Pergamon

Geochimica et Cosmochimica Acta, Vol. 68, No. 17, pp. 3599–3606, 2004

0016-7037/04 $30.00 + .00

doi:10.1016/j.gca.2004.02.011

Oxygen-isotopic compositions of relict and host grains in chondrules in the Yamato 81020 CO3.0 chondrite

TAKUYA KUNIHIRO,[1,*,2] ALAN E. RUBIN,[1] KEVIN D. MCKEEGAN,[2] and JOHN T. WASSON[1]

[1]Institute of Geophysics and Planetary Physics, University of California, Los Angeles, Los Angeles, CA 90095-1567, USA
[2]Department of Earth and Space Sciences, University of California, Los Angeles, Los Angeles, CA 90095-1567, USA

(*Received June* 11, 2003; *accepted in revised form February* 6, 2004)

Abstract—We report the oxygen-isotope compositions of relict and host olivine grains in six high-FeO porphyritic olivine chondrules in one of the most primitive carbonaceous chondrites, CO3.0 Yamato 81020. Because the relict grains predate the host phenocrysts, microscale in situ analyses of O-isotope compositions can help assess the degree of heterogeneity among chondrule precursors and constrain the nebular processes that caused these isotopic differences. In five of six chondrules studied, the $\Delta^{17}O$ ($=\delta^{17}O - 0.52 \cdot \delta^{18}O$) compositions of host phenocrysts are higher than those in low-FeO relict grains; the one exception is for a chondrule with a moderately high-FeO relict. Both the fayalite compositions as well as the O-isotope data support the view that the low-FeO relict grains formed in a previous generation of low-FeO porphyritic chondrules that were subsequently fragmented. It appears that most low-FeO porphyritic chondrules formed earlier than most high-FeO porphyritic chondrules, although there were probably some low-FeO chondrules that formed during the period when most high-FeO chondrules were forming. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

Porphyritic chondrules exhibit two dominant textures: low-FeO porphyritic (type-I) chondrules generally have many small (<20 μm) mafic silicate grains, whereas high-FeO porphyritic (type-II) chondrules tend to have fewer and larger (>40 μm) grains (McSween, 1977; Scott and Taylor, 1983). In unequilibrated chondrites there is a strong relationship between textural type and composition; olivine fayalite values [FeO/(FeO+MgO) × 100, Fa] in the central area of type-I CO chondrules are commonly ≤6 mol.%, whereas those in type-II chondrules are generally >10 mol.%. We use the terms low-FeO and high-FeO olivine with a boundary of ~Fa9 ± 1 in this study. In this paper, chondrules referred to as textural type I have low FeO contents and type II have high FeO contents.

Relict grains, i.e., those that did not crystallize in situ in the host chondrule, are found in both type-I and type-II chondrules (Nagahara, 1981; Rambaldi, 1981); they are unmelted materials from a previous generation of chondrules. The existence of relicts in chondrules shows that the final melting events did not produce completely liquid droplets. Most type-II chondrules in CO3 chondrites contain low-FeO relict olivine grains (Steele, 1989; Jones, 1992; Jones, 1993; Wasson and Rubin, 2003). The chemical compositions of the low-FeO relict grains suggest that the relicts were derived from type-I chondrules (Jones, 1996). The ubiquity of low-FeO relicts in type-II CO chondrules indicates that these chondrules formed relatively late during the chondrule-forming epoch (Wasson and Rubin, 2003).

Studies of the O-isotope compositions of relict grains can help identify their provenance. Numerous studies of the O-isotope compositions of meteorites have shown that, in general, chondritic materials show differences in their detailed isotopic signatures (i.e., Clayton, 1993 and references therein; Choi et al., 1998; Hiyagon and Hashimoto, 1999; Krot et al., 2002; McKeegan et al., 1998; Yurimoto et al., 1998). Because relicts formed earlier than host chondrules, relicts and hosts provide information about the O-isotope evolutionary history of solid materials. Microscale in situ analyses of O-isotope compositions can help assess the degree of heterogeneity among chondrule precursors preserved as relict grains, and help constrain those nebular processes that result in changes in the isotopic composition of solids.

CO3.0 Yamato 81020 (hereafter Y-81020; Kojima et al., 1995) is one of the most primitive (unaltered) carbonaceous chondrites; thus it should show minimal disturbance of the O-isotope record by parent-body processes. We used an ion microprobe to study the oxygen-isotope compositions of relict grains in type-II chondrules in Y-81020. We obtained data for six relict olivine grains (five low-FeO and one moderately high-FeO) and coexisting high-FeO grains of the "host" chondrules. Our chief goal was to obtain correlated petrographic and isotopic evidence regarding the compositional evolution of the solar nebula, especially during the period of chondrule formation.

2. MATERIAL AND METHODS

2.1. Petrographic Techniques

As discussed in several recent papers, the CO3.0 carbonaceous chondrite Y-81020 experienced very little thermal metamorphism or aqueous alteration (e.g., Itoh and Yurimoto, 2003; Kojima et al., 1995; Wasson et al., 2001). We studied two chondrules in thin section 51-1 and four from thin section 56-4 from the National Institute of Polar Research (NIPR) in Tokyo.

Backscattered electron (BSE) images were made with a LEO-1430VP scanning electron microscope. Preliminary studies of the thin sections were made of mosaics of BSE images with 2 μm resolution. We then surveyed every ≥200-μm type-I and type-II chondrule in the images looking for objects with relict grains. We found only six chondrules containing relict grains coarse enough (≥20 μm across) to analyze optimally with our ion microprobe. We characterized these olivine grains by determining the concentrations of 10 elements using a JEOL JXA-8200 electron microprobe with a wavelength-dispersive system.

* Author to whom correspondence should be addressed (tky@ucla.edu).

2.2. Isotopic Techniques

Oxygen-isotope measurements were performed by secondary ion mass spectrometry with the Cameca IMS-1270 instrument at the University of California, Los Angeles (UCLA). Analytical details are essentially identical to those described by McKeegan et al. (1998). Briefly, a primary ion beam of 20 keV Cs^+ was defocused to produce a uniformly illuminated 15-μm-diameter spot at the sample surface with an ion intensity of 0.2 nA. Negative secondary ions corresponding to $^{16}O^-$, $^{17}O^-$, and $^{18}O^-$ were analyzed in a peak-jumping mode at a mass resolution of ~7000, sufficient to eliminate quantitatively all molecular ion interferences. A normal-incidence electron gun was used to flood the analysis area with low-energy electrons for charge compensation. One run typically consisted of 20 blocks of three cycles each (3, 10, 5 s integration times). The ion intensities were determined by pulse-counting with an electron multiplier for $^{17}O^-$ and $^{18}O^-$, and $^{16}O^-$ ions were collected on a Faraday cup. The $^{18}O^-$ secondary ion intensity was between 8×10^4 and 1.5×10^5 counts per second. Appropriate corrections were made for detector deadtime.

