotopic compositions of olivine and bulk chondrule.

5. Discussion

The following processes have been proposed as possible origins of magnetite in Allende and other oxidized CV chondrites:

1. crystallization of magnetite from a cooling, oxidized chondrule melt [2,3];
2. oxidation of metallic nodules within chondrules while in the solar nebula [4–6];
3. oxidation of metallic nodules on the CV parent asteroid [7,8].

The first two scenarios are set in the solar nebula, while the third takes place in an asteroidal setting. In the first model the magnetite nodules precipitated upon cooling of chondrule melts, while in the latter two the magnetite formed by corrosion of pre-existing metal nodules.

Oxygen isotopes can, in principle, help discriminate amongst these competing hypotheses. If magnetite formed by crystallization in a presumably well mixed chondrule melt, then the oxygen isotopic compositions of the magnetite and olivine should plot along a common mass fractionation line; that is, they should have the same $\Delta^{17}O$ values. In addition, because the degree of isotopic fractionation between minerals is small at high temperatures ($\Delta^{18}O_{\text{olivine-magnetite}} < 2‰$ at $T > 1400$ K, [37]), the magnetite $\delta^{18}O$ value should be only about 1–2‰ less than that in the olivine.

Three chondrules (C2, C4 and C6) were measured for the O isotopic compositions of both magnetite

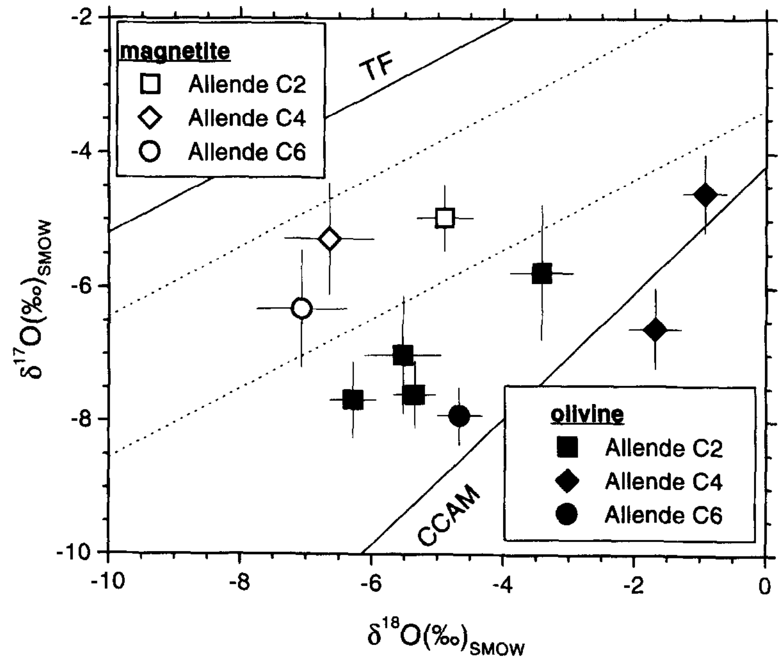

Fig. 5. Average oxygen isotope compositions of coexisting magnetite and olivine grains in C2, C4, and C6 PO chondrules. The broken lines show 95% confidence interval of the mean $\Delta^{17}O$ of three magnetite grains; no olivine grains fall in this range. See text for details.

and olivine. The average O isotopic compositions of these magnetite and olivine grains (Fig. 5) demonstrate that these coexisting phases are not in equilibrium. Broken lines parallel to the TF line in Fig. 5 show the 95% confidence interval of the mean $\Delta^{17}O$ of three magnetite grains. None of the olivine has an O isotopic composition in this range. The differences in $\Delta^{17}O$ values between coexisting magnetites and olivines from the same chondrules vary from 1.6 ± 1.1 to 3.9 ± 1.1‰ (1σ errors). Moreover, the $\Delta^{18}O_{\text{olivine-magnetite}}$ values do not show the expected high temperature equilibrium fractionation of about 1–2‰, but vary from −1.4‰ to 5.8‰. In summary, these data are inconsistent with the hypothesis that magnetite formed during chondrule crystallization.

