Evidence in CO3.0 chondrules for a drift in the O isotopic composition of the solar nebula

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Abstract–Several recent studies have shown that materials such as magnetite that formed in asteroids tend to have higher $\Delta^{17}O$ ($= \delta^{17}O - 0.52 \times \delta^{18}O$) values than those recorded in unaltered chondrules. Other recent studies have shown that, in sets of chondrules from carbonaceous chondrites, $\Delta^{17}O$ tends to increase as the FeO contents of the silicates increase. We report a comparison of the O isotopic composition of olivine phenocrysts in low-FeO ($\leq Fa_1$) type I and high-FeO ($\geq Fa_{15}$) type II porphyritic chondrules in the highly primitive CO3.0 chondrite Yamato-81020. In agreement with a similar study of chondrules in CO3.0 ALH A77307 by Jones et al. (2000), $\Delta^{17}O$ tends to increase with increasing FeO. We find that $\Delta^{17}O$ values are resolved (but only marginally) between the two sets of olivine phenocrysts. In two of the high-FeO chondrules, the difference between $\Delta^{17}O$ of the late-formed, high-FeO phenocryst olivine and those in the low-FeO cores of relict grains is well-resolved (although one of the relicts is interpreted to be a partly melted amoeboid olivine inclusion by Yurimoto and Wasson [2002]). It appears that, during much of the chondrule-forming period, there was a small upward drift in the $\Delta^{17}O$ of nebular solids and that relict cores preserve the record of a different (and earlier) nebular environment.

INTRODUCTION

There is abundant evidence that the mean O isotopic composition of the solar nebula varied with time and/or place. For example, magnetite, produced by aqueous alteration on asteroids and, thus, a proxy for asteroidal H_2O, records $\Delta^{17}O$ ($= \delta^{17}O - 0.52 \times \delta^{18}O$) values around 7‰ in the LL3 chondrites Semarkona and Ngawi but values around –1‰ in the CV3 chondrites Kaba, Mokoia, and Allende (Choi et al. 1997, 1998, 2000). Because chondrules have low porosities and permeabilities and low surface/volume ratios, they tend to resist aqueous alteration and, thus, play an especially important role in preserving the record of nebular processes. In the chondrites in which magnetite and chondrules have been studied, the chondrule phases have lower $\Delta^{17}O$ values than the magnetite. As a result, Choi et al. (1998) raised the possibility that the O isotopic composition of nebular gas evolved with time at the formation locations of the various chondrite groups. Wasson (2000) summarized additional results supporting such a view. H_2O was the last phase to condense (possibly as hydrated minerals) from the inner solar nebula, and this suggests an upward drift in $\Delta^{17}O$ with time.

The latter conclusion must be tempered by reports that the mean initial $^{26}Al/^{27}Al$ ratio in CO3.0 chondrules (Kunihiro et al. 2004a) is about 2× lower than in LL3.0 chondrules (Kita et al. 2000). If Al isotopes were well-mixed at all places and times in the solar nebula, then the higher initial $^{26}Al/^{27}Al$ ratio implies that the $\Delta^{17}O$ in LL chondrules was established earlier than the lower $\Delta^{17}O$ in CO chondrules. As discussed in more detail in Kunihiro et al. (2004a), either $^{26}Al/^{27}Al$ cannot be used as a chronometer, or there was not a monotonic upward drift in $\Delta^{17}O$ in the nebula.

Porphyritic chondrules in primitive chondrites are divided into two textural-chemical types: the low-FeO type I chondrules and the high-FeO type II chondrules. Because Fe in equilibrium solids is reduced at high and oxidized at low nebular temperatures, one might expect that an upward drift in the $\Delta^{17}O$ of the nebular gas would result in lower values in low-FeO chondrules and higher values in high-FeO chondrules. This is the trend observed by Jones et al. (2000) in a study of the CO3.0 Allan Hills A77307 and reported in an abstract by Wasson et al. (2001), which was a preliminary report of the present study. The abstract by Leshin et al. (2000) on carbonaceous-chondrite olivine showed similar

trends but with exceptions that were interpreted to be inconsistent with this picture.

The CO3.0 chondrites are especially well-suited for such study because they have experienced minimal aqueous or thermal alteration and because the range in $\Delta^{17}O$ is large enough to be characterizable with the ion microprobe. The CO3.0 chondrite Yamato-81020 has preserved a remarkably fresh record of the solar nebula. Y-81020 is relatively unweathered, but patches of limonite occur in the matrix throughout the meteorite; opaque spherules near the surfaces of some chondrules also have rinds containing limonite and other weathering products. Y-81020 experienced minor asteroidal aqueous alteration, but to date, no effects due to thermal metamorphism have been reported (e.g., Kojima et al. 1995). Brecciation and other impact-produced effects are relatively minor.

Studies of the oxygen isotopes in some of the same Yamato-81020 chondrules have previously been reported by Yurimoto and Wasson (2002) and Wasson et al. (2000). Wasson and Rubin (2003) studied many high-FeO chondrules in Yamato-81020 and found that >90% contained low-FeO relict grains.