Olivine data were corrected for instrumental mass fractionation by using the $\delta^{18}O$ for San Carlos olivine (+5.25‰ relative to SMOW; Eiler et al., 1995) and assuming a linear mass-fractionation law. An additional correction to account for the changes in instrumental mass discrimination of 0.5‰ for each 10% change in fayalitic content of the olivine (Leshin et al., 1997) was not applied. The reported uncertainties include both the internal measurement precision on an individual analysis and an additional factor that represents the point-to-point reproducibility, estimated by the standard deviation of the mean (in both $\delta^{18}O$ and $\delta^{17}O$) for measurements of the standard during a given analytical session.

3. RESULTS

3.1. Petrographic Observations

BSE images of the chondrules are shown in Figure 1. Fayalite-composition zoning profiles from the cores of the relict grains to the edges of the host phenocrysts (Fig. 2) follow the traverses shown in Figure 1. The chemical compositions of center cores and outer host phenocrysts in the zoning profiles are given in Table 1. In each section chondrules are named based on their coordinates in a grid superposed on the section images.

The analyzed chondrules are all type-II porphyritic-olivine (PO) chondrules ranging in size from 100 × 170 μm to 300 × 350 μm. All chondrules contain accessory to minor amounts of opaque phases. Most grains are troilite; all chondrules except B5y also contain a few small grains of kamacite. Small (≤5 μm) chromite grains occur in G3v, J3s, E6b and B5y; E6b and J3s also contain a few 20-μm-size subhedral chromite grains. Chondrule A5y contains a large (100 × 140 μm) subhedral olivine phenocryst and three smaller (30-70 μm) olivine grains (Fig. 1a). In the large grain, there is a 70-μm low-FeO relict with a minimum fayalite composition of Fa1. The maximum fayalite composition of the host grain is Fa29.

Chondrule G3v contains two large (100 μm) subhedral olivine phenocrysts, 10 somewhat smaller (30-50 μm) olivine grains, and many even smaller (<30 μm) olivine grains (Fig. 1b). In the largest phenocryst there is a 40-μm low-FeO relict with a minimum fayalite composition of Fa6. The outer part of the host grain is more ferroan, ranging up to Fa36. This chondrule was previously called YcM in the study of Wasson and Rubin (2003).

Chondrule M3d contains two large (70-100 μm) subhedral olivine phenocrysts, nine smaller (30-40 μm) olivine grains, and many even smaller (<30 μm) olivine grains (Fig. 1c). A 40-μm-size phenocryst at the edge of the chondrule contains a 20-μm-size low-FeO relict core with a minimum fayalite composition of Fa1. Several of the smaller olivine grains also contain relicts. The host grain reaches ~Fa25 near the outer margin.

Chondrule J3s is a fragment containing one large phenocryst that encloses a ~20 × 80 μm low-FeO relict core (Fig. 1d) with a minimum fayalite composition of Fa1. The host olivine reaches ~Fa25 near the edge.

Chondrule E6b contains two large (70-100 μm) subhedral olivine phenocrysts, four intermediate (10-30 μm) olivine grains, and many small (1-10 μm) olivine grains. In the largest phenocryst, there is a 50-μm-size low-FeO relict (Fig. 1e) with a minimum fayalite composition of Fa2. The host grain reaches Fa29 at the margin.

Chondrule B5y has a single large (180 × 210 μm) subhedral olivine phenocryst and an elongated, segmented, moderately skeletal grain (~80 × 350 μm) that curves around the margin of the chondrule (Fig. 1f). The central grain contains a relatively dark, 65-μm-size moderately angular relict, with a minimum fayalite composition of Fa18. The host olivine ranges up to Fa63. This chondrule was called YcK by Wasson and Rubin (2003).

3.2. Oxygen Isotopes

A total of 22 O-isotope measurements were made on relict olivine grains and their host phenocrysts in six chondrules; the results are shown in Table 2 and Figure 3. The spots analyzed are marked in Figure 1. Fayalite compositions of the spots were estimated by averaging ~6 electron probe spot analyses around the ion microprobe analyzed spots. In chondrule M3d, the size of the relict grain is the same as the spot size; its composition was calculated by averaging values of electron probe analyses that were carried out before the ion probe analysis.

In the five chondrules (A5y, G3v, M3d, J3s, and E6b) with low-FeO (Fa1-6) relict grains, the ranges for the relicts are $\delta^{17}O = -8.7$ to -3.9‰, $\delta^{18}O = -6.4$ to -0.9‰ (Table 2 Fig. 3a–e). The host phenocrysts have mean compositions of Fa15-34 and O-isotope ranges of $\delta^{17}O = -4.1$ to 0.5‰ and $\delta^{18}O = -1.2$ to 4.9‰. The $\Delta^{17}O$ compositions of the host phenocrysts are consistently less negative than the relict grains. The differences in $\Delta^{17}O$ between the relicts and hosts range from 0.2 to 3.6‰.

Chondrule B5y is different from the others. This chondrule has a moderately high-FeO relict grain (Fa18-27) with $\delta^{17}O \sim 3.7$‰ and $\delta^{18}O \sim 7.5$‰ (Table 2; Fig. 3f), whereas the ranges in the host phenocrysts are $\delta^{17}O = -1.2$ to 1.0‰ and $\delta^{18}O =$ 3.7 to 5.7‰. The mean $\Delta^{17}O$ value of the host phenocrysts is 2.5‰ more negative than the mean of the relict. The ion-microprobe spots sampled a host phenocryst compositional range of Fa54-63.