The disequilibrium between the O-isotope compositions of the magnetite and the coexisting olivine indicates that the magnetites formed from pre-existing chondrule metal by oxidation with a gas or a fluid having a less negative $\Delta^{17}O$ than the olivine. If the magnetite formed by corrosion of metal (either in the nebula or on a parent asteroid), the $\Delta^{17}O$ of the magnetite should be equivalent to that of the oxidant, which was probably H_2O [38]. Because temperature effects on O isotopic composition of magnetite oxidized by gaseous H_2O are minor (~ 4‰ between 1000 and 400 K [37]), oxidation in the "infinite" O isotope reservoir of the nebula could be expected to yield a fairly homogeneous O isotope composition for the magnetite grains. On the other hand, oxidation on the parent asteroid having a low H_2O content would probably result in more heterogeneous magnetite compositions having similar $\Delta^{17}O$, but following a fractionation trend on a 3-isotope plot. The variation in $\delta^{18}O$ observed in the six magnetites, about 4.5‰, may not be sufficient to distinguish whether the magnetite was oxidized by an "infinite" or a "limited" oxygen reservoir.

An alternative approach to discriminating between nebular and asteroidal oxidation is to compare magnetite O isotope compositions with independent evidence regarding the O isotope compositions of nebular gas. A variety of evidence indicates that, in carbonaceous chondrites, the least negative $\Delta^{17}O$

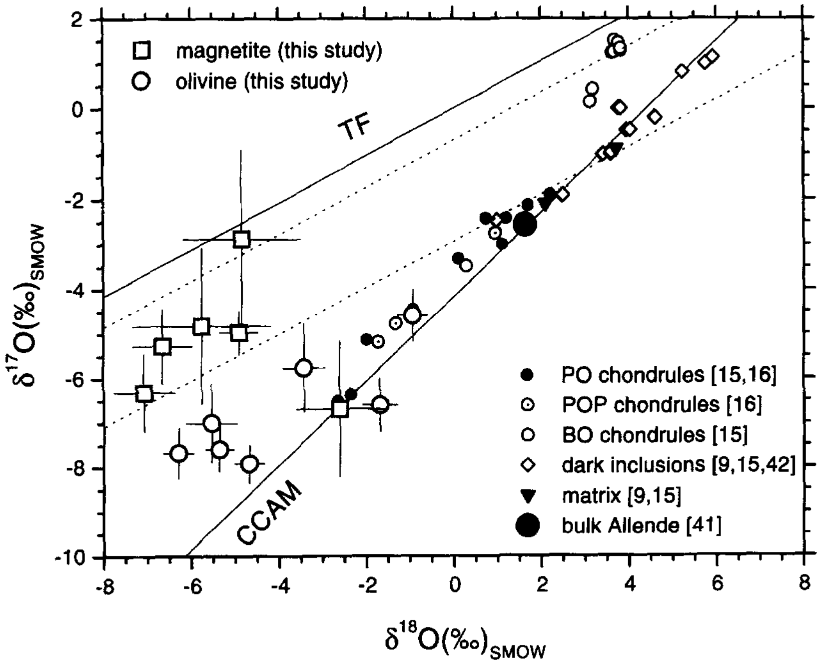

Fig. 6. Oxygen isotopic compositions of Allende magnetite and olivine measured by the UCLA Cameca ims 1270 ion microprobe and other oxygen bearing components of Allende measured by Clayton and coworkers [9,15,16,41,42]. The broken lines show 95% confidence interval of the mean $\Delta^{17}O$ of five magnetite grains (excluding TS486M2). Oxygen isotopic compositions of BO chondrules, dark inclusions, and matrix fall in this range.

