



## Oxygen isotopes in R-chondrite magnetite and olivine: Links between R chondrites and ordinary chondrites

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**Abstract**—Ion-microprobe studies yield  $\Delta^{17}\text{O}$  ( $=\delta^{17}\text{O} - 0.52 \cdot \delta^{18}\text{O}$ ) values in magnetite from the Rumuruti chondrite (RC) PCA91241 (which is paired with PCA91002) of +3.1 to +3.9‰, slightly higher than that in O from whole-rock R samples. Despite  $\Delta^{17}\text{O}$  values in whole-rock RCs that are much (by ca. 1.6‰) higher than in whole-rock LL chondrites, the  $\Delta^{17}\text{O}$  in R magnetite is much lower (by ca. 2‰) than the values (+4 to +7‰) from LL3 Semarkona and Ngawi (Choi et al., 1998). The  $\delta^{18}\text{O}$  values in PCA magnetite (−15 to −10‰) are the lowest known in meteorites, well below the range in Semarkona (−4 to +9‰). On a  $\delta^{17}\text{O}$ – $\delta^{18}\text{O}$  diagram both magnetite data sets form linear arrays with slopes of ca. 0.7, indicating mixing of O from different isotopic reservoirs; the slopes and intercepts of the two arrays are similar enough to permit them to be segments of a single array. This suggests that, in RCs and LL chondrites, magnetite formed from the same raw materials by the same processes, probably by aqueous alteration of metal in an asteroidal setting. We observed  $\Delta^{17}\text{O}$  values in olivines and pyroxene from RCs ranging from −1.2 to +2.9‰ and  $\delta^{18}\text{O}$  from +1.4 to +9.1‰. These compositions scatter in the same general range observed in chondrules from ordinary chondrites. The similarity in the O-isotopic composition of minerals that preserve a record of formation in the solar nebula supports a model in which RCs formed from nebular components similar to those in H chondrites, but with a matrix/chondrule ratio several times higher in the RCs, and with more extensive aqueous alteration in the RCs than in known H chondrites. We postulate that the matrix in R chondrites has  $\Delta^{17}\text{O}$  higher than whole-rock values. We suggest that the original  $\Delta^{17}\text{O}$  value of  $\text{H}_2\text{O}$  in the RC body was similar to that incorporated into the ordinary chondrites, previously estimated by Choi et al. (1998) to be ca. +7‰ in the LL parent body. Copyright © 2000 Elsevier Science Ltd

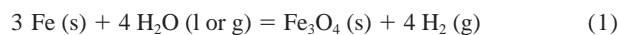
### 1. INTRODUCTION

Choi et al. (1998) found that magnetite in the unequilibrated ordinary chondrites LL3.0 Semarkona and LL3.5 Ngawi (for brevity these data are referred to as LL3 magnetite) has the highest  $\Delta^{17}\text{O}$  values (+4 to +7‰; all O-isotope compositions are relative to the SMOW standard) known in meteoritic materials. The magnetite also has a large range in  $\delta^{18}\text{O}$  and a slope of ca. 0.7 on a  $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$  diagram, indicating mixing of oxygen from two different reservoirs. Choi et al. inferred that one of these reservoirs was  $\text{H}_2\text{O}$  with  $\Delta^{17}\text{O}$  ca. +7‰. Because Rumuruti group chondrites (RCs) have the highest whole-rock  $\Delta^{17}\text{O}$  compositions known in meteorites and are relatively unequilibrated, we studied the only known RC magnetite-bearing assemblage with the goal of gaining new insights into the O-isotopic composition of the (nebular)  $\text{H}_2\text{O}$  incorporated into asteroids, and with the idea that O-isotopic compositions more extreme than those in the LL3 chondrites might be discovered.

RCs (Rubin and Kallemeyn, 1989; Weisberg et al., 1991; Kallemeyn et al., 1996) constitute a major new noncarbonaceous chondrite group characterized by moderate volatile element abundances, high matrix/chondrule ratios, high degree of oxidation, and medium-size chondrules (similar in size to H chondrites). Most RCs are breccias, with the petrographic type

of the host materials in the range 3.6 to 3.8 (Kallemeyn et al., 1996); some RCs contain Type 5 and Type 6 clasts. The most distinguishing characteristic of the RCs is their elevated whole-rock  $\Delta^{17}\text{O}$  values (+2.9‰ in Rumuruti, the only RC fall; Schulze et al., 1994), the highest of any chondrite group.