4. DISCUSSION

4.1. Relict Grains in Type-II Chondrules

Most researchers agree that chondrules formed in the solar nebula by the flash melting of preexisting solid precursor grains (e.g., Hewins and Connolly, 1996; Rubin, 2000). The low-FeO relict cores are preserved from grains that did not melt during the last melting event experienced by the host chondrule (Jones, 1992; Jones, 1996). Most relicts seem to be minerals (or chondrule fragments) formed during earlier generations of chon-

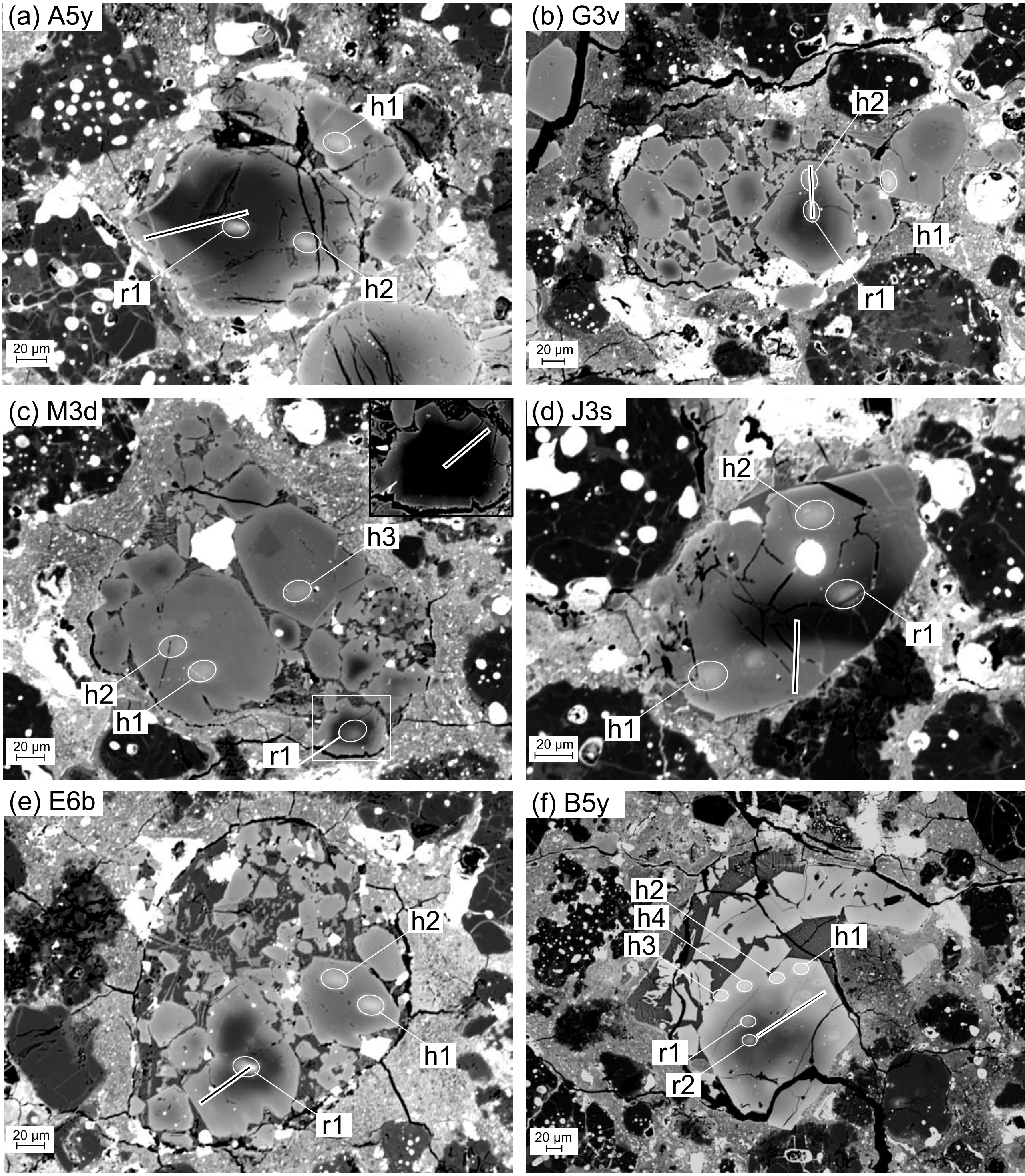

Fig. 1. Backscattered electron (BSE) images of six FeO-rich type-II porphyritic olivine chondrules: (a) A5y, (b) G3v, (c) M3d, (d) J3s, (e) E6b, and (f) B5y. Chondrules A5y, G3v, M3d, J3s, and E6b contain low-FeO (≤Fa6) relict grains whereas B5y contains a moderately high-FeO (~Fa18) relict grain. An enlarged image of the relict grain in M3d is shown in the upper right corner. Ellipses show locations of ion-microprobe spots (the spots appear brighter because of sputtering effects in the ion probe). The locations labels "r" and "h" correspond to relict and host in Table 2. Lines in each figure show the positions of the electron probe traverses illustrated in Figure 2. The oxygen-isotopic compositions of each spot are shown in (Table 2

drule formation. The existence of relict grains provides strong evidence that some chondrule components experienced multiple melting events and thus that the chondrule heating mechanism was capable of recurring (Rubin and Krot, 1996; Wasson, 1993). Wasson and Rubin (2003) combined their data with those of Jones (1992) and found that low-FeO relict grains are

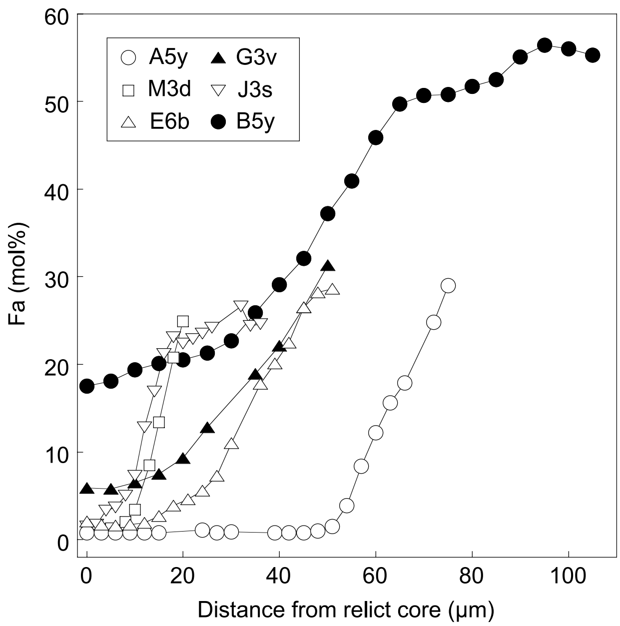

Fig. 2. Fayalite composition zoning profiles in olivine phenocrysts from cores of relict grains to the rims of the host chondrules obtained by electron microprobe. The Fa compositions of relict grain cores for A5y, G3v, M3d, J3s, E6b, and B5y are 1, 6, 1, 1, 2, and 18 mol.%, respectively. The chemical composition obtained by the electron probe of the center of cores and the edges of the profiles are shown in Table 1. The positions of the traverses are shown in Figure 1.

present in essentially all (>90%) type-II chondrules in CO3.0 chondrites. They suggested that the cores of coarse high-FeO phenocrysts are also relicts, thereby implying that recycled chondrule materials constitute a major component of type-II chondrules.

