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Oxygen isotopes in magnetite and fayalite in CV chondrites Kaba and Mokoia

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Abstract–We report *in situ* measurements of O-isotopic compositions of magnetite and primary and secondary olivine in the highly unequilibrated oxidized CV chondrites Kaba and Mokoia. In both meteorites, the magnetite and the secondary olivine (fayalite, Fa_{90-100}) have O-isotopic compositions near the terrestrial fractionation (TF) line; the mean $\Delta^{17}O$ (= $\delta^{17}O$–0.52 × $\delta^{18}O$) value is about –1‰. In contrast, the compositions of nearby primary (chondrule), low-FeO olivines (Fa_{1-2}) are well below the TF line; $\Delta^{17}O$ values range from –3 to –9‰. Krot *et al.* (1998) summarized evidence indicating that the secondary phases in these chondrites formed by aqueous alteration in an asteroidal setting. The compositions of magnetite and fayalite in Kaba and Mokoia imply that the O-isotopic composition of the oxidant was near or somewhat above the TF line. In Mokoia the fayalite and magnetite differ in $\delta^{18}O$ by ~20‰, whereas these same materials in Kaba have virtually identical compositions. The difference between Mokoia magnetite and fayalite may indicate formation in isotopic equilibrium in a water-rich environment at low temperatures, ~300 K. In contrast, the similar compositions of these phases in Kaba may indicate formation of the fayalite by replacement of preexisting magnetite in dry environment, with the O coming entirely from the precursor magnetite and silica. The $\Delta^{17}O$ of the oxidant incorporated into the CV parent body (as phyllosilicates or H_2O) appears to have been much (7–8‰) lower than that in that incorporated into the LL parent body (Choi *et al.*, 1998), which suggests that the O-isotopic composition of the nebular gas was spatially or temporally variable.

INTRODUCTION

The CV (Vigarano-group carbonaceous) chondrites are among the most studied chondrites. McSween (1977) divided CV chondrites into the less common reduced subgroup and the more common oxidized subgroup largely on the basis of their abundances of reduced phases such as metal and oxidized phases such as magnetite. Krot *et al.* (1995) showed that the oxidized CV have experienced extensive alteration resulting in the formation of secondary nepheline, sodalite, fayalitic olivine, fayalite, salite-hedenbergitic pyroxenes, phyllosilicates, awaruite, and magnetite, whereas the reduced CV largely escaped extensive alteration. The oxidized CV were recently divided into the Bali- and Allende-like lithologies (Weisberg *et al.*, 1997; Krot *et al.*, 1998). The Bali lithology is characterized by the presence of abundant secondary fayalite (Fa_{90-100}) and phyllosilicates, whereas the Allende lithology virtually lacks these minerals and contains fayalitic olivine (Fa_{40-60}), nepheline, and sodalite instead. Krot *et al.* (1998) suggested that the Allende lithology experienced asteroidal alteration at higher temperatures than the Bali lithology. The observed excess of ^{53}Cr in Mokoia fayalite with the initial $^{53}Mn/^{55}Mn$ ratio of (2.3 ± 0.2) × 10^{-6} suggests that fayalite formed about 7–10 Ma after crystallization of the Allende calcium-aluminium-rich inclusions (CAIs), which is consistent with an asteroidal origin (Hutcheon *et al.*, 1998).

Our team used the University of California at Los Angeles's Cameca ims 1270 ion microprobe to study magnetite in CV3 Allende (Choi *et al.*, 1997) and in the unequilibrated LL3 chondrites Semarkona and Ngawi (Choi *et al.*, 1998). The mean $\Delta^{17}O$ (= $\delta^{17}O$ – 0.52 × $\delta^{18}O$) in LL3 magnetite was found to be ~5.2‰, the highest $\Delta^{17}O$ value reported in meteorite samples that clearly formed in the solar system. The data were interpreted to indicate that the oxidant (probably H_2O) responsible for the formation of the magnetite had $\Delta^{17}O$ ~7%.

We report O-isotopic data for several magnetite and fayalite grains in the oxidized CV chondrites Kaba and Mokoia. Key questions addressed in this paper are (1) the nature of the asteroidal process that produced the magnetite and fayalite (2) the nebular source of the oxidant that produced the magnetite and (3) the number and nature of the major nebular reservoirs (in particular, their O-isotopic compositions) and whether the composition of the gaseous reservoir changed with time or location. A preliminary report of the Mokoia data was given by Krot *et al.* (1998).

SAMPLES AND ANALYTICAL PROCEDURES

Polished thin sections of Kaba (JSC 75.1-K1, off ASU 75.1), Mokoia (JSC 35794-M1, off BM35794) and USNM2166 were studied using optical microscopy, backscattered electron imaging, and electron probe microanalysis. Backscattered electron images were obtained with a Zeiss DSM962 scanning electron microscope using a 15 keV accelerating voltage and 1–2 nA beam current. Electron probe microanalysis was performed with a Cameca-microbeam SX50 electron microprobe using a 15 keV accelerating voltage, 10–20 nA beam current, and beam size of about 1–2 μm using wavelength dispersive x-ray spectroscopy. For each element, counting times on both peak and background were 30 s (10 s for Na and K). Matrix effects were corrected using PAP procedures.

Oxygen-isotopic measurements on the Cameca 1270 were carried out during 1997–1998. A defocused Cs^+ beam of 0.1–0.5 nA was used to sputter craters ~12 to 25 μm in diameter on carbon-coated polished thin sections. Negative ^{16}O ions were measured by a Faraday cup; the other isotopes were collected on an electron multiplier. In many analyses of olivine and some on magnetite, $^{17}O^-$ peaks were fully separated from $^{16}OH^-$ peaks with mass resolving power of ~7000. Some spots on magnetite had relatively large