Magnetite assumes special importance in the study of O reservoirs because, during its formation from metal or FeS, all O comes from the oxidant (probably  $\text{H}_2\text{O}$ ), e.g.:



As demonstrated by Bridges et al. (1995, 1999), the O-isotopes of silica polymorphs, glass, and plagioclase from unequilibrated chondrites have also recorded alteration effects.

We undertook an in situ ion-microprobe study of magnetite, olivine and pyroxene in an unequilibrated magnetite-rich clast that Rubin and Kallemeyn (1994) discovered in a thin-section of R chondrite Pecora Escarpment 91241 (hereafter PCA91241), as well as mafic silicates in a non-magnetite-bearing thin section and a thin section from the paired meteorite PCA91002.

### 2. SAMPLES AND ANALYTICAL METHODS

Our studies were carried out on three thin sections of PCA91002 and its paired specimen, PCA91241. Section PCA91241,10 contained the unequilibrated magnetite-bearing clast (Rubin and Kallemeyn, 1994), section PCA91241,14 contained another unequilibrated clast, and section PCA91002,29 contained an R5 clast. To save space we abbreviated the names of samples according to the scheme listed in Table 1. The first letter in the abbreviation indicates whether the assemblage was a

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Table 1. Thin-section provenance of samples and nomenclature.

Sample	Notes
PCA91241,10	
c17px	Grain in POP chondrule in unequil. clast A
c18ol	Grain in POP chondrule in unequil. clast A
c18px	Grain in POP chondrule in unequil. clast A
c20ol	Chondrule fragment in unequil. clast A
c21ol	Chondrule fragment in unequil. clast A
g25ol	Isolated grain (chondrule fragment?) in unequil. clast A
g35ol	Isolated grain (chondrule fragment?) in unequil. clast A
m1mt	Magnetite nodule in unequil. clast A
m3mt	Magnetite nodule in unequil. clast A
PCA91241,14	
c4px	Grain in chondrule in unequil. clast B
c5ol1	Grain in chondrule in unequil. clast B
c5ol2	Grain in chondrule in unequil. clast B
g6ol	Isolated grain (chondrule fragment?)
g7ol	Isolated grain (chondrule fragment?)
g8ol	Isolated grain (chondrule fragment?)
g9ol	Isolated grain (chondrule fragment?)
PCA91002,29	
c3ol	Unequilibrated chondrule near equil. clast
e1ol	Grain (chondrule fragment?) in R5 equilibrated clast
e3ol	Grain (chondrule fragment?) in R5 equilibrated clast
e4ol	Grain (chondrule fragment?) in R5 equilibrated clast

Silicate samples and magnetite nodules were designated chondrules, (c), equilibrated clast (e), isolated grains (g), or magnetite (m). Minerals were abbreviated: olivine (ol); low-Ca pyroxene (px) and magnetite (mt).

chondrule (c), a grain (or grain assemblage) in an equilibrated clast (e), an isolated grain (g), or a magnetite nodule (m).

Electron-microprobe analyses of magnetite, olivine and pyroxene were obtained with the Cameca CAMEBAX (Paris, France) at UCLA. Analytical conditions were a 15-kV accelerating potential, 10- or 20-nA beam currents, 20-s counting times, and a focused beam. Mineral standards and PAP (ZAF) matrix corrections were employed.

Oxygen-isotope measurements were obtained in situ with the UCLA Cameca ims 1270 ion microprobe with a defocused Cs<sup>+</sup> beam to sputter a 12- to 18- $\mu$ m diameter crater. Standards were LP204 magnetite, San Carlos olivine (Fa<sub>11</sub>), and synthetic fayalite. The three measurements of low-Ca pyroxene were corrected with San Carlos olivine. Samples were C coated except those in the March 1999 runs, which were Au coated; standards were Au coated except in the October 1998 and May 1999 sessions. A normal incident electron gun was used to compensate for sample charging. A high mass resolving power (>6000) was used to eliminate molecular interferences, particularly OH<sup>-</sup>. Data were collected without energy filtering by measuring <sup>16</sup>O (>5  $\times$  10<sup>7</sup> cps) in a Faraday cup (FC) equipped with an electrometer, and measuring <sup>17</sup>O and <sup>18</sup>O with an electron multiplier (EM). Oxygen-isotope measurements of olivine, pyroxene, and magnetite were interspersed with measurements of standards. The raw data were corrected for deadtime, instrumental mass fractionation, EM yield, and for the negligible (<0.1%) tail of the <sup>16</sup>OH<sup>-</sup> peak under the <sup>17</sup>O<sup>-</sup> peak (McKeegan, 1987). Uncertainties include allowance for scatter in the analyses of the standards. Our method for determining the oxygen-isotope composition of magnetite is similar to that described by Choi et al. (1998). Magnetite data were obtained in two analytical sessions (October 1998 and May 1999).