Y-81020 is petrologic subtype 3.0 (Chizmadia et al., 2002; Kojima et al., 1995). Amoeboid olivine inclusions in Y-81020 lack fayalite rims around their forsterite grains in contrast to the ubiquity of such rims in CO3.2 Kainsaz and more equilibrated CO chondrites (Chizmadia et al., 2002). Because fayalite rims are a sensitive indicator of parent-body aqueous and thermal alteration (Chizmadia et al., 2002), it is clear that Y-81020 experienced minimal hydrothermal alteration and that the compositional zoning in olivine grains in chondrules is not derived from parent-body metamorphism. Zoning across the boundary between relict grains and their host phenocrysts (Fig. 2) may have been produced by partial resorption of the relicts in boundary-layer melts coupled with incomplete mixing in the melt. There may also have been some Fe-Mg diffusion between the relict and the newly grown olivine rim (Jones et al., 2000). The cores of the relict grains in chondrules A5y, M3d, J3s, and E6b have Fa < 2. The O-diffusion rate in olivine is much smaller than the Fe-Mg diffusion rates by a factor of 1000 at 1300 K and by higher factors at lower temperatures (Buening and Buseck, 1973; Chakraborty, 1997; Jaoul et al., 1980; Ryerson et al., 1989). Because of this difference and because Fe-Mg zoning is preserved, solid-state diffusion would have produced only negligible changes in the O-isotope composition of the relict grain during the final chondrule melting event.

The core of the relict grain in chondrule G3v is Fa6; it is difficult to assess whether the fayalite composition of the G3v relict-grain core was increased by Fe-Mg interdiffusion. We estimate the contribution of diffusion exchange to the observed O-isotope composition assuming Fe-Mg interdiffusion occurred. If we assume that the core and host of G3v originally were Fa0 and Fa30, the G3v composition (Fa6) could reflect 20% Fe-Mg exchange. The maximum difference in $\Delta^{17}O$ is 20‰ in chondrules. If the O-diffusion rate was $10^3 \times$ smaller than the Fe-Mg diffusion rate, the change in $\Delta^{17}O$ resulting from diffusion is <0.1‰. Thus, we conclude that the O-isotope compositions of relict grains accurately reflect those of earlier chondrule generations.

The core of the relict grain in chondrule B5y has a fayalite

Table 1. Typical electron-probe analyses (wt%) of olivine grains in chondrules from Yamato 81020 (CO3.0).

Chondrule	SiO_2	Cr_2O_3	Na_2O	MnO	K_2O	Al_2O_3	TiO_2	MgO	FeO	CaO	Total	Fa mol%
A5y (51-1)	100 × 170 μm											
Relict	42.4	0.3	n.d.	n.d.	n.d.	0.1	n.d.	56.3	0.9	0.16	100.2	1
Host	37.9	0.5	n.d.	0.2	n.d.	n.d.	n.d.	36.2	26.3	0.18	101.3	29
G3v (56-4)[1]	170 × 310 μm											
Relict	41.4	n.d.	n.d.	n.d.	n.d.	0.1	n.d.	52.1	5.8	0.67	100.3	6
Host	37.6	0.2	n.d.	0.3	n.d.	n.d.	n.d.	34.2	27.8	0.36	100.5	31
M3d (56-4)	170 × 260 μm											
Relict	41.9	0.5	n.d.	n.d.	n.d.	0.2	n.d.	55.3	1.2	0.30	99.6	1
Host	38.3	0.2	n.d.	0.3	n.d.	n.d.	n.d.	38.7	22.8	0.29	100.6	25
J3s (56-4)	100 × 170 μm											
Relict	41.8	0.2	n.d.	n.d.	n.d.	0.1	n.d.	55.0	1.5	0.37	99.1	1
Host	37.6	0.4	n.d.	0.2	n.d.	0.1	n.d.	38.6	22.4	0.25	99.7	25
E6b (51-1)	200 × 250 μm											
Relict	42.1	0.4	n.d.	0.1	n.d.	0.1	n.d.	55.5	2.1	0.23	100.6	2
Host	37.7	0.4	n.d.	0.3	n.d.	n.d.	n.d.	36.4	26.0	0.33	101.1	29
B5y (56-4)[2]	300 × 350 μm											
Relict	39.6	0.3	n.d.	0.1	n.d.	n.d.	n.d.	44.0	16.6	0.35	100.9	18
Host	34.3	0.2	n.d.	0.3	n.d.	n.d.	n.d.	20.3	44.8	0.14	100.0	55

[1] Chondrule was designated YcM by Wasson and Rubin (2003).
[2] Chondrule was designated YcK by Wasson and Rubin (2003).
n.d.: below detection limits (3σ, in wt%); 0.2 for Cr_2O_3; 0.1 for Na_2O, MnO, K_2O, Al_2O_3 and TiO_2.

Table 2. Result of oxygen isotopic analyses of chondrules from Yamato 81020 (CO3.0).

Chondrule		δ^{17}O ± $1\sigma_M$ ‰	δ^{18}O ± $1\sigma_M$ ‰	Δ^{17}O ± $1\sigma_M$ ‰	Fa mol%
A5y (51-1)					
Relict	1	−4.8 ± 1.1	−1.1 ± 1.1	−4.3 ± 0.9	1
Host	1	−1.5 ± 1.1	2.6 ± 1.0	−2.8 ± 0.9	24
	2	0.2 ± 1.1	4.9 ± 1.1	−2.4 ± 0.8	15
G3v (56-4)					
Relict	1	−7.0 ± 1.1	−3.4 ± 1.1	−5.2 ± 0.9	8
Host	1	0.5 ± 1.1	4.1 ± 1.0	−1.6 ± 0.9	34
	2	−1.5 ± 1.0	3.5 ± 1.1	−3.3 ± 0.8	24
M3d (56-4)					
Relict	1	−8.7 ± 1.2	−6.4 ± 1.1	−5.3 ± 0.9	3
Host	1	−2.4 ± 1.3	−1.2 ± 1.2	−1.7 ± 1.2	23
	2	−2.0 ± 1.2	0.2 ± 1.1	−2.2 ± 1.0	24
	3	−1.5 ± 1.1	3.2 ± 1.1	−3.1 ± 0.8	20
J3s (56-4)					
Relict	1	−3.9 ± 1.1	−0.9 ± 1.0	−3.4 ± 0.9	8
Host	1	0.2 ± 1.2	4.6 ± 1.1	−2.2 ± 1.0	26
	2	−1.6 ± 1.1	3.1 ± 1.1	−3.2 ± 0.9	25
E6b (51-1)					
Relict	1	−8.0 ± 1.1	−4.5 ± 1.1	−5.7 ± 0.8	5
Host	1	−4.1 ± 1.2	1.3 ± 1.1	−4.7 ± 1.0	21
	2	−2.2 ± 1.1	0.8 ± 1.1	−2.6 ± 0.9	21
B5y (56-4)					
Relict	1	4.0 ± 1.1	7.4 ± 1.0	0.2 ± 0.9	27
	2	3.4 ± 1.1	7.6 ± 1.0	−0.6 ± 1.0	18
Host	1	−0.4 ± 1.2	5.7 ± 1.1	−3.4 ± 1.0	63
	2	1.0 ± 1.1	4.9 ± 1.1	−1.5 ± 1.0	58
	3	−0.7 ± 1.3	3.7 ± 1.1	−2.6 ± 1.1	61
	4	−1.2 ± 1.2	3.7 ± 1.0	−3.2 ± 1.0	54