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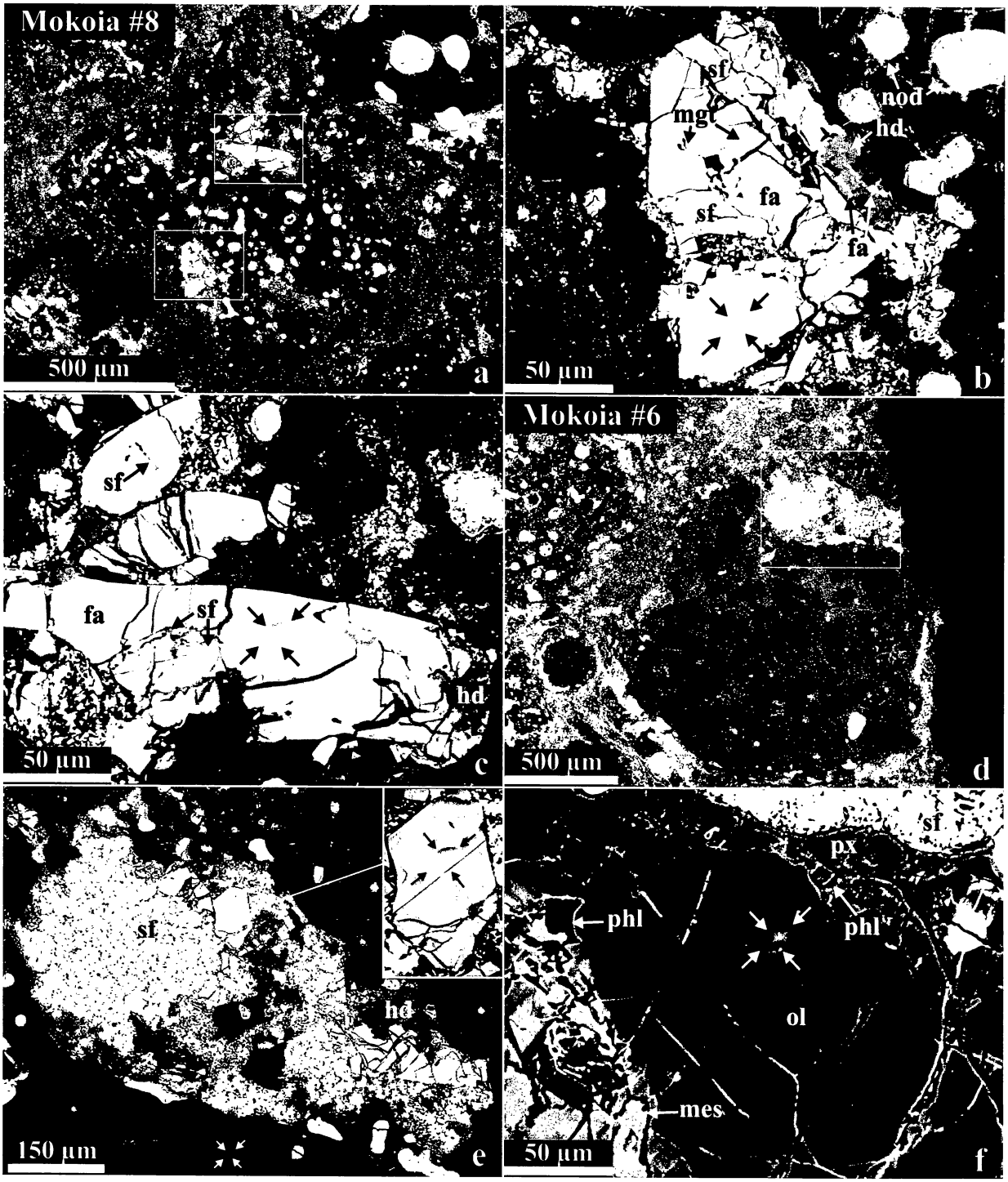

FIG. 1. Backscattered electron micrographs of the fayalite-hedenbergite-magnetite-bearing chondrules #8 (a, b, c) and #6 (d, e, f) from Mokoia. (a–c) Regions outlined in (a) are shown in detail in (b) and (c). Fayalite (fa) grains occur in the outer portion of the chondrule. These grains contain inclusions of Ni-bearing sulfide (sf) and magnetite (mgt) associated with hedenbergitic pyroxene (hd); some sulfide inclusions have elongated shapes. Low-Ca pyroxene (px) grains and mesostasis are replaced by phyllosilicates (phl). Forsteritic olivine (ol) phenocrysts and fayalite do not show evidence of replacement by phyllosilicates. Ion probe spots in fayalite grains analyzed are indicated by arrows in (b) and (c). (d–f) Large opaque nodule in the periphery of chondrule #6 outlined in (d) is shown in detail in (e–f). The large nodule consists of Ni-bearing sulfide (sf), fayalite (fa), and hedenbergitic pyroxene (hd). Low-Ca pyroxene (px) and anorthitic mesostasis (mes) are replaced by phyllosilicates (phl); forsteritic olivine (ol) and fayalite appear to be unaltered. The inset in (d) shows a more detailed view of the ion probe spot on the fayalite grain. The ion probe spot in forsteritic olivine indicated near the bottom of (e) is shown in more detail in (f).

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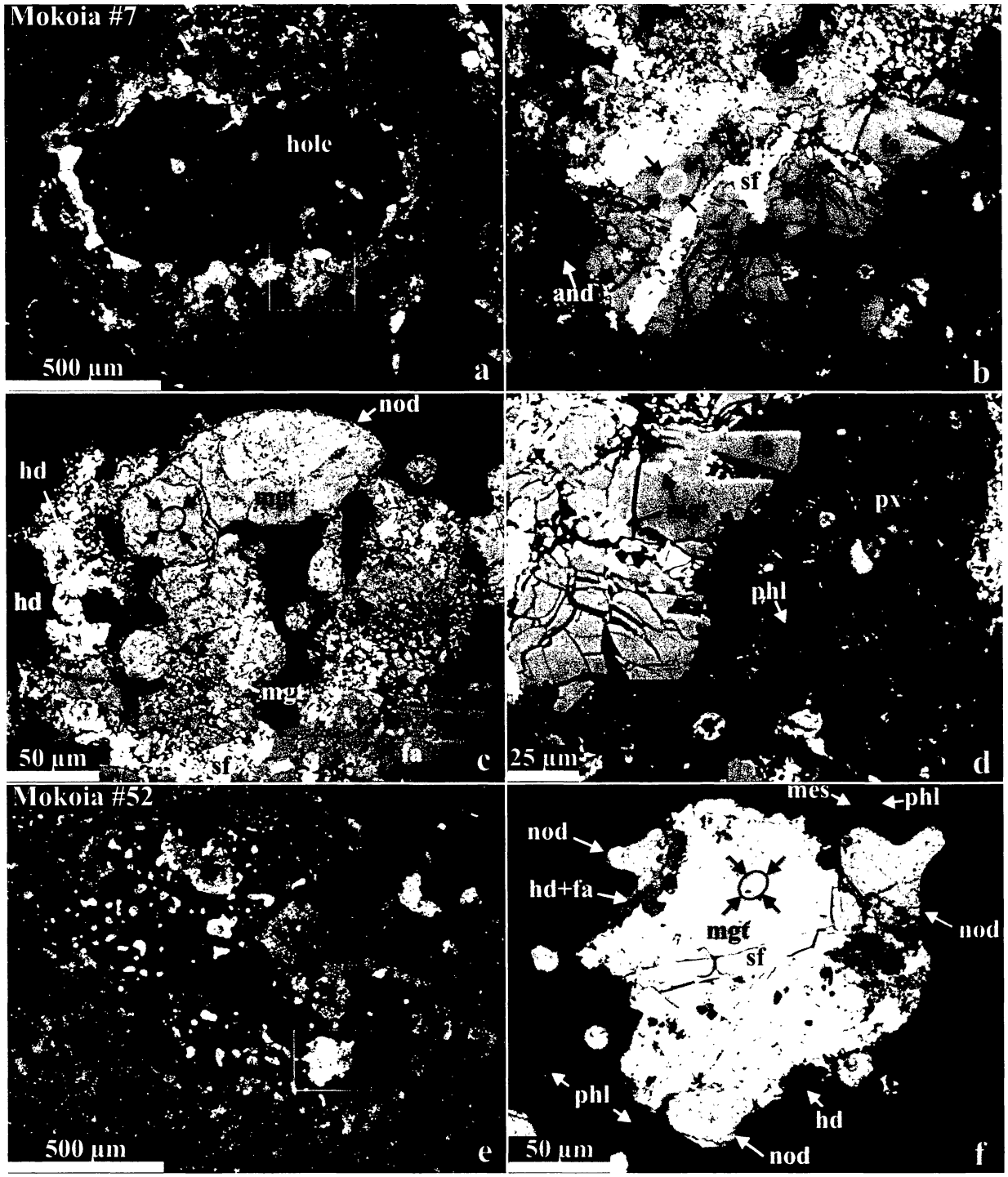