SAMPLES AND EXPERIMENTAL PROCEDURES

Six relatively large chondrules were selected from Yamato-81020 section 56-4. Three have type I structures, low-FeO contents, low Na_2O contents in the mesostases, and high contents of metal. The other three have type II structures, high-FeO contents, sodic mesostases, and low metal contents. The chondrules were assigned names based on a grid superposed on a BSE image of the thin section.

Petrographic Techniques

Thin sections were studied microscopically in transmitted and reflected light. Backscattered electron (BSE) images were made with the LEO 1430 scanning electron microscope (SEM) at a range of magnifications; the phases were identified by EDS. Mineral analyses were made at UCLA with the Cameca "Camebax-microbeam" electron microprobe and, since late 2002, with the JEOL JXA-8200 electron microprobe using natural and synthetic standards, an accelerating voltage of 15 keV, a 15 nA sample current, and 20 sec counting times. Cameca data were corrected with a PAP protocol, JEOL data with a ZAF protocol.

Ion-Probe Techniques

Oxygen isotopes were analyzed using the Cameca 1270 ion microprobe (IMP) at the Tokyo Institute of Technology. The primary ion beam was mass-filtered positive 20 keV Cs ions; the typical spot size was 4 μm. The primary beam current was ≈3 pA, adjusted to obtain a count rate of ≈4 × 10^5 cps for

negative ^{16}O ions. A normal-incidence electron gun was used for charge compensation. Negative secondary ions corresponding to the ^{16}O tail, ^{16}O, ^{17}O, ^{16}OH, and ^{18}O were analyzed at a mass resolution of ≈6000. Additional analytical procedures are described in Yurimoto et al. (1998). An olivine (SC) from San Carlos, Arizona, USA and a spinel (SPU) from Russia were employed as O isotope standards. No corrections were made for matrix effects. If these are similar to those measured in olivine by Leshin et al. (1997) on the UCLA Cameca 1270 (a decrease of 0.5‰ in $\delta^{18}O$ for each 10 mol% increase in Fa), the range between our extreme $\delta^{18}O$ values would increase by about 3‰.

PETROGRAPHIC STUDIES

Images of the chondrules are shown in Fig. 1. Five chondrules are relatively circular in outline and, seemingly, largely intact. The remaining chondrule (B5y) is a fragment, but the intact exterior arc is ≥210°. When discussing features in these chondrules, the orientations are assumed to be those in Fig. 1. The ranges of phase compositions measured in the mafic minerals of the six chondrules are listed in Table 1. We will first discuss the low-FeO and then the high-FeO chondrules.

Low FeO, Type I Chondrules

Chondrule I6w (Earlier Called Chondrule J; Fig. 1a; D = 410 μm)

This porphyritic olivine-pyroxene chondrule shows the irregularly lobate surface morphology common to low-FeO type I chondrules in Yamato-81020 (Rubin and Wasson Forthcoming). It contains four opaque nodules with long dimensions >30 μm and eight others with long dimensions ≥8 μm. It seems to have terrestrial-corrosion (limonitic) rinds on every opaque grain, particularly those near the chondrule surface. Many tiny fractures are also filled with terrestrial corrosion products. The irregular shape and the porosity of the mesostasis are features shared with many amoeboid olivine inclusions (AOI); in the AOI, the anorthite-diopside regions are the "mesostasis." Terrestrial weathering can produce porosity, but the absence of recognizable weathering products (e.g., limonite) indicates that these are preterrestrial. One of the analyzed points is near the largest metal nodule, the other is in a moderately large olivine crystal not near any metal in the plane of the section.

Chondrule J6j (Earlier Called Chondrule H; Fig. 1b; D = 400 μm)