composition of Fa18; this is in the high-FeO range and is significantly higher than those of the five low-FeO (Fa1-6) relict grains. A composition of Fa18 is relatively common in the centers of phenocrysts in type-II chondrules in CO3.0; among 11 type-II chondrules studied by Wasson and Rubin (2003), six have cores ranging from Fa15 to Fa18.

4.2. Oxygen Isotopes in Relict and Host Grains

The Δ^{17}O values in five low-FeO relict grains in type-II chondrules from Y-81020 are more negative than those in their high-FeO host phenocrysts. These data confirm and extend earlier studies (Jones et al., 2000; Wasson et al., 2004) showing that, in most cases, the O-isotopic compositions of low-FeO relict grains in CO3.0 chondrites are more ^{16}O-rich than those in "younger" more-ferroan olivine. Combining these results with those of Jones et al. (2000) shows that low-FeO relict grains in six of six CO3.0 type-II chondrules have Δ^{17}O values that are more negative than their host grains.

Electron and ion-microprobe data on chondrules and isolated olivine grains in the ALHA77307 and Y-81020 CO3.0 chondrites show that every ^{16}O-rich grain (Δ^{17}O from −9.0 to −3.5) has a low FeO content near Fa1 (Jones et al., 2000; Leshin et al., 2000; Wasson et al., 2004). The relationship between FeO content and O-isotopic composition is less clear among relatively ^{16}O-poor materials. Although most relatively ^{16}O-depleted grains (Δ^{17}O from −3.5 to +1.7) in these data sets (Jones et al., 2000; Leshin et al., 2000; Wasson et al., 2004) are high FeO (Fa20-40), a few of these grains have low FeO contents (Fa1-5). The mean O-isotope compositions of high-FeO olivine phenocrysts in the five type-II chondrules in Y-81020 measured in this study range in Δ^{17}O from −3.7 to −2.3‰, consistent with previous papers. Although the analytical uncertainty is not negligible and there is significant overlap, the high-FeO olivines in type-II chondrules generally have higher Δ^{17}O than the low-FeO olivines in type-I chondrules. The mean O-isotope compositions of low-FeO relict grains in the five type-II chondrules in Y-81020 range in Δ^{17}O from −5.7 to −3.4‰. All low-FeO relict grains have O-isotopic compositions within the range previously reported for low-FeO type-I chondrules in CO3.0 chondrites (Jones et al., 2000; Leshin et al., 2000; Wasson et al., 2004).

Both the fayalite content and O-isotope compositions of low-FeO relict grains are consistent with the grains having been derived from type-I chondrules. It is significant that the O-isotopic compositions of the relict grains in this study are not near the Δ^{17}O value ∼ −25‰ that appears to be typical of refractory inclusions or amoeboid olivine inclusions in pristine carbonaceous chondrites. From this we conclude that the relict olivine grains did not originate as amoeboid olivine inclusions, the other major potential source of forsterite (Hiyagon and Hashimoto, 1999; Imai and Yurimoto, 2003; Krot et al., 2002). The relicts in our study differ from those analyzed by Jones et al. (2002) and Yurimoto and Wasson (2002), who found Δ^{17}O values ≤−15‰ in unusual relict grains from two chondrules from CV3 Mokoia and one chondrule from Y-81020.

The O-isotope composition of the moderately high-FeO relict grain in chondrule B5y is located at the upper end of a cluster formed by the host phenocrysts from type-II chondrules (Fig. 3f). The fayalite compositions of ion-microprobe spots in the other type-II chondrule host phenocrysts are in the range Fa15-34, whereas the moderately high-FeO relict points in chondrule B5y are Fa18 and Fa27. The fayalite composition of this relict grain in chondrule B5y may suggest that it was recycled from type-II chondrules. In this case, the Δ^{17}O of B5y can be used to help define the O-isotope compositional variation among type-II chondrules. As discussed below, the high Δ^{17}O value of the B5y relict may reflect stochastic sampling. A more complex explanation is that this grain came from a different nebula location having higher mean Δ^{17}O, such as the ordinary-chondrite forming region. On the other hand, the Δ^{17}O of the host phenocrysts in chondrule B5y is close to the mean Δ^{17}O of the host phenocrysts in the other type-II chondrules (even though the B5y host-phenocryst fayalite compositional range, Fa54-63, is significantly higher than those of the other host phenocrysts). Additional analyses of type-II chondrules are needed to assess (1) the variation of O-isotopic composition among type-II chondrules, (2) the general O-isotope composition relationship between moderately high-FeO relicts (i.e., B5y) and their host chondrules, and (3) the origin of the B5y ferroan host and relict.

Jones et al. (2000) observed one isolated olivine (Fa4) grain in CO3.0 ALHA77307 with a mean Δ^{17}O of +1.7‰. The Δ^{17}O in the B5y relict is consistent with the observation that Δ^{17}O values in some high-FeO chondrules in CO3.0 chondrites are >0‰. The Δ^{17}O of nebular gas at the time the last chondrule precursors formed was at least this high.