FIG. 2. Backscattered electron micrographs of the fayalite-hedenbergite-magnetite-bearing chondrules #7 (a–d) and #52 (e, f) from Mokoia. Regions outlined in (a) and (e) are shown in detail in (b) through (d) and (f), respectively. (a–b) Fayalite (fa) forms massive grains containing inclusions of Ni-bearing sulfide (sf) and magnetite (mgt); black area is plucked. Some sulfide inclusions have elongated shapes suggesting infilling of cracks. (c) The magnetite/fayalite ratio increases toward the chondrule's core. Hedenbergitic pyroxenes (hd) occur as rounded nodules surrounded by sulfides. (d) Low-Ca pyroxene (px) phenocrysts in the chondrule's periphery are replaced by phyllosilicates (phl) and rimmed by bronzitic pyroxene (thin light-gray layers along phyllosilicate–pyroxene boundaries). (e, f) In chondrule 52, magnetite occurs as massive grains containing elongated inclusions of Ni-bearing sulfides and as rounded nodules (nod) containing tiny inclusions of Ca-, P-, Cr-, Ni-, and S-rich phases, possibly phosphates, chromite, and Ni-bearing sulfides. Massive magnetite appears to be replaced by fayalite and hedenbergitic pyroxene; nodular magnetite appears not to alter to those silicates. Anorthitic mesostasis (mes) is replaced by phyllosilicates (phl). Fayalite and magnetite grains analyzed by ion probe are outlined and indicated by arrows in (b), (c), and (f).

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$^{16}OH^-$ peaks whose tails gave a minor contribution to $^{17}O^-$. The interference was monitored and corrected: The maximum $^{16}OH^-$ interference to the $^{17}O^-$ signal was 0.5‰, and typically <0.1‰. A terrestrial magnetite LP204 (Valley and Graham, 1991) was used as the magnetite standard and a synthetic fayalite as primary standard for fayalite. Olivine grains from the San Carlos peridotite were used as the secondary olivine standards and to evaluate the matrix effect of olivine composition on the instrumental mass fractionation. Analytical procedures are described in more detail in Choi *et al.* (1997).

MINERALOGY AND PETROGRAPHY

In Kaba and Mokoia, fayalite occurs in peripheral portions of magnesian (Type I) chondrules, fine-grained chondrule rims, and in matrix. These fayalite-bearing assemblages have similar mineralogy and compositions, probably indicating similar formation mechanism(s) (Hua and Buseck, 1995; Krot *et al.*, 1998). The petrologic settings of the representative forsterite, fayalite, and magnetite grains from Kaba and Mokoia studied for O-isotopic compositions are illustrated in Figs. 1–4 and summarized in Table 1. Because of the small grain size, the O-isotopic composition of fayalite in fine-grained rims was not studied.

Fayalite in chondrules forms large subhedral-to-anhedral grains that commonly contain inclusions of Ni-bearing sulfides (troilite and Ni-poor pentlandite) and magnetite; the latter is nearly pure Fe_3O_4. In some cases, sulfide inclusions in fayalite have elongated morphologies (Figs. 1b,c and 2b). Texturally similar sulfides are present in massive magnetite grains (Figs. 2f and 3d). Our observations and those described by Hua and Buseck (1995) and by Krot *et al.* (1998) suggest that fayalite in Kaba and Mokoia chondrules replaced magnetite-sulfide assemblages. Fayalite-magnetite assemblages are closely associated with hedenbergitic pyroxenes (Figs. 1b,c; 2c,f; and 3d).

The host chondrules have igneous porphyritic olivine-pyroxene textures with forsteritic olivines (Fa_{1-2}) poikilitically enclosed by low-Ca pyroxene phenocrysts (Fs_{1-2}) that are surrounded by anorthitic mesostasis (with high-Ca pyroxene crystallites (Table 2). Low-Ca pyroxenes are replaced to various degrees by low-Al phyllosilicate and bronzitic pyroxene, whereas anorthitic mesostasis