This porphyritic olivine-pyroxene chondrule is similar in its irregularly lobate outline to chondrule I6w, but the mean size of the metal grains and the metal abundance are both smaller. Most low-Ca pyroxene grains occur near the chondrule surface. Again, there is appreciable porosity visible in the (very low-Na) mesostasis. There is evidence of corrosion at the edges of some metal grains, but the fraction altered is less
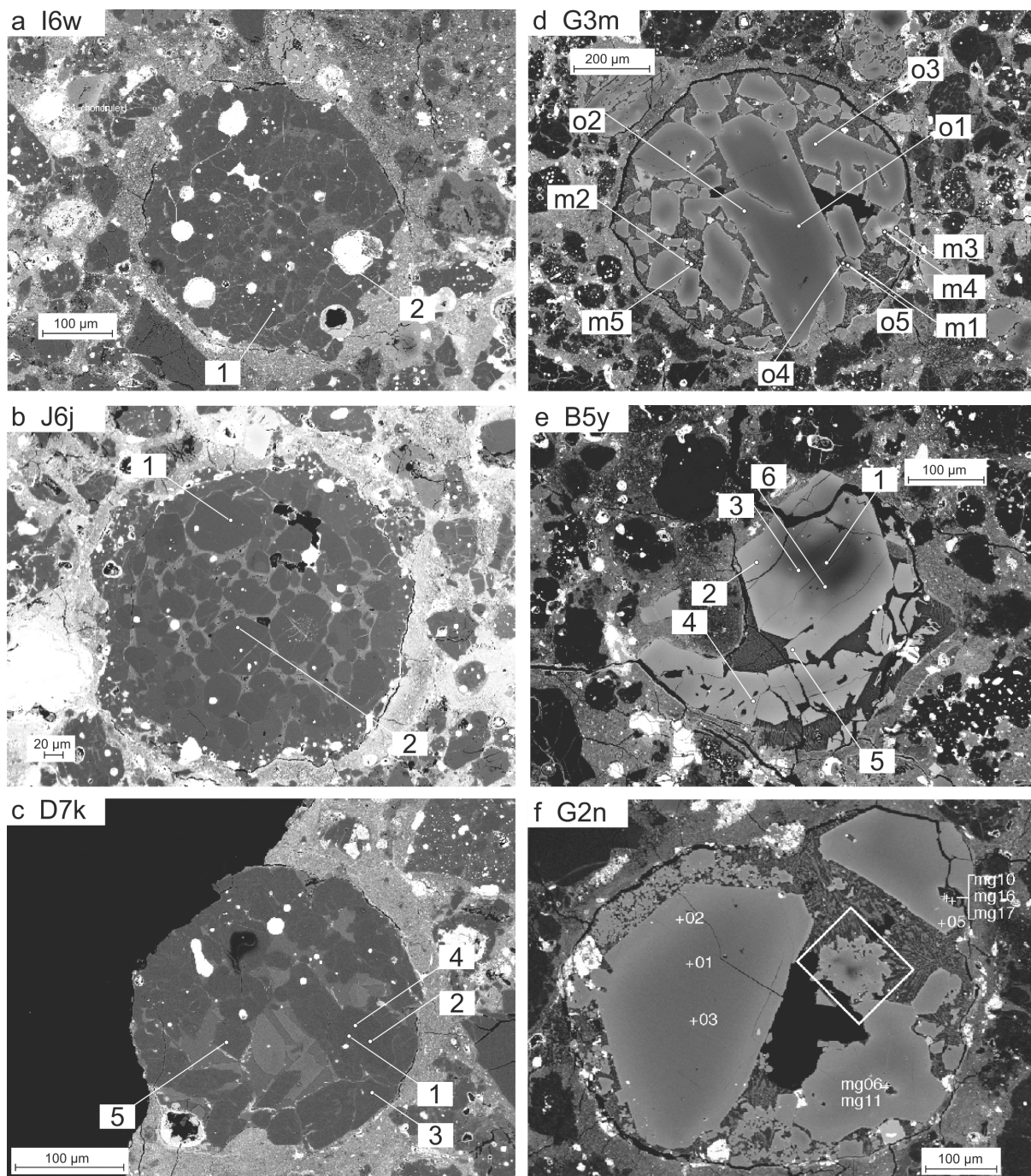
Fig. 1. Backscattered electron images of the six porphyritic chondrules in which we determined O isotope compositions using the Cameca 1270 ion microprobe. The first set of three (left column) are low-FeO chondrules with type I (smaller mafic minerals, abundant metal grains) structures; the second set (right column) consists of high-FeO chondrules with type II (large olivine grains, low contents of metal) structures. In the first five images, small white points mark the SIMS analytical points; in (f), the points are marked by +s. In (a), (b), (c), and (e), the points mark O isotope analyses; in the other two chondrules, analyses of both O and Mg were completed, and the points are marked with an "o" or "m(g)," respectively: a) chondrule I6w; metal shows terrestrial corrosion, mesostasis and some mafic minerals show porosity that appears to be preterrestrial; b) chondrule J6j; mesostasis shows porosity; two olivine grains show alignments of dusty metal; point 2 is in the overgrowth region of one of these dusty grains; c) chondrule D7k; about 20% of the area is Ca-pyroxene; mesostasis does not show porosity; d) chondrule G3m; there are two low-FeO relict grains, one at the o5 analytical point, the other just above the small hole bisected by the line connected to point o2; e) chondrule B5y; Wasson and Rubin (2003) inferred that the large dark relict inside the pentagonal olivine phenocryst shows two growth zones; point 1 is inside the first, point 3 the second, and point 6 may overlap both zones; f) chondrule G2n; this chondrule was imaged and discussed in detail by Yurimoto and Wasson (2002); the area inside the rectangle mainly consists of an olivine-rich relict "crystal clot" with a very low $\Delta^{17}O$ of −23‰ that appears to have originated as an amoeboid olivine inclusion.

Table 1. Mean olivine and $\Delta^{17}O$ compositions in different chondrule lithologies of Yamato-81020-56-4. The old chondrule names used in earlier publications are also listed.