Ion-microprobe measurements of oxygen-isotope ratios of 15 olivine and three pyroxene grains were collected in three analytical sessions from January through March 1999. With several duplicate or triplicate analyses, partly in separate sessions, we report a total of 21 oxygen-isotope measurements of olivine and pyroxene. We employed a modified version of the analytical method for olivine described by Leshin et al. (1997), who showed that, at low Fa contents,  $\delta^{18}\text{O}$  requires a matrix correction of ca. 0.5‰ for a change of 10 mol.% Fa. Although the relationship may not be linear (Eiler et al., 1995), the deviation from linearity is not well defined and probably minor.

The Fa contents of olivine analyzed in January 1999 are (in mol.%) ca. 10, 20, and 25; although a small (ca. 1‰) matrix correction is indicated for the latter data, we did not analyze a high-Fa standard and the listed data are uncorrected. The instrumental mass fractionation between pyroxene and olivine for the low-energy secondary ions measured by the UCLA Cameca ims 1270 are typically <2‰ for  $\delta^{18}\text{O}$  (McKeegan et al., 1998; Shearer et al., 1999). The olivine analyses measured in the March 1999 analytical session were corrected for matrix effects based on data for San Carlos olivine (Fa<sub>11</sub>) and synthetic fayalite (Leshin et al., 1997). A linear correction of 0.7‰ in  $\delta^{18}\text{O}$  for each 10 mol.% change in fayalite content of olivine was indicated; one low-Ca pyroxene grain (Fs<sub>27</sub>) was corrected with this slope.

### 3. PETROGRAPHY AND MINERALOGY

Most RC, including the paired specimens PCA91002 and PCA91241, are breccias; for example, Figure 4 of Rubin and Kallemeyn (1994) shows two chondrules with Type I structures but very different compositions. One preserves the low-FeO olivine (Fa<sub>3,4</sub>) characteristic of unmodified Type I chondrule structures, exhibiting only minor alteration to fayalitic olivine around grain margins. Olivine in the other chondrule has been completely altered to a value near that (Fa<sub>38-40</sub>) commonly observed in equilibrated RCs. From an extensive data set we list several representative olivine, pyroxene, and magnetite analyses (Table 2).

The olivine and pyroxene grains analyzed by ion probe are from chondrules and isolated grains within three clasts and from matrix regions of the meteorite outside these clasts. Clast A is a 1.8  $\times$  2.4 mm clast in PCA91241,10 that contains magnetite, clast B is an equilibrated clast in PCA91241,14, and clast C is a ca. 2  $\times$  4 mm R5 clast in PCA91002,29.

The 1.8  $\times$  2.4 mm unequilibrated clast (clast A) in PCA91241,10 has approximately 6 vol.% magnetite (Fig. 1). Magnetite is concentrated in a small region of the clast, where it forms a complex intergrowth with sulfides (Fig. 2). Clast A also contains two well-defined chondrules, several chondrule fragments, and numerous isolated olivine and pyroxene grains. The unequilibrated nature of this clast is indicated by the large range in olivine Fa values (Fa<sub>0,8-40</sub>) and the apparent lack of textural integration of the chondrules and surrounding fine-grained matrix material. Ion-microprobe analyses were made on one olivine and two low-Ca pyroxene phenocrysts from a Type I porphyritic-olivine-pyroxene (POP) chondrule, two olivine grains from a chondrule fragment, two isolated olivine grains, and two magnetite grains; their locations within the clast are shown in Figure 1. Petrographic descriptions of the chondrules are in the Appendix.

Clast A itself appears to be a breccia with components that experienced different degrees of alteration. Two isolated olivine grains (g25ol and g35ol) within the clast have rim compositions of Fa<sub>40</sub> in contact with the matrix material in the clast. However, some olivine phenocrysts including those in the POP chondrule (c18ol) are zoned only to Fa<sub>21</sub> even though they are in contact with adjacent matrix; this indicates that the chondrule has not equilibrated after it was incorporated into the current generation of breccia. Hence, the isolated olivine grains, chondrules, and chondrule fragments record different prior alteration histories.