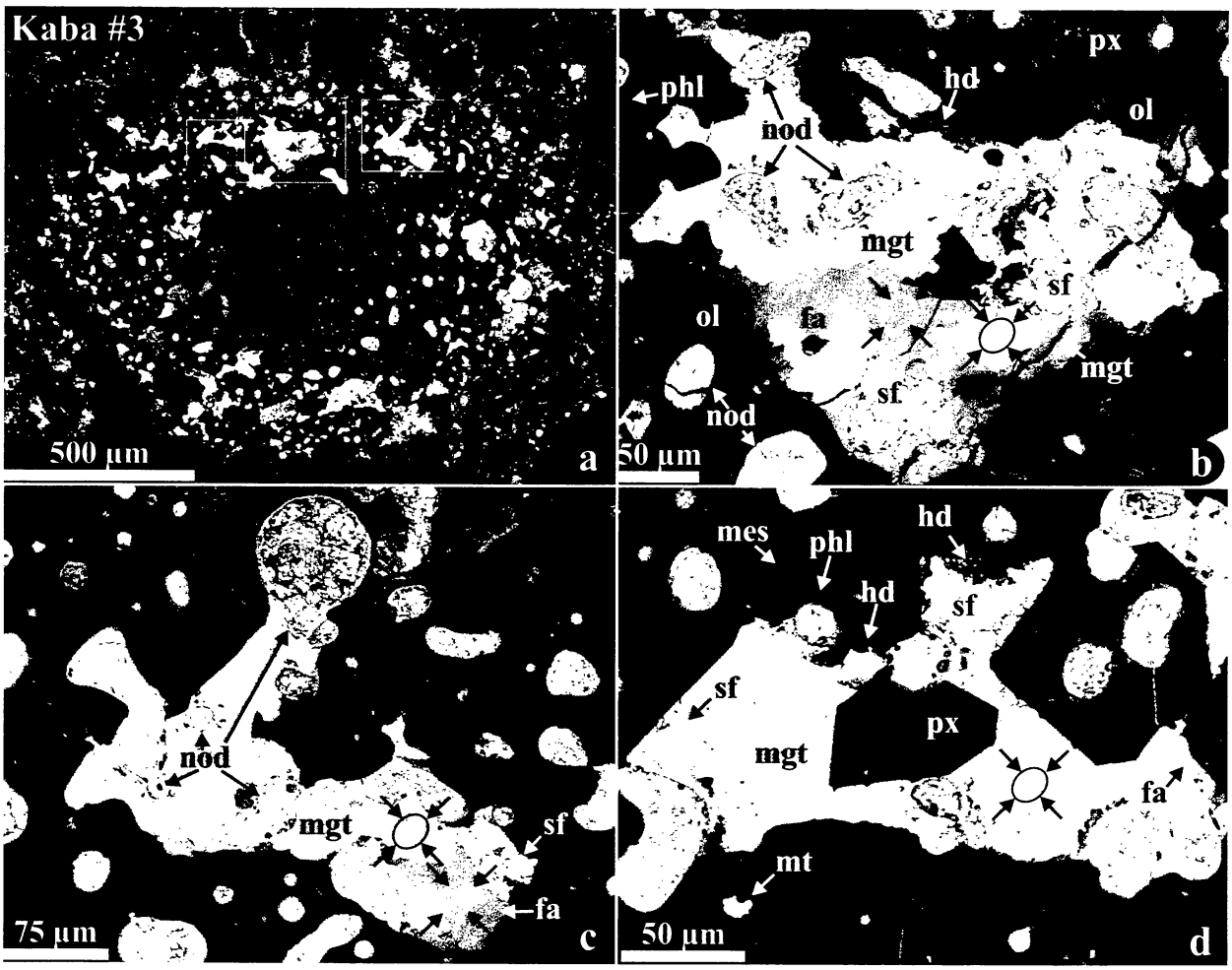

FIG. 3. Backscattered electron micrographs of the fayalite-hedenbergite-magnetite-bearing chondrule #3 from Kaba. Regions outlined in (a) are shown in detail in (b) through (d). Magnetite (mgt) occurs as massive grains associated with large grains of Ni-bearing sulfides (sf) and enclosing rounded magnetite nodules (nod) rich in tiny inclusions of Ca-, P-, Cr-, Ni-, and S-rich phases, probably phosphates, chromite, and Ni-bearing sulfides. Massive magnetite and sulfide is corroded by fayalite (fa) and hedenbergitic pyroxenes (hd). Low-Ca pyroxene phenocrysts (px) (and anorthitic mesostasis (mes)) are corroded by phyllosilicates (phl); forsteritic olivine grains (ol) show no evidence for the replacement, but some have higher FeO enrichment along the boundaries with fayalite (see (b)), and the latter have higher MgO. Regions of fayalite and magnetite grains analyzed by ion probe are indicated by arrows in (b) through (d).

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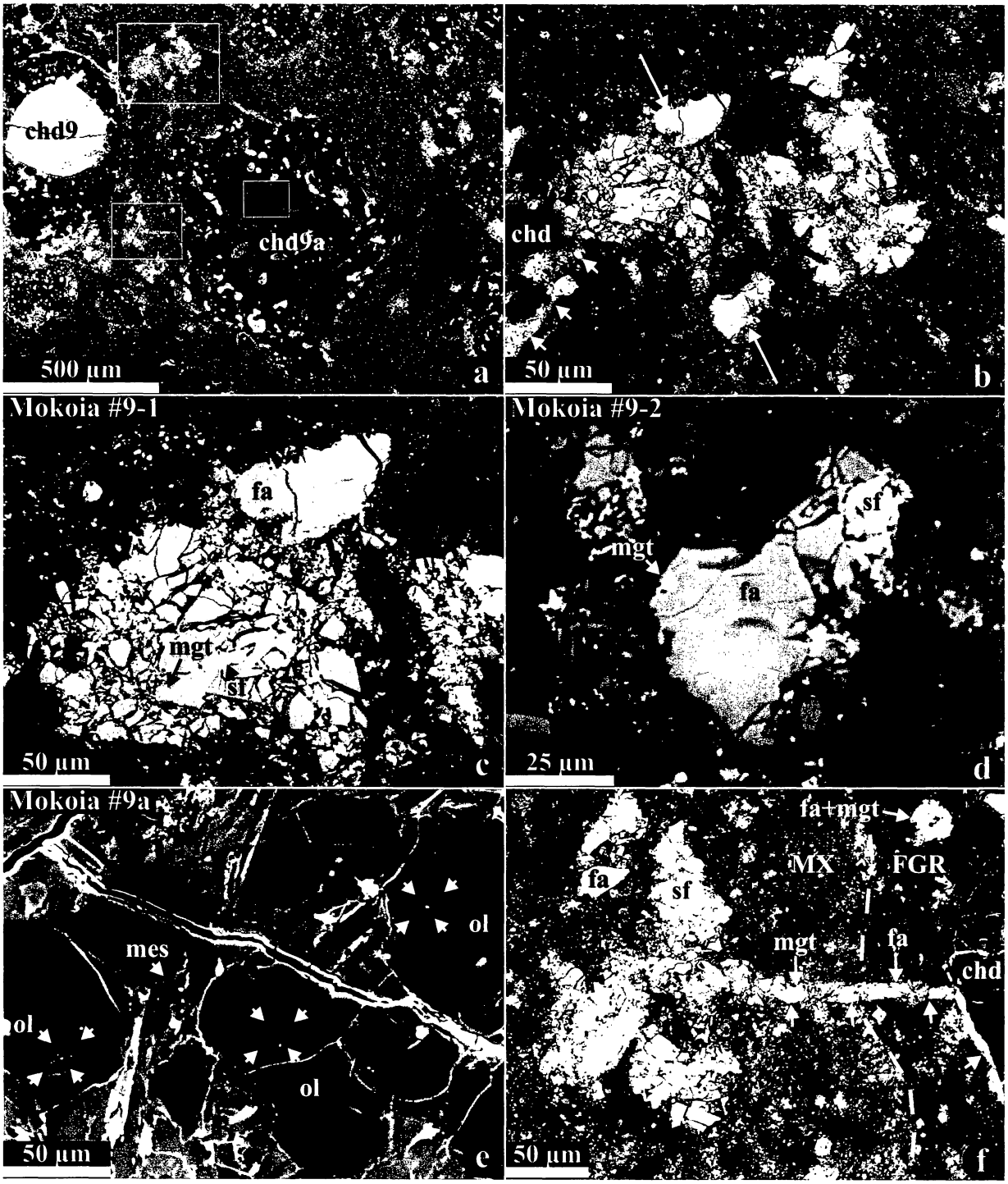

FIG. 4. Backscattered electron micrographs of the neighboring chondrules #9 and #9a from Mokoia. Regions outlined in (a) are shown in detail in (b) through (f). Fayalite-magnetite-sulfide-bearing assemblages occur in the outer portions of the chondrules, their fine-grained rims, and in matrix. Both occurrences are connected through a fayalite-magnetite-sulfide vein (indicated by arrows in (f)) crosscutting the fine-grained rims around the chondrules. The dashed line in (f) marks the boundary between the fine-grain rim (FGR) of chondrule #9a and adjacent matrix (MX). Ion probe spots in forsteritic olivine phenocrysts (ol) and fayalite analyzed are indicated by arrows in (c), (d), and (e) (three spots).