Lithology	Old name	Olivine (%Fa)	$\Delta^{17}O$ (‰)
Low-FeO chondrules, olivine phenocrysts			
Chdrl I6w	J	0.8–1.0	−3.5
Chdrl J6j	H	0.2–0.3	−2.4
Chdrl D7k	C	0.6–1.0	−7.0
High-FeO chondrules, olivine phenocrysts			
Chdrl G3m	A	20–25	−1.9
Chdrl B5y	F (and K)	34–65	−0.3
Chdrl G2n	I	20–40	−0.4
High FeO chondrules, low-FeO olivine relicts			
Chdrl G3m	A	5.6	−3.4
Chdrl B5y	F (and K)	20–30	−1.9[a]
Chdrl G2n	I	15	−23[b]

[a]Mean of three points; additional data and discussion in Kunihiro et al. (2004b).
[b]From Yurimoto and Wasson (2002).

than in chondrule I6w. In two large olivines near the center, there are chains of dusty metal; in the lower of these, there are also transverse arrays leading off the main array. The dusty-metal-rich portions of these olivines appear to be relict grains. The first O isotopic analysis was on a large non-dusty olivine grain, the second in the outer dust-free "overgrowth" portion of an olivine having a dusty core.

Chondrule D7k (Earlier Called Chondrule C; Fig. 1c; D = 270 µm)

Although it has a similarly irregular outline, this porphyritic olivine-pyroxene chondrule is quite different from the other two type I chondrules: a) its mesostasis is more abundant and shows no porosity; and b) it includes large BSE-bright, euhedral and subhedral Ca-pyroxene grains that appear to have nucleated on olivine grains. The high content of diopside and mesostasis reflects Ca and Al contents that are at least 2× greater than those in typical low-FeO chondrules such as J6j and I6w. There are bright, small, feathery Ca-pyroxene grains at the edge of some mesostasis fields, especially near the bottom of the chondrule. Coarse low-Ca pyroxene phenocrysts also occur throughout the chondrule but are not resolvable from olivine in Fig. 1c. Reliable oxygen isotopic compositions were measured at four points; two in olivine and two in low-Ca pyroxene, including one very low $\Delta^{17}O$ value in grain 3 near the bottom right edge. A fifth point (in olivine) yielded poor quality data that are not listed.

High-FeO Chondrules

The three high-FeO chondrules are fascinating in their complexity, and all show O isotopic evidence of relict olivine. We discuss them in order of increasing amounts of O data.

Chondrule G3m (Earlier Called Chondrule A; Fig. 1d; D = 800 µm)

This porphyritic-olivine chondrule is large by CO standards for type II chondrules; it was discussed in some detail by Wasson and Rubin (2003), who concluded that the ~5 µm of overgrowth observed on a low-FeO relict grain (just above the ellipsoidal hole in left center) was a measure of the amount of growth on all olivine following the last melting event. Many olivine phenocrysts are euhedral to subhedral and relatively large; the largest is 600 × 120 µm. Some mesostasis is uniformly glassy, other parts show bright feathery crystals of calcic pyroxene. In contrast to two of the low-FeO chondrules, the mesostasis is not porous. The scatter in $\Delta^{17}O$ values range from −0.1 to −3.9‰; the scatter may largely reflect relict phases. Point 5 (−3.4‰) is certainly a relict; point 4, which is ≈20 µm away, is −0.1‰. Although adjacent to mesostasis, microscopic examination shows that the latter analysis point is entirely on olivine. Point 2 (−3.9‰) is in the interior of the large pyroxene; this may also be a relict phase.

Chondrule B5y (Earlier Called Chondrule F and also K; Fig. 1e; D = 420 µm)

This chondrule fragment has an arcuate shape. The surface may be intact for about 210° on the bottom, but the high abundance of mesostasis on or near the surface through much of this region suggests that the surface is missing. Wasson and Rubin (2003) reported a remarkably high fayalite content (Fa_{77}) near the outer periphery of the chondrule in a large olivine that seems to be a single (but fractured) curved grain about 300 µm long. The other coarse olivine consists of a large, almost rhomboid phenocryst about 200 µm in its longest dimension. It has an irregularly shaped dark center that appears to be a relict; Wasson and Rubin (2003) interpreted the BSE image and the compositional data to show that this is a two-generation relict, i.e., formed in two independent melting events that predated the final melting event experienced by the chondrule. The mesostasis is variable; in some places, there are abundant subparallel bars of Ca-pyroxene; in other regions, Ca-pyroxene is rare, and the mesostasis forms a uniform matte texture. There is no visible porosity in the mesostasis.

Chondrule G2n (Earlier Called Chondrule I; Fig. 1f; D = 590 µm)

Yurimoto and Wasson (2002) discussed this chondrule in detail; it includes an olivine crystal clot having a mean $\Delta^{17}O$ of −23‰. This porphyritic olivine chondrule is largely intact, but some material may have been lost from the upper edge. The olivine mainly consists of three large grains having centers only slightly darker than the edges; the largest is subhedral and 400 × 240 µm. There are many small irregular grains (5–20 µm) near these large grains, especially on the right side of the large grain; Wasson and Rubin (2003) described these as "cauliflower" and inferred that they grew from small nuclei following the last melting event. The

crystal clot, outlined by a rectangle in Fig. 1f, is slightly smaller (80 × 90 μm) than the smallest of the three large phenocrysts and has a much darker center. The mesostasis has abundant exsolved calcic pyroxene, but there are small patches that are fine-grained and matte in appearance; there is no porosity in the mesostasis.