Olivine and pyroxene from two chondrules, one porphyritic olivine (PO) and the other barred olivine-pyroxene (BOP), within a different unequilibrated clast (clast B from thin-section

Table 2. Representative electron microprobe analyses of olivine, pyroxene, and magnetite in PCA91241 and PCA91002.

	g7ol1	g8ol1	c5ol1	e1ol1	c3ol1	c18px	mt3
SiO <sub>2</sub>	42.1 (2)	36.0 (1)	40.0 (2)	35.7 (1)	41.9 (2)	58.3 (2)	0.35 (1)
TiO <sub>2</sub>	0.02	0.03	<0.02	0.04 (1)	0.02	0.07 (1)	<0.02
Al <sub>2</sub> O <sub>3</sub>	<0.02	<0.02	<0.02	<0.02	0.12 (1)	0.52 (1)	0.03
Cr <sub>2</sub> O <sub>3</sub>	0.38 (3)	<0.02	0.11 (2)	0.08 (2)	0.21 (3)	0.84 (5)	0.42 (3)
FeO	4.41 (9)	33.8 (2)	15.7 (2)	33.4 (2)	1.25 (5)	5.05 (9)	92.5 (3)
MnO	0.24 (2)	0.41 (2)	0.25 (2)	0.37 (2)	0.03	0.43 (2)	0.03
NiO	0.02	0.26 (2)	<0.02	0.22 (2)	<0.02	0.08 (1)	0.22 (2)
MgO	53.0 (2)	29.0 (1)	43.5 (2)	28.8 (1)	55.0 (2)	35.2 (1)	0.08 (1)
CaO	0.04 (1)	0.03	0.03	<0.02	0.41 (2)	0.41 (1)	0.07 (1)
Na <sub>2</sub> O	nd	nd	nd	nd	nd	nd	nd
K <sub>2</sub> O	nd	nd	nd	nd	nd	nd	nd
Total	100.21	99.53	99.59	98.61	98.94	100.9	93.7
Fa/Fs	4.5	39.5	16.9	39.4	1.3	Fs7.4	—

Units are wt% except Fa/Fs, mol%. Numbers in parentheses represent error in the last decimal place from counting statistics; not reported if less than unity. nd = not determined.

PCA91241,14) as well as several isolated olivine grains outside this clast were also analyzed by ion microprobe. Their petrographic descriptions are also in the Appendix. The occurrence outside clast B of an olivine grain (g6ol1) that has one edge with

an equilibrated composition (Fa<sub>40</sub>) and another edge with a Fa<sub>21</sub> composition in sharp contact with Fa<sub>40</sub> olivine grains in adjacent matrix material (Appendix) suggests that some metamorphic equilibration occurred before brecciation.