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TABLE 1. Description of the samples in which the O-isotopic compositions are determined.

Chondrite	Section	Sample	Grains*	Descriptive notes
Mokoia	JSC 35794-M1	chd8	fa8-1, 2	Subhedral fayalite, magnetite and sulfide inclusions (Fig. 1)
			fo8	Forsteritic olivine enclosed in low-Ca pyroxene phenocryst
Mokoia	JSC35794- M1	chd6	fa6	Subhedral fayalite associated with hedenbergite (Fig. 1)
			fo6-1, 2	Forsteritic olivine enclosed in low-Ca pyroxene phenocrysts
Mokoia	JSC35794--M1	chd52	mt52	Massive magnetite with elongated sulfide inclusions (Fig. 2)
Kaba	JSC 75.1-K1	chd3	fa3-1, 2	Fayalite replacing massive magnetite (Fig. 3)
			mt3-1,2,3,4	Massive magnetite
			fo3-1, 2	Forsteritic olivine phenocrysts
Mokoia	JSC 35794-M1	mx9-1,2	fa9-1, 2	Fayalite with magnetite and sulfide inclusions (Fig. 4)
Mokoia	USNM2166	chd61	mt61-1, 2	Nodular magnetite
Mokoia	USNM2166	chd62	mt62	Nodular magnetite
Mokoia	USNM2166	chd66	mt66	Nodular magnetite

*Abbreviations: fa = fayalite; fo = forsterite; mt = magnetite.

and high-Ca pyroxene are commonly replaced by phyllosilicates with higher Al contents (Figs. 1–4; Table 2). Forsteritic olivine phenocrysts show no evidence for alteration (at magnifications up to 5000), even in direct contact with phyllosilicates (Figs. 1f and 3d). Oxygen-isotopic compositions of forsteritic olivine phenocrysts in fayalite-bearing and fayalite-free chondrules were studied (Table 1).

All fayalite-hedenbergite-bearing chondrules studied contain a high abundance of opaque nodules composed of magnetite and Ni-bearing sulfides (Figs. 1–4). Rare relic Fe,Ni-metal nodules were found only inside chondrule phenocrysts (Fig. 3d). There are two textural types of magnetite in chondrules: rounded nodules and massive grains; both types commonly coexist (Figs. 2 and 3). The nodular magnetites have detectable concentrations of CaO (0.2–0.3 wt%), NiO (0.2–0.3 wt%), and Cr_2O_3 (0.3–1.5 wt%), possibly because of submicron inclusions of Ca-phosphates, chromite, and Ni-bearing sulfides. The massive magnetite grains are compositionally pure Fe_3O_4 (CaO, NiO, Cr_2O_3 <0.03 wt%) and commonly contain coarse-grained Ni-bearing sulfide inclusions; the latter are occasionally elongated (Figs. 2f and 3c), similar to those observed inside fayalite grains (Figs. 1b and 2b). It appears that only massive, compositionally pure magnetite grains are replaced by fayalite and hedenbergite; the coexisting nodular magnetite shows no evidence for this replacement (Fig. 3). Oxygen-isotopic compositions of both textural types of magnetite were studied (Table 1).

We studied two coarse fayalite grains in Mokoia matrix that occur near two fayalite-bearing chondrules (Fig. 4). These are similar to the chondrule fayalite grains in that they contain abundant inclusions of Ni-bearing sulfides and rare inclusions of magnetite. Fine-grained rims on neighboring chondrules are crosscut by fayalite-magnetite-sulfide veins that connect with the fayalite-magnetite-sulfide assemblages in the matrix (Fig. 4f), an indication that fayalite formation postdated accretion, compaction, and lithification of the fine-grained rims and matrix materials (Krot *et al.*, 1998).

OXYGEN-ISOTOPIC COMPOSITION OF THE MAGNETITE AND OLIVINE

Our O-isotopic data on Kaba and Mokoia magnetite and olivine are summarized in Tables 3 and 4 and plotted in a $\delta^{17}O$ *vs.* $\delta^{18}O$ diagram (Fig. 5). All listed uncertainties are 1σ. The O-isotopic compositions of magnetite and fayalite fall near the terrestrial fractionation (TF) line. Weighted mean $\Delta^{17}O$ values of magnetite and fayalite in Kaba are –1.0 ± 0.7‰ and –0.6 ± 0.5‰, respectively, and those in Mokoia are –0.9 ± 0.5‰ and 0.1 ± 0.5‰, respectively. Standard deviations of $\Delta^{17}O$ calculated from the grain to grain scatter are about –1‰. The mean magnetite $\Delta^{17}O$ values in Kaba and Mokoia are thus about –1‰, marginally higher than the mean $\Delta^{17}O$ of –2.2 ± 0.4‰ observed in Allende magnetite (Choi *et al.*, 1997). The O-isotopic composition of the forsteritic olivines in both meteorites scatter around the carbonaceous chondrite anhydrous minerals (CCAM) line, with $\Delta^{17}O$ values in the range –3 to –9‰.

The O-isotopic compositions of fayalite in each chondrite are quite homogenous. Although in each meteorite the mean $\Delta^{17}O$ values in the fayalite samples are slightly higher than those in the magnetite, the differences are not significant within 2σ. More important is that these are essentially the same as those in magnetite. As discussed in more detail below, this suggests that the $\Delta^{17}O$ of the

TABLE 2. Kaba and Mokoia chondrules. Representative microprobe analyses (in wt%) of primary olivine (ol), low-Ca pyroxene (px), mesostasis (mes), fayalite (fay), hedenbergite (hed), andradite (and), and secondary phyllosilicates (phl) differing in Al_2O_3 and H_2O contents.

	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO*	MnO	MgO	CaO	Na_2O	K_2O	Total	Phase (mol%)
ol	42.1	0.03	0.03	0.54	1.0	0.12	56.1	0.21	<0.03	<0.03	100.1	$Fa^{1.0}$
px	58.2	0.15	0.90	0.61	0.77	0.11	38.5	0.60	<0.03	<0.03	99.8	$Fs^{1.1}$, $Wo^{1.1}$
mes	45.7	0.05	35.3	<0.03	0.20	0.04	0.83	17.6	1.4	<0.03	101.2	$Ab^{12.7}$, $Fs^{87.2}$
fay	28.8	<0.03	<0.03	<0.03	70.2	0.27	0.18	<0.03	<0.03	<0.03	99.3	$Fa^{99.3}$
hd	47.0	0.10	<0.03	<0.03	27.0	0.30	0.80	22.0	<0.03	<0.03	98.0	$Fs^{48.0}$, $Wo^{50.0}$
and	33.8	0.11	0.09	0.06	34.2	<0.03	0.35	31.6	<0.03	<0.03	100.2	–
phl	40.2	0.05	9.1	0.66	3.2	0.03	17.8	0.11	1.7	0.33	73.2	–
phl	38.2	0.18	17.5	0.30	3.9	0.04	17.8	0.27	1.3	0.49	79.9	–
phl	36.0	<0.03	25.5	0.03	4.8	0.04	19.0	0.67	2.2	0.42	88.6	–

*As Fe_2O_3 in andradite.