OXYGEN ISOTOPE STUDIES

Our O isotopic results are summarized in Table 2 and in Fig. 2. Individual phenocryst points are shown together with 1σ errors in Fig. 2a and mean phenocryst compositions in

Fig. 2b. As in the petrographic section, we first discuss the low-FeO chondrules, then the high FeO chondrules.

In the petrographic section, we noted that two of the low-FeO chondrules (I6w and J6j) are quite similar in texture. We analyzed O isotopic compositions of two points each on the phenocrysts of these chondrules. One of the phenocrysts in I6w was later found to be pyroxene and was excluded from the mean. As shown in Fig. 2b, the mean phenocryst compositions plot near the CCAM line, but the $\delta^{18}O$ values differ, with that of I6w being ~5‰ lower than that of J6j. The $\Delta^{17}O$ values of the two chondrules differ by about 1‰.

We noted above that D7k, the third low-FeO chondrule,

Table 2. Oxygen isotope data for olivine and low-Ca pyroxene in three low-FeO and three high-FeO chondrules of Yamato-81020-56-4.

| Point	Fa or Fs (mol%)	$\delta^{17}O$ (‰)	σ (‰)	$\delta^{18}O$ (‰)	σ (‰)	$\Delta^{17}O$ (‰)	σ (‰)	Notes
Chdrl I6w								
1-oliv	2.0	−5.8	2.7	−4.4	1.1	−3.5	2.9	
2-pyx	$Fs_{0.86}$	−9.1	3.0	−7.6	1.1	−5.1	3.2	
Olivine phenocryst mean		−5.8		−4.4		−3.5		
Chdrl J6j								
1-oliv	0.32	−2.1	2.6	0.9	1.2	−2.6	2.9	
2-oliv	0.26	−2.2	2.1	0.2	1.0	−2.3	2.3	
Phenocryst mean		−2.2		+0.5		−2.4		
Chdrl D7k								
1-oliv	0.63	Poor isotopic data						
2-oliv	0.54	−7.7	2.3	−0.6	1.3	−7.3	2.6	
3-pyx	$Fs_{0.62}$	−17.6	2.1	−10.6	1.1	−12.0	2.4	
4-oliv	3.0	−11.2	2.2	−8.6	1.4	−6.7	2.7	
5-pyx	$Fs_{1.3}$	−13.7	2.7	−12.5	1.4	−7.2	3.1	
Olivine phenocryst mean		−9.4		−4.6		−7.0		Exclude pts 3, 5
Chdrl G3m								
1-oliv	17	1.2	2.1	6.5	1.0	−2.1	2.3	
2-oliv	21	−3.2	2.4	1.3	1.1	−3.9	2.6	
3-oliv	24	1.0	2.4	4.7	0.9	−1.5	2.6	
4-oliv	37	5.1	2.4	10.0	1.3	−0.1	2.7	
5-oliv	5.6	3.0	2.7	12.2	1.5	−3.4	3.1	Relict
Phenocryst mean		+1.9		+6.5		−1.5		Exclude pt 5, pt 4 ½ wt
Chdrl B5y								
1-oliv	20	2.1	2.1	2.4	1.4	0.9	2.6	Relict
2-oliv	57	−1.1	2.2	−5.4	0.9	1.6	2.4	
3-oliv	30	−3.0	2.4	1.8	1.2	−3.9	2.7	Relict
4-oliv	62	2.0	2.3	4.6	1.0	−0.4	2.5	
5-oliv	68	−0.7	3.0	2.8	1.2	−2.1	3.3	
6-oliv	26	1.0	2.2	6.0	1.0	−2.1	2.5	Relict
Phenocryst mean		+0.7		+0.1		−0.3		Exclude pts 1, 3, 6
Chdrl G2n								
1-oliv	72	3.4	2.4	3.6	1.1	1.5	2.6	
2-oliv	57	−0.1	2.5	5.4	1.2	−2.9	2.8	
3-oliv	73	0.6	2.5	5.0	1.1	−2.0	2.7	
5-oliv	44	5.5	2.6	3.5	1.0	3.6	2.8	
Additional O isotopic data reported by Yurimoto and Wasson (2002)								
Phenocryst mean		+1.9		+4.5		−0.4		Pt 5 ½ wt
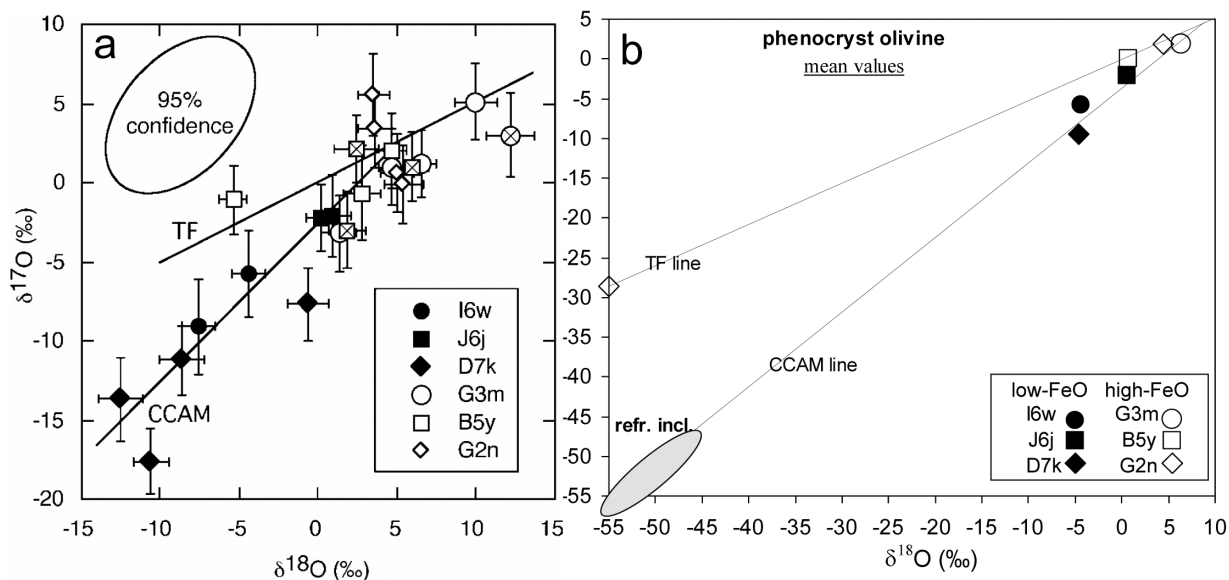
Fig. 2. Individual and mean O isotope compositions in olivine phenocrysts in Y-81020 chondrules are plotted on these oxygen 3-isotope diagrams: a) individual values show moderate scatter, consistent with the 95% error ellipse plotted in the upper left. Nonetheless, two trends are recognizable: 1) most high-FeO phenocrysts (open symbols) plot near the TF line ($\Delta^{17}O = 0$), while low-FeO phenocrysts have more negative $\Delta^{17}O$ values; and 2) the points scatter about the CCAM line based on carbonaceous-chondrite anhydrous minerals. Relict grains (crosses inside open symbols) in high-FeO chondrule B5y scatter around or near the high-FeO phenocrysts, with one exception; the relict in G3m plots below (at a more negative $\Delta^{17}O$ value) the points measured in high-FeO phenocrysts; b) mean O isotopic compositions of the six chondrules plot near the intersection of the CCAM and TF lines. The position occupied by refractory inclusions from pristine CO chondrites studied by ion microprobe is shown schematically. Although the three low-FeO chondrules (filled symbols) plot further down the CCAM line than do the three high-FeO chondrules (open symbols), their mean $\Delta^{17}O$ values differ by only about 3‰. In contrast, the gap between the mean $\Delta^{17}O$ values of low-FeO chondrules and refractory inclusions is about 20‰. Several kinds of evidence indicate that low-FeO chondrules formed earlier than high-FeO chondrules; thus, these data indicate that the $\Delta^{17}O$ of chondrule-precursor solids evolved upward with time.