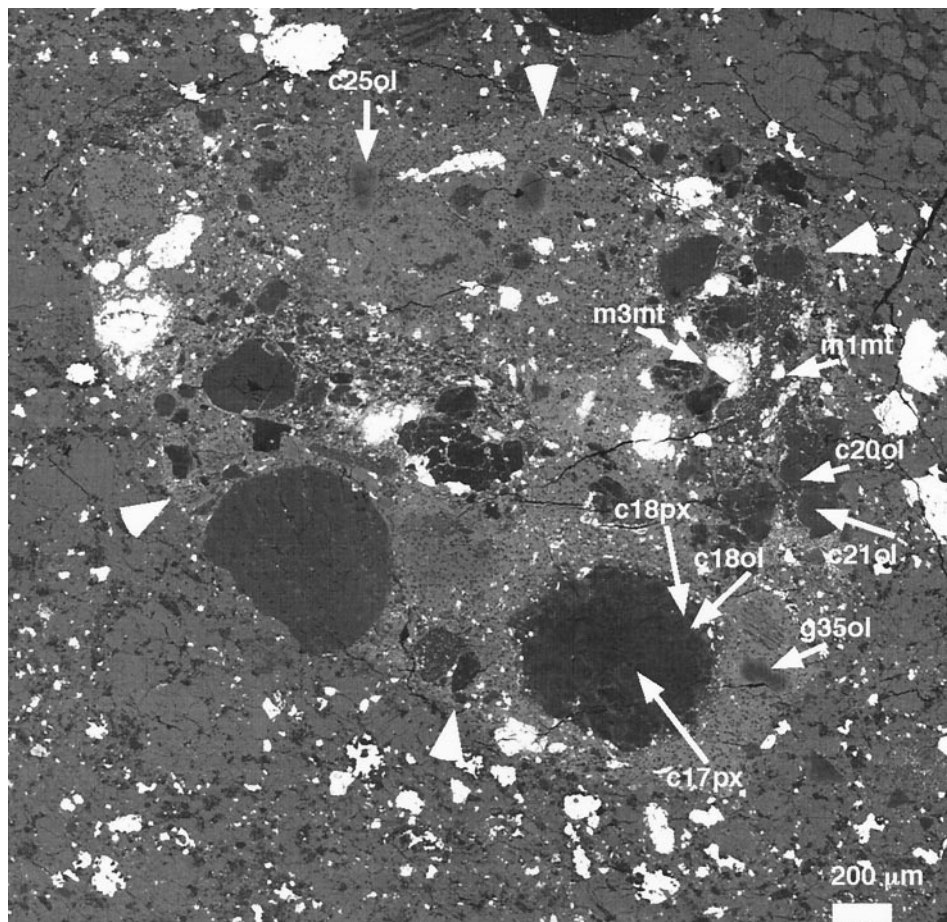


Fig. 1. BSE image of unequilibrated magnetite-bearing clast A (tips of triangles show boundaries) in RC thin-section PCA91241,10. Identified are the magnetite (mt), olivine (ol), and pyroxene (px) grains analyzed by ion microprobe (data in Tables 3 and 4).

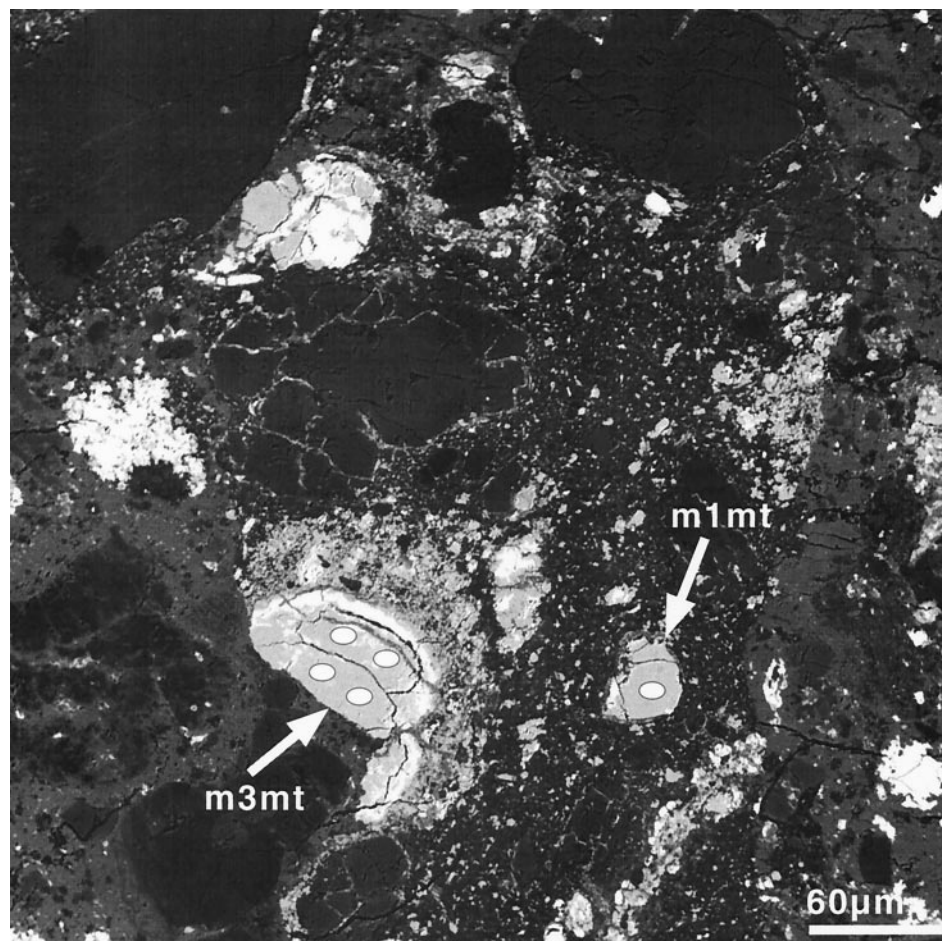


Fig. 2. BSE image of magnetite-rich region of clast A shown in Figure 1. Magnetite grains (m1mt and m3mt) analyzed for oxygen isotopes by ion microprobe are shown. White ellipses show locations of analyzed spots (data in Table 3).