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TABLE 3. Oxygen-isotopic composition of magnetite in Kaba and Mokoia.*

Meteorite	Grain	Host	$\delta^{18}O$ (‰)	1σ	$\delta^{17}O$ (‰)	1σ	$\Delta^{17}O$ (‰)	1σ
1997 June 25								
Kaba	mt3-1	chd3	9.5	± 0.9	4.2	± 1.0	–0.8	± 1.3
Kaba	mt3-2	chd3	11.4	± 1.0	5.5	± 1.1	–0.4	± 1.4
Kaba	mt3-3	chd3	12.6	± 0.9	4.0	± 1.0	–2.5	± 1.3
Kaba	mt3-4	chd3	11.4	± 1.0	5.6	± 1.0	–0.3	± 1.4
1997 July 07								
Mokoia	mt51	chd52	2.4	± 0.8	0.8	± 0.7	–0.4	± 1.1
Mokoia	mt51	chd52	2.5	± 1.0	1.2	± 0.9	–0.2	± 1.3
Mokoia	mt61-1	chd61	0.4	± 0.8	–2.7	± 0.8	–2.9	± 1.1
Mokoia	mt61-2	chd61	3.4	± 0.7	1.1	± 0.8	–0.7	± 1.1
Mokoia	mt62	chd62	2.3	± 0.6	0.6	± 0.8	–0.6	± 1.0
Mokoia	mt66	chd66	–0.2	± 0.9	–0.8	± 0.8	–0.7	± 1.2

*See Table 1 for descriptions of the host chondrules and matrix.

O incorporated into the fayalite was similar to that in the magnetite, which is consistent with formation of both minerals from the same O reservoir.

We can summarize the O-isotopic compositions of magnetite and fayalite in Kaba and Mokoia CV chondrites as follow: (1) Magnetite in grains in Kaba and Mokoia have relatively narrow O-isotopic compositions (*e.g.*, $\delta^{18}O$) compared to those in the ordinary chondrite Semarkona (Choi *et al.* 1998). However, we cannot rule out the possibility that this observation simply reflects the fewer analytical points in Kaba and Mokoia magnetite relative to ordinary chondrite magnetite. (2) Magnetite and fayalite in Mokoia have different O-isotopic compositions ($\delta^{18}O_{fayalite} - \delta^{18}O_{magnetite} \approx 20‰$), whereas these two phases in Kaba have similar O-isotopic compositions. (3) Magnetite and fayalite in Kaba and Mokoia show the highest $\Delta^{17}O$ values yet observed in CV chondrites (but are about 2–3‰ lower than the highest values measured in carbonaceous chondrites, 1.6–1.8‰ in CI magnetite; Rowe *et al.*, 1994).

TABLE 4. Oxygen-isotope composition of fayalite (fa) and fayalitic olivine (fo) in Kaba and Mokoia.*

Meteorite	Grain	Fa (mol%)	Host	Date	$\delta^{18}O$ (‰)	1σ	$\delta^{17}O$ (‰)	1σ	$\Delta^{17}O$ (‰)	1σ
Kaba	fa1-1	Fa100	chd1	97Oct24	10.7	± 0.9	4.0	± 1.0	–1.5	± 1.3
Kaba	fa1-2	Fa100	chd1	97Oct24	9.6	± 0.7	4.1	± 0.9	–0.9	± 1.1
Kaba	fa1-2	Fa100	chd1	98Oct09	13.3	± 1.2	5.4	± 1.1	–1.5	± 1.6
Kaba	fa3-1	Fa100	chd3	97Jun24	11.1	± 0.7	6.4	± 0.8	0.6	± 1.1
Kaba	fa3-1	Fa100	chd3	97Oct24	10.8	±1.0	4.6	± 0.6	–1.0	± 1.2
Kaba	fa3-2	Fa100	chd3	97Jun24	12.2	± 1.1	7.4	± 1.2	1.0	± 1.7
Kaba	fa3-2	Fa100	chd3	97Oct24	10.9	± 0.7	5.0	± 0.8	–0.7	± 1.0
Kaba	fa3-2	Fa100	chd3	98Oct09	10.0	± 1.8	4.7	± 1.1	–0.5	± 2.2
Mokoia	fa6	Fa99.8	chd6	97Jun23	21.1	± 0.7	10.6	± 0.9	–0.3	± 1.2
Mokoia	fa8-1	Fa99.4	chd8	97Jun23	20.8	± 0.9	11.5	± 0.8	0.7	± 1.2
Mokoia	fa8-2	Fa99.4	chd8	97Jun23	21.0	± 0.7	12.1	± 1.0	1.2	± 1.2
Mokoia	fa9-1	Fa99.3	mx9	97Jun23	19.8	± 0.8	10.3	± 0.8	0.0	± 1.1
Mokoia	fa9-2	Fa99.3	mx9	97Jun24	20.7	± 1.0	9.4	± 1.2	–1.4	± 1.5
Kaba	fo3-1	FaO.5	chd3	97Jun24	–2.5	± 1.4	–10.2	± 1.3	–8.9	± 1.9
Kaba	fo3-2	FaO.5	chd3	97Jun24	–2.4	± 1.1	–7.7	± 1.3	–6.5	± 1.7
Mokoia	fo6-1	Fa0.2	chd6	97Jun23	–1.5	± 1.1	–9.1	± 1.2	–8.3	± 1.6
Mokoia	fo6-2	Fa0.4	chd6	97Jun23	–1.0	± 1.0	–8.3	± 1.0	–7.8	± 1.4
Mokoia	fo8	Fa1.1	chd8	97Jun23	–2.3	± 0.8	–8.2	± 0.9	–7.0	± 1.2
Mokoia	fo9-1	Fa0.8	mx9	97Jun23	4.0	± 1.3	–1.3	± 1.2	–3.4	± 1.8
Mokoia	fo9-2	Fa0.8	mx9	97Jun23	1.2	± 0.9	–5.0	± 1.1	–5.5	± 1.4
Mokoia	fo9-3	Fa0.9	mx9	97Jun24	5.3	± 1.3	–2.4	± 1.3	–5.2	± 1.8

*See Table 1 for descriptions of the host chondrules and matrix.

FORMATION OF MAGNETITE AND FAYALITE ON THE CV PARENT BODY

Both nebular and asteroidal origins for CV magnetite, fayalite, and other alteration products have been proposed (Hua and Buseck, 1995; Krot *et al.*, 1995; Choi *et al*, 1997). Some of the magnetite grains in Figs. 1 to 4 show textural evidence of formation after chondrule and matrix were compacted (*i.e.*, in an asteroidal setting). The massive euhedral to subhedral shapes of the fayalites seem consistent with slow growth into voids during hydrothermal formation. Krot *et al.* (1995, 1998) have made a strong case for concluding that the alteration of Kaba and Mokoia mainly, if not exclusively, occurred within the parent body. We will not repeat those arguments here but content ourselves with pointing our the ways in which the O-isotopic evidence either supports or is consistent with formation in asteroidal processes.