is quite different in texture from those just discussed. It contains abundant low-Ca pyroxene and diopside and appears to be substantially enriched in Ca and Al compared to typical low-FeO chondrules. This suggests that the precursor materials included a substantial amount of a refractory component, perhaps in the form of a refractory inclusion fragment. As shown schematically in Fig. 2b, ion-microprobe studies show that the refractory inclusions in primitive CO3.0 chondrites scatter around the CCAM line at about $\delta^{18}O = -50‰$, $\Delta^{17}O = -25‰$ (e.g., Wasson et al. 2001). Thus, it is not surprising that the olivine phenocryst $\Delta^{17}O$ value, $-7.0‰$, is much more negative than those in the low-FeO chondrules that are not particularly enriched in refractories. One of our two analyses of low-Ca pyroxene (point 3) gave a very negative $\Delta^{17}O$ of $-12‰$; this pyroxene grain is more reduced than the other pyroxene grain. We suspect that this very low $\Delta^{17}O$ value indicates the presence of an incompletely digested refractory pyroxene relict.

The high-FeO chondrule G3m was discussed in some detail by Wasson and Rubin (2003). They noted the thin overgrowth on one low-FeO relict grain and inferred that the thickness of new olivine grown following the last melting event was on the order of 5 μm. One of our O isotope analyses (point o5 on Fig. 1d) was on the other low-FeO relict grain; its $\Delta^{17}O$ value was $-3.4‰$, substantially more negative than the

mean of the four phenocryst points (and we assigned only 1/2 weight to the most positive phenocryst value). On the other hand, the $\Delta^{17}O$ in one phenocryst (point 2) was slightly more negative than the relict, although the difference was small compared to the uncertainties on individual values.