Compositional zoning profiles from two coarse olivines in what was originally a Type II chondrule (Fig. 3) demonstrate a range of alteration effects (both were ion probed). The olivine traverse across c50l1 (Fig. 4) shows a steady and steep increase in Fa content toward the grain margin from (Fa<sub>12-26</sub>); this grain exhibits normal zoning characteristic of primary igneous crystallization in olivine from Type II chondrules (e.g., Fig. 12 of Jones, 1996); it has been little affected by metamorphism or aqueous alteration. In contrast, the traverse across c50l2 (Fig. 4) has a shallow slope and limited range (Fa<sub>33-42</sub>); the Fa value at the grain margin is near the equilibrated RC olivine composition; the shallow slope and relatively high Fa value in the center of the profile (Fa<sub>33</sub>) suggest partial equilibration during thermal metamorphism. The contrast with its sibling c50l1 requires an explanation; we suggest that the exposed part of c50l1 was relatively close (perhaps within 10 μm) to grain surface(s) including fracture surfaces. Also shown in Figure 4 is a zoning profile from the rim to interior of an isolated olivine grain (g7ol) shown in Figure 5 (see Appendix).

Clast C is a ca. 2 × 4 mm R5 clast in PCA91002,29 that was briefly described in Rubin and Kallemeyn (1994). Three equilibrated olivine grains within clast C (e1ol, e3ol, e4ol) and one unequilibrated olivine grain (c3ol) from a PO chondrule outside the clast were analyzed by ion probe. The three olivine grains

from the R5 clast appear to be from the same poorly defined chondrule. The grains are all Fa<sub>39-40</sub>, the equilibrated olivine composition of RC. The interstitial area between these large olivine grains is filled with small grains of augite, olivine (Fa<sub>39-40</sub>), sodic plagioclase, and accessory chromite.

A highly unequilibrated PO chondrule outside clast C contains partially devitrified mesostasis. The analyzed olivine grain has a Fa<sub>7</sub> rim and a core of Fa<sub>1-2</sub> (the ion-probe spot is in the core). Small olivine grains near the chondrule surface are Fa<sub>32</sub>, suggesting that this chondrule underwent partial Fe/Mg exchange during moderate metamorphism.

The occurrence of R5 clasts, enstatite grains (Fig. 2 of Rubin and Kallemeyn, 1994), partially equilibrated mafic silicates, and Fa<sub>66</sub> overgrowths in PCA91241 confirm that the rock is a multigenerational breccia consisting of clasts that record very different styles and degrees of alteration.

#### 4. OXYGEN ISOTOPIC COMPOSITIONS OF RC MINERALS

##### 4.1. Magnetite and Olivine in the PCA91241,10 Magnetite-Bearing Clast

Oxygen-isotope compositions of magnetite and olivine grains are listed in Tables 3, 4, and 5 and shown in Fig. 6. The