The precise reactions that produced magnetite and fayalite are not known. A set of possible reactions are discussed in Krot *et al.* (1998). Their preferred reactions for the formation of magnetite and fayalite are:

$$3\ Fe\ (s) + 4\ H_2O\ (g) = Fe_3O_4 + 4\ H_2\ (g) \quad (1)$$

$$2\ Fe\ (s) + SiO_2\ (aq) + 2\ H_2O\ (g) = Fe_2SiO_4\ (s) = 2\ H_2\ (g) \quad (2)$$

$$2\ Fe_3O_4\ (s) + 3\ SiO_2\ (aq) + 2\ H_2\ (g) = 3\ Fe_2SiO_4\ (s) + 2\ H_2O \quad (3)$$

We will also show that another reaction not involving H_2O may have formed the fayalite in Kaba:

$$Fe_3O_4\ (s) + Fe\ (s) + 2\ SiO_2\ (s) = 2\ Fe_2SiO_4\ (s) \quad (4)$$

In addition to metal, Fe(s) could be produced by the oxidation of schreibersite or an iron sulfide. The fact that all magnetite and fayalite data in both meteorites fall within experimental uncertainties of a fractionation line suggests that these phases formed from the same O-isotopic reservoir. This is consistent with the conclusions of Krot *et al.* (1998) that both phases formed during low-temperature aqueous alteration on the CV parent body.

Nonetheless, the very different natures of the O-isotopic magnetite-fayalite "fractionations" between Kaba and Mokoia indicate important differences in processes, conditions, or both. The extremely large fractionation in $\delta^{18}O$ between magnetite and fayalite in Mokoia provides strong evidence for this having occurred at low temperatures in an aqueous environment. As shown in Fig. 6, $\Delta^{18}O_{fayalite-magnetite}$ increases with decreasing temperature ($\Delta^{18}O$ is the difference in $\delta^{18}O$ between two phases formed under equilibrium conditions). The observed difference, ~20‰, implies formation at low temperatures (~300 K) if fayalite and magnetite were in isotopic equilibrium. Because it is very difficult to reequilibrate grains by volume diffusion after their formation at such low temperatures, this large isotopic fractionation seems best understood in terms of the simultaneous growth of both phases. Other, more complex, models involving sequential formation of magnetite and fayalite not in equilibrium are also possible.

The measured range in $\delta^{18}O$ in Mokoia fayalite and magnetite is relatively small, <4‰ in each phase (the actual range could be smaller, if the experimental

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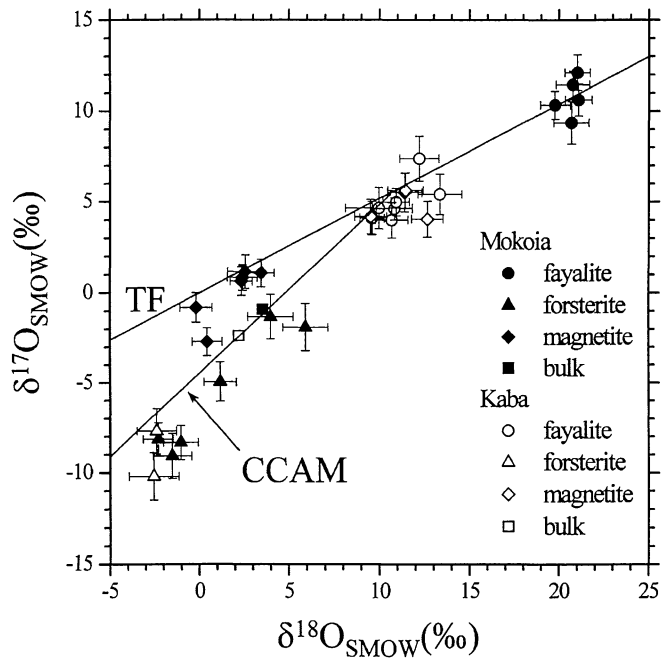

FIG. 5. Oxygen-isotopic compositions of magnetite, fayalite, and forsteritic olivine in magnetite-bearing assemblages in Kaba and Mokoia. The TF and CCAM lines are shown for reference. In Mokoia, the magnetite and fayalite differ in $\delta^{18}O$ by ~20‰, whereas in Kaba the compositions are nearly identical, and very close to the intersection of the TF and CCAM lines. Bulk Kaba and Mokoia compositions from Clayton and Mayeda (1999) are shown.

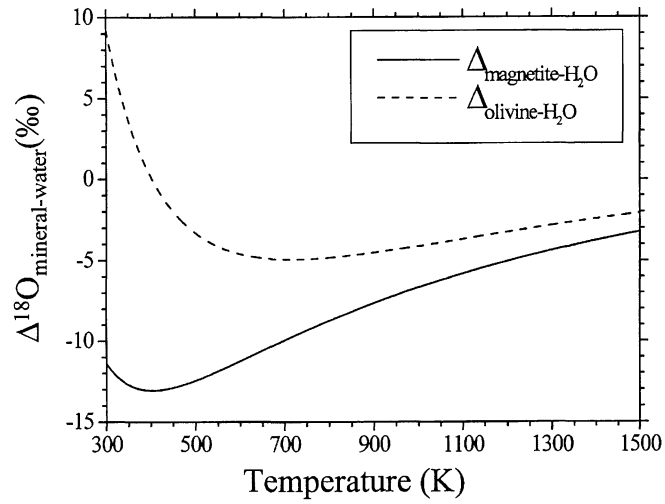

FIG. 6. A plot of $\Delta^{18}O$ *vs.* temperature for magnetite-H_2O and olivine-H_2O. Data were extrapolated to low temperatures using the reduced partition functions for olivine (forsterite) and magnetite from Clayton and Kieffer (1991), for H_2O from Hattori and Halas (1982). A small difference of <1‰ is expected between forsterite and fayalite. At isotopic equilibrium, magnetite has lower $\delta^{18}O$ than H_2O, whereas olivine has high $\delta^{18}O$ than H_2O at temperatures above 400 K. At ~300 K, the equilibrium fractionation between magnetite and olivine is ~20‰, as observed in Mokoia.

uncertainty plays an important role, or larger, if there is zoning on a scale smaller than our beam size, typically ~12 μm). This small range contrasts with observations in Semarkona, where Choi *et al.* (1998) observed a 13‰ range in $\delta^{18}O$ in the magnetite. As noted by Choi *et al.* (1998), when Fe-Ni metal (or sulfides) are oxidized to form magnetite by a limited supply of H_2O, the O of H_2O might undergo appreciable fractionation because of preferential incorporation of lighter O isotopes into magnetite.