The high-FeO chondrule fragment B5y has a complex O isotope composition. One of the two large phenocrysts has a large relict high-FeO (taking the traditional border between low- and high-FeO chondrule olivine to be about $Fa_{9\pm1}$) core that Wasson and Rubin (2003) interpreted to have formed during two different melting events that predated the final melting event. Our point 1 was in the darker (Fa_{20}) first-growth region, and our points 3 and 6 were in the slightly lighter (Fa_{26-30}) second growth region of this relict. There is no clear pattern in our data; the mean $\Delta^{17}O$ values of three points on the relict grains and the mean for the phenocrysts are about the same and are relatively high. The quoted errors (largely based on counting statistics) are large. Kunihiro et al. (2004b) studied the same chondrule using a higher beam current and a larger spot size that produced better precision. They found the intriguing result that $\Delta^{17}O$ was higher in the relicts than in the measured phenocrysts, the opposite of the usual trend. They noted that these are high-FeO relicts and that this is probably a stochastic sampling variation; however, more complex explanations are also possible. We

defer to the more extensive discussion in that paper regarding this result.

The high-FeO chondrule G2n (under the name chondrule I) was the target of a detailed study by Yurimoto and Wasson (2002). They showed that the relict grain outlined by a rectangle in Fig. 1f consists of a clot of low-FeO olivine. The core olivine (with Fa <30 mol%) was found to have $\Delta^{17}O$ <−21‰ with a mean of −23‰, supporting their inference that this olivine-rich region was originally an amoeboid olivine inclusion rather than a chondrule fragment. We list the compositions obtained for four phenocryst points in Table 2. These show considerable scatter; after assigning a weight of 0.5 to (the most deviant) point 5, we calculated a mean of −0.4‰, 22‰ higher than in the relict phase (a record range of $\Delta^{17}O$ for one CO chondrule); this is a chondrule of O isotope extremes.

OXYGEN ISOTOPE EVOLUTION OF THE NEBULA AT THE CO FORMATION LOCATION

Our chondrule data are separated into three categories and are summarized in Table 1. With the exception of the high-FeO relict in chondrule B5y, our data reveal a consistent trend; $\Delta^{17}O$ increases from low-FeO olivine and low-Ca pyroxene (as whole chondrules or as relict grains in high-FeO chondrules) to high-FeO phenocryst olivine. The range in mean $\Delta^{17}O$ values in high-FeO phenocrysts is from −1.9 to −0.4‰; the range in low-FeO phenocrysts is −7.0 to −2.4‰. If we exclude the value for the Ca-Al-rich chondrule D7k, the low-FeO range is reduced to −4.3 to −2.4‰.

The chondrules in type 3.0 chondrites are valuable for studying the O isotopic composition of the nebula because these objects have remained (essentially) closed systems since formation in the nebula. The following discussion is largely based on section 7 of the Wasson (2000) review paper. Clayton and Mayeda (1984) thought that the $\Delta^{17}O$ of the nebular gas was higher than those of chondrule melts and that exchange occurred during the brief period when chondrules were molten. Wasson (2000) noted that chondrules evaporate at temperatures about 600 K lower than the temperature at which they melt and, thus, concluded that chondrules must have formed in a nebula in which ambient temperatures were much lower than these melting temperatures. The consequence of this is that the surface of chondrules cooled quickly following the flash-melting events. As soon as the surface crystallized or chilled to a glass, isotopic exchange rates became negligible.

Wasson (2000) agreed with Clayton and Mayeda (1984) and others that the meteoritic evidence implies that the $\Delta^{17}O$ of the nebular gas was more positive than that of the mean solids during the period when chondrule formation was occurring. He suggested that the O isotopic composition of the solids drifted toward higher values because extensive evaporation occurred during chondrule formation, and the recondensed

solids were in isotopic equilibrium (or nearly so) with the gas. The mean FeO/(FeO + MgO) ratio of the solids also increased because, at low nebular temperatures, the Fe that was present as metal before evaporation recondensed as FeO.

Leshin et al. (2000) presented O isotope data (as diagrams) for olivine from carbonaceous chondrites and concluded that "there is no simple relationship between mineral chemistry and oxygen-isotopic composition." Most of the olivine O isotope data in the Leshin et al. diagrams were obtained on chondrules and grains from chondrules that experienced appreciable asteroidal aqueous alteration. Their data on CO3.0 ALH A77307 (a chondrite that largely avoided asteroidal alteration) are similar to those we present for CO3.0 Yamato-81020.

The Wasson (2000) evaporation/recondensation model leads to the prediction that, in new-growth olivine that crystallized following chondrule melting events, the $\Delta^{17}O$ should, on average, be higher in high-FeO olivine. The generally accepted scenario of relict grain formation is that these are fragments of phenocrysts from earlier generations of chondrules. This leads to the prediction that the $\Delta^{17}O$ of low-FeO relict grains should be more negative than those in the high-FeO host phenocrysts. With the one complication of the relict in chondrule B5y (which is high-FeO rather than low-FeO and is discussed together with more precise data by Kunihiro et al. [2004b]), our present data set supports this simple model.