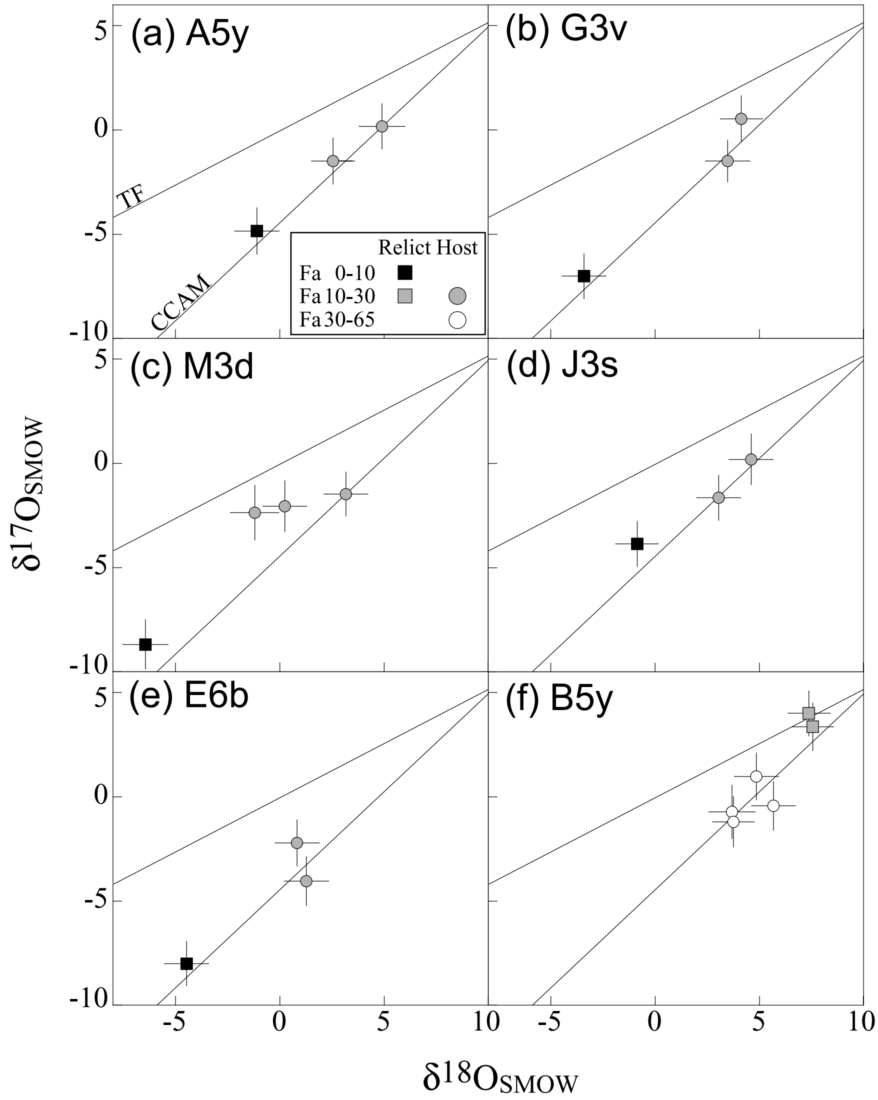

Fig. 3. Oxygen-isotope composition of relict and host olivine grains for individual chondrules from Yamato 81020 (CO3.0). Rectangles and circles show relict and host respectively. Filled, gray, and open symbols show $0 < \mathrm{Fa} < 10$, $10 < \mathrm{Fa} < 30$, and $30 < \mathrm{Fa} < 65$, respectively. Error bars are $1\sigma_M$. The terrestrial fractionation line and carbonaceous chondrite anhydrous minerals line (Clayton, 1993) are shown as solid lines. The five low-FeO relict grains (a–e) have more negative Δ^{17}O than the host phenocrysts. The differences in Δ^{17}O between the relicts and hosts range from 0.2 to 3.6‰. Chondrule B5y (f; which contains a moderately high-FeO relict) shows the opposite trend; the mean Δ^{17}O composition of the host phenocrysts is 2.5‰ less negative than the mean of the relict.

4.3. Earlier Formation of Type-I Chondrules

Relict grains formed before their host phenocrysts. Both the fayalite and O-isotope compositions of low-FeO relict grains are consistent with the grains having been derived from type-I chondrules. Thus, it is clear that some low-FeO type-I chondrules formed before high-FeO type-II chondrules.

Wasson and Rubin (2003) showed that low-FeO relicts are ubiquitous in type-II chondrules. Although high-FeO (Fa6 or higher) relicts would be easy to recognize in BSE images of low-FeO chondrules, none were found. In other chondrite groups some type-I chondrules include relict dusty olivine grains containing numerous small metallic Fe grains formed by reduction of FeO during the last chondrule melting event (Nagahara, 1981; Rambaldi, 1981). The initial Fa contents of these olivine grains were moderately high, ≥3 mol.%. We surveyed a total of ~300 low-FeO type-I chondrules in the two available thin sections of Y-81020, and we found only one chondrule that contained dusty olivine. Thus, dusty olivine grains seem to occur in ≤1% of CO chondrules. From these observations, it is clear that high-FeO relict grains are rare in type-I CO chondrules although low-FeO relict grains are abundant in type-II CO chondrules.

There is reason to expect the FeO of nebular solids to increase gradually. When metal vaporizes at low (<500 K) ambient nebular temperatures, the Fe recondenses as FeO; this process incrementally converts reduced Fe metal to oxidized silicates, thereby increasing the FeO/(FeO+MgO) ratio in the solids (Wasson, 2000). Considering both this argument and the scarcity of relict grains in type-I chondrules, we conclude that most type-I chondrules formed earlier than most type-II chondrules although there may have been a significant overlap in their formation intervals. As discussed later, this evaporation/recondensation process may have also caused a shift in the mean O-isotope composition of nebular solids.

An alternative possible explanation for the relative rarity of high-FeO relict grains in CO chondrites is that there may be a bias against preservation of high-FeO relict olivine grains in type-I chondrules because high-FeO olivine melts at lower temperatures (e.g., 1930 K for Fa20 vs. 2160 K for Fa0). However, it seems probable that high-FeO relict material within type-I chondrules was mainly lost by resorption rather than by melting; Greenwood and Hess (1996) showed that, for phases below their melting temperatures, the amount of resorption depends more on the duration of the heat pulse than on the peak temperature. If chondrules were incompletely melted for brief (<10 s) periods, it seems probable that large (>20 μm) high-FeO relicts olivine could have survived. Because we do not find any (<1%), we conclude that they did not exist in significant numbers.