values (closer to the TF line) are found in phases that formed later in the nebula or were more equilibrated with nebular gas than the most refractory minerals [9,16,39,40]. This suggests that the $\Delta^{17}O$ of nebular gaseous oxygen where and when Allende formed was about the same or higher than that measured in barred olivine (BO) chondrules ($\Delta^{17}O = -0.4$‰, [15]). Previous measurements of O isotope compositions of magnetites in CI, CR2, and the ungrouped type-2 carbonaceous chondrite Essebi ($\Delta^{17}O = -0.38$ to $+1.79$‰, [11,12]) also constrain the composition of the gaseous oxygen; since the $\Delta^{17}O$ of the anhydrous phases in carbonaceous chondrites ≤ 0‰, that of the H_2O before any O isotope exchange reaction with the rock should have had a $\Delta^{17}O \geq 0$‰. It is, therefore, probable that the H_2O accreted to the CV parent asteroid had a $\Delta^{17}O \geq 0$‰.

In Fig. 6 we compare our data with the literature data of various components of Allende measured by Clayton and coworkers [9,15,16,41,42]. The 95% confidence range of the mean $\Delta^{17}O$ of five magnetite grains (excluding T486MT2) is shown by the dotted line. The magnetite $\Delta^{17}O$ values are similar to or more negative than those of BO chondrules, and in same range with those of dark inclusions (largely consisting of fayalitic olivine) and matrix. The fact that $\Delta^{17}O$ values of the magnetite grains in Allende fall between estimated initial H_2O composition and that of bulk Allende suggests that the oxidant H_2O had experienced some O isotope exchange with silicates prior to magnetite formation. This supports the hypothesis that the magnetite formed in an asteroid.

We can also estimate the $\delta^{18}O$ value of the oxidant. If the magnetite formed by oxidation of metal by liquid H_2O, the maximum equilibrium fractionation in $^{18}O/^{16}O$ ratio between magnetite and water ($\Delta^{18}O_{\text{magnetite-water}}$) would be -13.6‰ at a temperature ~ 390 K [12]. If Allende originated from a relatively shallow depth, where the overburden pressure was small, the oxidant was probably gaseous H_2O; the equilibrium $\Delta^{18}O$ between magnetite and gaseous water is nearly constant between 400 and 700 K at $\Delta^{18}O \approx -10 \pm 1$‰, based on the fractionation factors given in Clayton and Kieffer [37]. Therefore, it is possible that the oxidant water that reacted with metal to form Allende magnetite nodules had an oxygen isotopic composition similar to that observed in dark inclusions.

6. Summary

Most magnetite in oxidized CV3 chondrites occurs as spherical nodules in chondrules. In Allende, magnetite mainly occurs in PO chondrules, generally together with Ni-rich metal and sulfides. Several processes have been proposed to account for the origin of the magnetite in oxidized CV3 chondrites, including both nebular and asteroidal origins and both crystallization and alteration processes. Our augmentation of petrographic observations by O isotopic data indicates that the best model involves oxidation in an asteroidal setting.

We measured O isotope compositions of individual magnetite nodules and coexisting olivine grains in Allende PO chondrules using an in situ ion microprobe technique. Measurements from 6 magnetite grains yield O isotope compositions ranging from -4.8 to -7.1‰ in $\delta^{18}O$ and from -2.9 to -6.3‰ in $\delta^{17}O$, and -0.4 to -5.3‰ in $\Delta^{17}O$. If we exclude one magnetite from our early, less-precise run, the variation in $\Delta^{17}O$ is from -0.4 to -2.6‰. Comparison of the O isotopic compositions of the magnetites with coexisting olivine, whose O isotopic compositions range from -4.0‰ to -5.7‰ in $\Delta^{17}O$, shows that the magnetites and olivines are not in O isotopic equilibrium. The magnetite has $\Delta^{17}O$ values closer to the TF line, similar to those in high-FeO olivine, dark inclusions, and matrix. The most probable origin of the magnetite is alteration of Fe–Ni metal by H_2O having O isotope compositions similar in $\Delta^{17}O$ to that of the magnetite. The O isotope composition of this H_2O may reflect O isotope exchange between nebular H_2O having $\Delta^{17}O$ near or above 0‰ and fine-grained silicates or other oxides having $\Delta^{17}O < -3$‰.

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