However, if magnetite and fayalite form simultaneously during low-temperature oxidation of preexisting Fe-Ni metal or sulfide (such as reactions (1) and (2)), the residual H_2O may show only minimal change or even a decrease in $\delta^{18}O$, as observed in Semarkona. At low temperatures, magnetite has lower $\delta^{18}O$ than H_2O whereas olivine has higher $\delta^{18}O$ (Fig. 6). In other words, the direction and amount of shift in O-isotopic compositions of H_2O during the formation of magnetite and fayalite would be controlled by the magnitude of isotopic fractionation factors (a function of *T*) and relative amounts of magnetite and fayalite that formed. In any case, the magnitude of the increase in $\delta^{18}O$ would be expected to be smaller than that produced by forming magnetite only. We suggest that the large difference in $\delta^{18}O$ between magnetite and fayalite in Mokoia together with the relatively narrow ranges in each phase is an indication that, during alteration, similar amounts of these phase were forming.

The results for Kaba are very different. The $\delta^{18}O$ of the magnetite is ~10‰ higher than that in Mokoia, and the magnetite and fayalite in Kaba have identical O-isotopic compositions within analytical error bars. The mean compositions for each Kaba phase plot close to the intersection of the CCAM and TF lines. Although the coincidence in $\delta^{18}O$ of the Kaba phases might be coincidental, their physical proximity and similarity in $\Delta^{17}O$ suggests that this is not the correct interpretation. It is highly unlikely that the Kaba magnetite and fayalite formed in isotopic equilibrium with each other because this would require very high temperatures (>>1000 K), which is inconsistent with petrographic observations (Krot *et al.*, 1998; this study) and highly unequilibrated nature of this meteorite. A more plausible scenario of this is that magnetite formed first and that fayalite formed later by replacing some magnetite. If H_2O was no longer present, the fayalite may have formed by reaction (4). This reaction is spontaneous throughout the entire range of plausible asteroidal temperatures. Because SiO_2 is not found in x-ray maps, this hypothetical phase is either fine grained and dispersed or the SiO_2 was produced by the breakdown of another phase. If, following formation of magnetite during aqueous alteration, temperatures rose and the remaining water was expelled, reaction (4) would have occurred (providing all reactants were present in the microenvironment).

However, this scenario can only account for the similarity in $\delta^{18}O$ if there was no isotopic equilibrium between fayalite and the unreacted magnetite. Because half the fayalite O comes from the SiO_2, our scenario requires this O to be similar in $\delta^{18}O$ and $\Delta^{17}O$ to that in the magnetite. If the SiO_2 had been precipitated during the aqueous alteration that formed the magnetite, it would have had the same $\Delta^{17}O$ as the magnetite. The difficulty is in explaining the $\delta^{18}O$, because formation in equilibrium with the magnetite at ~300 K would leave the SiO_2 with a $\delta^{18}O$ much higher than that of the magnetite. A possible solution is that the labile SiO_2 had formed very late and that the $\delta^{18}O$ of the H_2O had drifted >10‰ lower by the time this part of the SiO_2 had formed.

EVOLUTION OF OXYGEN RESERVOIRS IN THE SOLAR NEBULA

Our Kaba data seem to provide the most definitive approximation of the composition of the high-$\Delta^{17}O$ endmember of the CCAM line (Fig. 3). This line is anchored at the low $\Delta^{17}O$ end

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by refractory inclusions, and particularly by the spinels in these inclusions. The line was originally defined on the basis of mineral separates from refractory inclusions, with melilite and anorthite generally defining the upper extreme at $\delta^{18}O$ ~1‰ (Clayton *et al.*, 1977; Ryerson and McKeegan, 1994).

However, other samples plot at still higher values. Rubin *et al.* (1990) reviewed the evidence and found that that the highest samples plotting near the CCAM line were CV Allende fine-grained matrix (Clayton *et al.*, 1976, 1983) and samples of coarse-grained rims removed from two Allende chondrules (one porphyritic pyroxene, the other porphyritic olivine). A reasonable working hypothesis is that Kaba magnetite and fayalite formed by the same process (inferred to be aqueous alteration) responsible for the generation of the other materials plotting near the upper end of the CCAM array. If the initial composition of the oxidant H_2O was the same everywhere on the CV parent body, it follows that the composition of the H_2O reservoir invoked in the previous section to explain the Mokoia data should be the one responsible for other alteration products plotting on the array (and, presumably, for the compositions of closely related materials such as dark inclusions that plot somewhat away from the array (Clayton and Mayeda, 1999)). Jabeen *et al.* (1998) and Ash *et al.* (1999) recently showed evidence of alteration related processes within chondrules of CV Allende.

Choi *et al.* (1997) noted that the difference in $\Delta^{17}O$ between magnetite and olivine in Allende indicate that the oxidant responsible for converting metallic Fe to magnetite had a higher $\Delta^{17}O$ than that incorporated in most chondrule olivine. A similar conclusion was reached by Rubin *et al.* (1990) based on their studies of coexisting chondrules and rims in Allende.

Although it is possible that the oxidant H_2O incorporated into the CV parent body is exotic (*i.e.*, that it originated in a part of the nebula well separated from the CV formation region in time or space), the simpler hypothesis is that this water is representative of the H_2O (g) that was the dominant O reservoir in the CV formation region. Our best estimate of the $\Delta^{17}O$ of this H_2O, −1‰, is much lower than the estimate (~7‰) of the $\Delta^{17}O$ of the oxidant at the LL formation region based on the Choi *et al.* (1998) studies of magnetite in Semarkona and Ngawi. Choi *et al.* (1998) mentioned the possibility that the composition of the nebular gas changed with time and that the simplest explanation of the correlation between $\Delta^{17}O$ and degree of oxidation observed in the bulk compositions of the three ordinary chondrite groups is that $\Delta^{17}O$ of the nebular gas increased with time. If we accept this picture and assume that the change was monotonic throughout the history of the solar nebula, the implication is that CV chondrites formed earlier than the ordinary chondrites. Wasson (2000) reviewed the age data and found them to be ambiguous, but there are some hints that the CV chondrites are indeed older that ordinary chondrites.

SUMMARY

Studies of two secondary (alteration) phases in the closely related CV chondrites Kaba and Mokoia show important differences and similarities. Although the $\Delta^{17}O$ values in both phases are the same within experimental uncertainties for both phases in both chondrites, $\delta^{18}O$ in the fayalite of Mokoia is ~20‰ higher than that in the magnetite, whereas $\delta^{18}O$ values in these two phases in Kaba are not resolvably different. We interpret these differences to primarily reflect differences in the formation sequence of magnetite and fayalite: magnetite and fayalite seemed to have formed simultaneously in Mokoia, whereas fayalite formed by replacement of magnetite in Kaba.

Our results show that the $\Delta^{17}O$ of the oxidant (probably H_2O) responsible for the formation of magnetite in the most primitive oxidized CV chondrites had $\Delta^{17}O$ ~0‰, considerably lower than the $\Delta^{17}O$ value of 7‰ inferred for the oxidant present in the LL3 parent body (Choi *et al.*, 1998). If we follow the suggestion of Choi *et al.* (1998) and interpret this difference in terms of a monotonic upward drift of the $\Delta^{17}O$ of nebular O with time, it follows that the CV chondrites formed earlier than the ordinary chondrites. We are carrying out similar studies on other primitive, magnetite-bearing chondrites to see if the same pattern (of higher $\Delta^{17}O$ in magnetite than in chondrules) is found.

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