Both type-I and type-II chondrules experienced multiple partial melting events (Rubin and Wasson, 2003; Wasson and Rubin, 2003), and the last melting event experienced by some low-FeO type-I chondrules may have been at a time and place where most of the chondrules being formed had high-FeO contents. The last melting event experienced by porphyritic chondrules seems to have been minor; upon cooling, only a small fraction of the overall phenocryst growth occurred. Wasson and Rubin (2003) reported evidence that overgrowth thicknesses of only 5 μm were produced during the final melting event in essentially all type-II CO chondrules, and Rubin and Wasson (2003) inferred from the abundance of grossly nonspherical type-I chondrules that this is also true for the type-I chondrules. If, as seems certain, there were low-FeO type-I chondrules and chondrule fragments in the region where high-FeO type-II chondrules were forming, some of the low-FeO material would have formed new low-FeO chondrules and the remelted object would still show the textural and compositional features of type-I chondrules even though melted in a space/time region where most melting events involved high-FeO chondrule precursor materials.

4.4. Implications for the Solar Nebula

As shown above, low-FeO relict grains are generally more ^{16}O-rich than the host phenocrysts. Because these relict grains predate the last chondrule-melting event in the host chondrules, this trend has implications for the oxygen-isotopic evolution of chondritic materials during the period of chondrule formation.

If low-FeO relicts (and their probable type-I chondrule precursors) and their host type-II chondrule phenocrysts formed in the same nebular region, then the observed O-isotopic heterogeneity between the two materials implies an upward drift in the Δ^{17}O in the solid particles with time (Rubin et al., 1990) in the CO region during the period of chondrule formation.

Both Clayton and Mayeda (1984) and Wasson (2000) proposed that chondrule materials had lower Δ^{17}O values than the nebular gas. The Clayton and Mayeda (1984) model involved solids that initially had $\Delta^{17}O < -20‰$ and gas with $\Delta^{17}O > 0‰$; they suggested that, during chondrule formation, O-isotopes exchanged between the melt and the gas. Thus, the mean O-isotopic composition of solid grains is expected to approach that of the gas (e.g., in terms of Δ^{17}O).

Another important example of isotopic processing involves evaporation and recondensation during chondrule formation; recondensation at low nebular temperatures is expected to cause the composition of the solid chondrule precursors to move towards the composition of the gas (Wasson, 2000). Wasson (2000) proposed that the Δ^{17}O of solids gradually approached that of the gas as a result of evaporation during chondrule formation followed by recondensation of metal oxides with Δ^{17}O values the same as or similar to that of the gas.

Our observation that low-FeO relict grains are generally more ^{16}O-rich than the host phenocrysts is consistent with these models. However, this simple relationship is not found in chondrule B5y, in which a moderately high-FeO relict has a Δ^{17}O higher than that of its host. This may reflect stochastic sampling of nebular grains having large grain-to-grain variations in their Δ^{17}O values. Thus, the correlation between Fa content and Δ^{17}O is not perfect. The precursor assemblages incorporated a wide range of materials including previous generations of chondrules as well as high-FeO fine particles produced when flash-evaporated solids recondensed. The Δ^{17}O of the latter particles should approach that of the ambient nebular gas. It seems possible that the precursor mix of the chondrule parental to the B5y relict had a smaller (or negligible) proportion of more negative Δ^{17}O grains than did the final host chondrule, despite the fact that the relict has a fayalite composition typical of olivine in type-II chondrules.

Alternatively, it is possible that the low-FeO relicts and their host type-II chondrule phenocrysts did not form in the same region. In this case, the precursors of low-FeO relict grains formed in the presence of a more ^{16}O-rich gas (more negative Δ^{17}O) than the gas where the precursors of high-FeO chondrule phenocrysts formed, and these early low-FeO relicts were subsequently mixed into the high-FeO chondrule region. This picture requires that the region where low-FeO relicts formed either had a lower mean O fugacity or the relict grains formed at higher temperatures relative to the high-FeO phenocrysts forming region. In either case, the preponderance of low-FeO relicts in high-FeO type-II chondrules shows that at least some type-I chondrules formed before high-FeO type-II chondrules.

We find it simpler and more plausible to form all the CO chondrules sequentially within a single region, with incomplete O-isotopic mixing between chondrule materials and gas throughout the entire period of chondrule formation. This view implies that the Δ^{17}O of the final gas was still higher than the mean Δ^{17}O of the high-FeO chondrules.

5. CONCLUSIONS

In high-FeO porphyritic (type-II) chondrules in CO3.0 chondrites, the oxygen-isotopic compositions of host phenocrysts are generally ^{16}O-depleted relative to those of low-FeO relict grains. Although one chondrule we studied contains a moderately high-FeO relict (with a higher Δ^{17}O value than the host phenocryst), all studied relicts with highly reduced (Fa $\leq$ 6 mol.%) cores are ^{16}O-rich compared to their host chondrules. Both petrographic observations and O-isotope data support the view that the low-FeO relict grains formed in an earlier generation of low-FeO porphyritic (type-I) chondrules. Textural observations and chemical and O-isotopic compositions indicate that some type-I chondrules formed earlier than some type-II chondrules. In fact, it seems likely that most type-I chondrules formed before most type-II chondrules. The data from this study imply that generations of chondrules within a single meteorite formed in different oxygen-isotopic reservoirs. This suggests either an upward drift in $\Delta^{17}O$ in chondrules or their precursor solids with time in the region where CO chondrites accreted, or isotopically distinct formation regions for type-I low-FeO and type-II high-FeO chondrules.

Acknowledgments—We thank Frank Kyte for help with the electron microprobe and Haibo Zou for help with the ion microprobe. We also thank Tim Fagan, Mariana Cosarinsky, and Rhian Jones for constructive reviews. This research was supported mainly by NSF grant EAR-0074076 (J. T. Wasson). K.D.M. receives support from NASA Grant NAG5-9789. The UCLA ion probe was made possible by a gift from the W. M. Keck Foundation and is mainly supported by a grant from the NSF Instrumentation and Facilities Program.

Associate editor: A. N. Krot

REFERENCES

Buening D. K. and Buseck P. R. (1973) Fe-Mg lattice diffusion in olivine. *J. Geophys. Res.* **78,** 6852–6862.

Chakraborty S. (1997) Rates and mechanisms of Fe-Mg interdiffusion in olivine at 980°-1300°C. *J. Geophys. Res.* **102,** 12317–12331.

Chizmadia L. J., Rubin A. E., and Wasson J. T. (2002) Mineralogy and petrology of amoeboid olivine inclusions in CO3 chondrites: Relationship to parent-body aqueous alteration. *Meteorit. Planet. Sci.* **37,** 1781–1796.