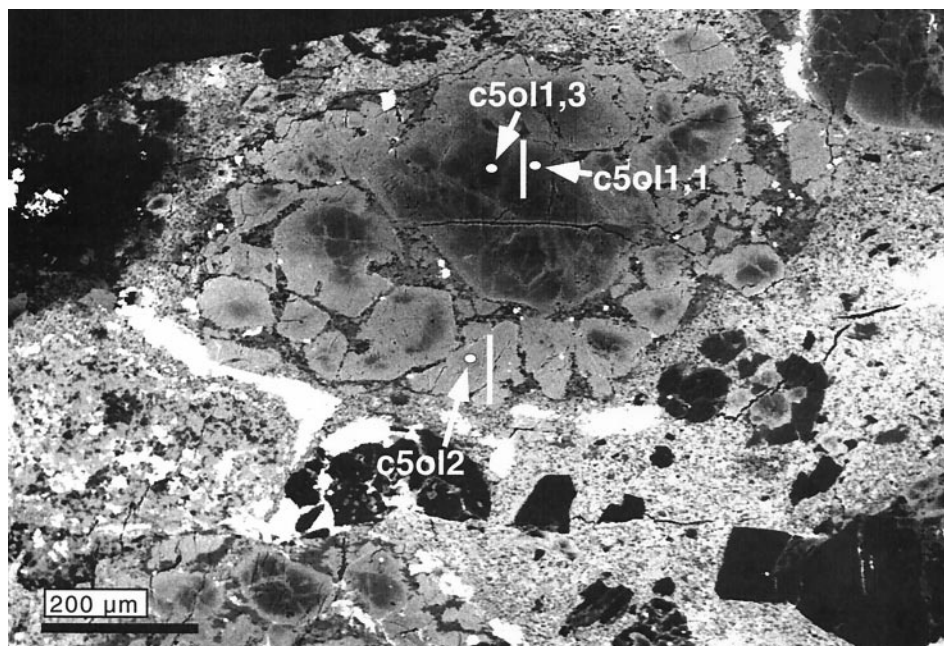


Fig. 3. BSE image of PO chondrule from an unequilibrated clast (clast B) in RC thin-section PCA91241,14. Shown are olivine grains (c5o11 and c5o12) analyzed by ion microprobe (data in Table 5 and Fig. 6). Dark areas have olivine compositions ca.  $\text{Fa}_{12-17}$ , bright edges have compositions near the equilibrated RC value ( $\text{Fa}_{38-40}$ ). FeO-enrichment can be seen from the chondrule exterior to the interior, as well as along cracks in olivine. Location of electron microprobe traverses (Fig. 4) through c5o11 (upper) and c5o12 (lower) are shown.

indicated uncertainties are  $1\sigma$ . Analyses of the magnetite grains were obtained in two ion-microprobe sessions (October 1998 and May 1999). One magnetite grain (m3mt) was large enough for four spots, three of which were analyzed in both sessions. Repeat analyses of the same spot in an individual session were averaged. Another magnetite grain (m1mt) was analyzed once in each session.

Our results (Fig. 6) suggest a systematic mass-dependent-fractionation error in  $\delta^{18}\text{O}$  (ca. 3‰) and  $\delta^{17}\text{O}$  between the two sessions. There was no systematic difference in  $\Delta^{17}\text{O}$ : mean values were  $+3.2 \pm 0.4\text{‰}$  and  $+3.4 \pm 0.8\text{‰}$  for m3mt and  $+3.8 \pm 1.2\text{‰}$  and  $+3.8 \pm 0.7\text{‰}$  for m1mt in the October 1998 and May 1999 sessions, respectively, confirming that the instrumental scatter roughly follows a mass fractionation (slope ca. 0.5) trend.

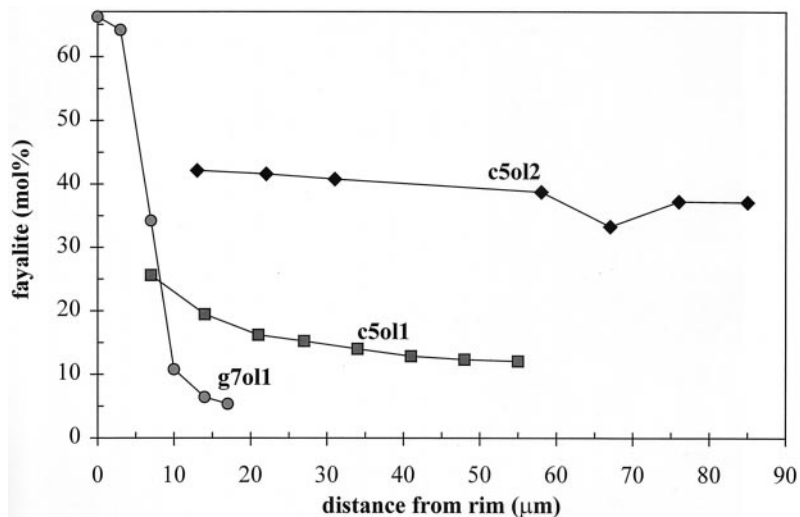


Fig. 4. Electron microprobe traverses across olivines c5o11 and c5o12 (Fig. 3) and g7o11 (Fig. 5). Rims correspond to zero on the distance scale. Fe/Mg zoning in c5o11 is consistent with normal igneous zoning during the crystallization of chondrule melt. Zoning in c5o12 is much shallower, consistent with near-complete diffusive exchange, suggesting that this traverse passes close (within ca. 10  $\mu\text{m}$ ) to one or more grain surfaces.