As can be seen in Fig. 2, the $\Delta^{17}O$ values of CO3.0 chondrules are very different from the very low values (<−20‰) in CO3.0 refractory inclusions. Similar values are also found in the olivine-rich amoeboid olivine inclusions (Itoh et al. 2002). A key question is why there is such a large gap between these and the lowest $\Delta^{17}O$ values measured in normal chondrules (about −8‰ in those in chondrules showing enhancements in Ca and Al, which is still higher in those having Ca/Si and Al/Si ratios similar to those in bulk CO chondrites). One possible answer is that the two kinds of materials formed at different places and times.

REFERENCES

Choi B. G., McKeegan K. D., Leshin L. A., and Wasson J. T. 1997. Origin of magnetite in oxidized CV chondrites: In situ

measurement of oxygen isotope compositions of magnetite and olivine in CV3 Allende. *Earth and Planetary Science Letters* 146:337–349.

Choi B. G., McKeegan K. D., Krot A. N., and Wasson J. T. 1998. Extreme oxygen-isotope compositions in magnetite from unequilibrated ordinary chondrites. *Nature* 392:577–579.

Choi B. G., Krot A. N., and Wasson J. T. 2000. Oxygen-isotopes in magnetite and fayalite in CV chondrites Kaba and Mokoia. *Meteoritics & Planetary Science* 35:1239–1248.

Clayton R. N. and Mayeda T. K. 1984. The oxygen isotope record in Murchison and other carbonaceous chondrites. *Earth and Planetary Science Letters* 67:151–161.

Jones R. H., Saxton J. M., Lyon I. C., and Turner G. 2000. Oxygen isotopes in chondrule olivine and isolated olivine grains from the CO3 chondrite Allan Hills A77307. *Meteoritics & Planetary Science* 35:849–857.

Kojima T., Yada S., and Tomeoka K. 1995. Ca-Al-rich inclusions in three Antarctic CO3 chondrites, Yamato-81020, Yamato-82050, and Yamato-790992: Record of low-temperature alteration. *Proceedings of the NIPR Symposium on Antarctic Meteorites* 8: 79–96.

Krot A. N., Scott E. R. D., and Zolensky M. E. 1995. Mineralogical and chemical modification of components in CV3 chondrites: Nebular or asteroidal processing? *Meteoritics* 30:748–775.

Kunihiro T., Rubin A. E., McKeegan K. D., and Wasson J. T. 2004a. Initial ^{26}Al/^{27}Al in carbonaceous-chondrite chondrules: Too little ^{26}Al to melt asteroids. *Geochimica et Cosmochimica Acta* 68: 2947–2957.

Kunihiro T., Rubin A. E., McKeegan K. D., and Wasson J. T. 2004b. Oxygen-isotopic compositions of relict and host grains in chondrules in the Yamato-81020 CO3.0 chondrite. *Geochimica et Cosmochimica Acta* 68: 3599–3606.

Leshin L. A., Rubin A. E., and McKeegan K. D. 1997. The oxygen isotopic composition of olivine and pyroxene from CI chondrites. *Geochimica et Cosmochimica Acta* 61:835–845.

Leshin L. A., McKeegan K. D., and Benedix G. K. 2000. Oxygen isotope geochemistry of olivine from carbonaceous chondrites (abstract #1918). 31st Lunar and Planetary Science Conference. CD-ROM.

Rubin A. E. and Wasson J. T. Forthcoming. Non-spherical lobate chondrules in CO3.0 Y-81020: General implications for the formation of low-FeO porphyritic chondrules in CO chondrites. *Geochimica et Cosmochimica Acta.*

Wasson J. T. 2000. Oxygen-isotopic evolution of the solar nebula. *Reviews of Geophysics* 38:491–512.

Wasson J. T. and Rubin A. E. 2003. Ubiquitous relict grains in type II chondrules, narrow overgrowths, and chondrule cooling rates following the last melting event. *Geochimica et Cosmochimica Acta* 67:2239–2250.

Wasson J. T., Yurimoto H., and Russell S. S. 2001. ^{16}O-rich melilite in CO3.0 chondrites: Possible formation of common, ^{16}O-poor melilite by aqueous alteration. *Geochimica et Cosmochimica Acta* 65:4539–4549.

Wasson J. T., Rubin A. E., and Yurimoto H. 2003. CO chondrule evidence for a drift in the nebular oxygen-isotopic composition (abstract). *Meteoritics & Planetary Science* 35:A166–A167.

Yurimoto H. and Wasson J. T. 2002. Extremely rapid cooling of a carbonaceous-chondrite chondrule containing very ^{16}O-rich olivine and a ^{26}Mg-excess. *Geochimica et Cosmochimica Acta* 66:4355–4363.

Yurimoto H., Ito M., and Nagasawa H. 1998. Oxygen isotope exchange between refractory inclusions in Allende and solar nebula gas. *Science* 282:1874–1877.