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.

Clayton R. N. (1993) Oxygen isotopes in meteorites. *Annu. Rev. Earth Planet. Sci.* **21,** 115–149.

Clayton R. N. and Mayeda T. K. (1984) The oxygen isotope record in Murchison and other carbonaceous chondrites. *Earth Planet. Sci. Lett.* **67,** 151–161.

Eiler J. M., Farley K. A., Valley J. W., Stolper E. M., Hauri E. H., and Craig H. (1995) Oxygen isotope evidence against bulk recycled sediment in the mantle sources of Pitcairn Island lavas. *Nature* **377,** 138–141.

Greenwood J. P. and Hess P. C. (1996) Congruent melting kinetics: Constraints on chondrule formation. In *Chondrules and the Protoplanetary Disk* (eds. R. H. Hewins, R. H. Jones, and E. R. D. Scott), pp. 205–211. Cambridge University Press.

Hewins R. H. and Connolly H. C. (1996) Peak temperatures of flash-melted chondrules. In *Chondrules and the Protoplanetary Disk* (eds. R. H. Hewins, R. H. Jones, and E. R. D. Scott), pp. 197–204. Cambridge University Press.

Hiyagon H. and Hashimoto A. (1999) ^{16}O excesses in olivine inclusions in Yamato-86009 and Murchison chondrites and their relation to CAIs. *Science* **283,** 828–831.

Imai H. and Yurimoto H. (2003) Oxygen isotopic distribution in an amoeboid olivine aggregate from the Allende CV chondrite: Primary and secondary processes. *Geochim. Cosmochim. Acta* **67,** 765–772.

Itoh S. and Yurimoto H. (2003) Contemporaneous formation of chondrules and refractory inclusions in the early Solar System. *Nature* **423,** 728–731.

Jaoul O., Froidevaux C., Durham W. B., and Michaut M. (1980) Oxygen self-diffusion in forsterite: Implications for the high-temperature creep mechanism. *Earth Planet. Sci. Lett.* **47,** 391–397.

Jones R. H. (1992) On the relationship between isolated and chondrule olivine grains in the carbonaceous chondrite ALHA77307. *Geochim. Cosmochim. Acta* **56,** 467–482.

Jones R. H. (1993) Effect of metamorphism on isolated olivine grains in CO3 chondrites. *Geochim. Cosmochim. Acta* **57,** 2853–2867.

Jones R. H. (1996) Relict grains in chondrules: Evidence for chondrule recycling. In *Chondrules and the Protoplanetary Disk* (eds. R. H. Hewins, R. H. Jones, and E. R. D. Scott), pp. 163–172. Cambridge University.

Jones R. H., Leshin L. A., and Guan Y. (2002) Heterogeneity and ^{16}O-enrichments in oxygen isotope ratios of olivine from chondrules in the Mokoia CV3 chondrite. *Lunar Planet. Sci.* **33,** Abstr. 1571.

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. *Meteorit. Planet. Sci.* **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. *Proc. NIPR Symp. Antarct. Meteorit.* **8,** 79–96.

Krot A. N., McKeegan K. D., Leshin L. A., MacPherson G. J., and Scott E. R. D. (2002) Existence of an ^{16}O-rich gaseous reservoir in the solar nebula. *Science* **295,** 1051–1054.

Leshin L. A., McKeegan K. D., and Benedix G. K. (2000) Oxygen isotope geochemistry of olivine from carbonaceous chondrites. *Lunar Planet. Sci.* **31,** 1918 Abstr.

Leshin L. A., Rubin A. E., and McKeegan K. D. (1997) The oxygen isotopic composition of olivine and pyroxene from CI chondrites. *Geochim. Cosmochim. Acta* **61,** 835–845.

McKeegan K. D., Leshin L. A., Russell S. S., and MacPherson G. J. (1998) Oxygen isotopic abundances in calcium-aluminum-rich inclusions from ordinary chondrites: Implications for nebular heterogeneity. *Science* **280,** 414–418.

McSween H. Y. (1977) Carbonaceous chondrites of the Ornans type: A metamorphic sequence. *Geochim. Cosmochim. Acta* **41,** 477–491.

Nagahara H. (1981) Evidence for secondary origin of chondrules. *Nature* **292,** 135–136.

Rambaldi E. R. (1981) Relict grains in chondrules. *Nature* **293,** 558–561.

Rubin A. E. (2000) Petrologic, geochemical and experimental constraints on models of chondrule formation. *Earth Sci. Rev.* **50,** 3–27.

Rubin A. E. and Krot A. N. (1996) Multiple heating of chondrules. In *Chondrules and the Protoplanetary Disk* (eds. R. H. Hewins, R. H. Jones, and E. R. D. Scott), pp. 173–180. Cambridge University Press.

Rubin A. E. and Wasson J. T. (2003) Non-spherical lobate low-FeO porphyritic chondrules in the Y-81020 CO3.0 chondrite: Evidence for small degrees of melting. *Meteorit. Planet. Sci.* **38,** A46 (abstr.).

Rubin A. E., Wasson J. T., Clayton R. N., and Mayeda T. K. (1990) Oxygen isotopes in chondrules and coarse-grained chondrule rims from the Allende meteorite. *Earth Planet. Sci. Lett.* **96,** 247–255.

Ryerson F. J., Durham W. B., Cherniak D. J., and Lanford W. A. (1989) Oxygen diffusion in olivine: Effect of oxygen fugacity and implications for creep. *J. Geophys. Res.* **94,** 4105–4118.

Scott E. R. D. and Taylor G. J. (1983) Chondrules and other components in C, O, and E chondrites: Similarities in their properties and origins. *Proc. Lunar Planet. Sci. Conf.* **14,** B275–B286.

Steele I. M. (1989) Compositions of isolated forsterites in Ornans (C3O). *Geochim. Cosmochim. Acta* **53,** 2069–2079.

Wasson J. T. (1993) Constraints on chondrule origins. *Meteoritics* **28,** 14–28.

Wasson J. T. (2000) Oxygen-isotopic evolution of the solar nebula. *Rev. Geophys.* **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. *Geochim. Cosmochim. Acta* **67,** 2239–2250.

Wasson J. T., Rubin A. E. and Yurimoto H. (2004) Evidence in CO3.0 chondrules for a drift in the O-isotopic composition of the solar nebula. *Meteorit. Planet. Sci*. (in press).

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. *Geochim. Cosmochim. Acta* **65,** 4539–4549.

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

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. *Geochim. Cosmochim. Acta* **66,** 4355–4363.