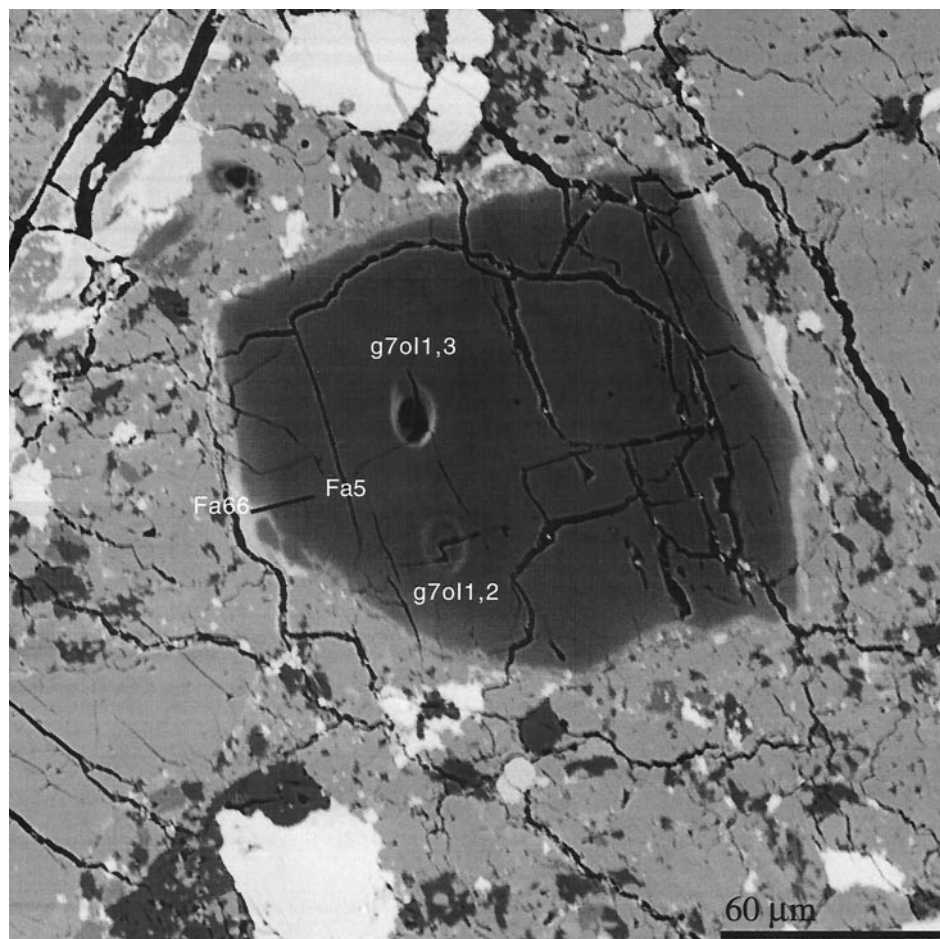


Fig. 5. BSE image of isolated olivine grain g7o11 showing locations of two ion microprobe spots in the core and the track of an electron microprobe traverse. A highly ferroan olivine rim (Fa<sub>66</sub>) does not completely surround the forsteritic olivine (Fa<sub>5</sub>) grain. The electron microprobe traverse extends from the Fa<sub>66</sub> rim to the Fa<sub>5</sub> core (see Fig. 4). Steep zoning probably results from the overgrowth of a highly ferroan (Fa<sub>66</sub>) olivine layer on a low-FeO olivine core, probably during aqueous alteration.

Zinner (1989) noted two effects that can affect the isotopic abundance ratios measured by ion probes: instrumental mass fractionation and differential response of the detection system. Both the ionization probability during sputtering and selection effects of the secondary ions between emission from the sample and collection in the detector lead to overabundances of the light isotopes relative to the heavy isotopes. For <sup>16</sup>O, <sup>17</sup>O, and <sup>18</sup>O this leads to fractionation in a mass-dependent sense (i.e., slopes of ca. 0.5 in  $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$  space), with the absolute magnitude of the fractionation depending on secondary ion-emission angle and velocity, as well as the composition of the sample. In our protocol, <sup>16</sup>O is measured in a Faraday cup, whereas <sup>17</sup>O and <sup>18</sup>O are measured on an electron multiplier. Differences in the relative gain between these two detectors would produce errors along a slope ca. 1 line in  $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$  space. Hence, in our data-set mass fractionation errors were dominant.

We analyzed olivine and pyroxene in the unequilibrated magnetite-bearing clast (clast A) in two ion microprobe sessions in January 1999. Two isolated olivine grains (Fa<sub>20</sub>, Fa<sub>25</sub>), two olivine grains from a chondrule fragment (both Fa<sub>20</sub>), as well as two pyroxene grains (Fs<sub>5</sub>, Fs<sub>7</sub>) and one olivine (Fa<sub>10</sub>)

Table 3. Oxygen isotopic composition of magnetite in the unequilibrated magnetite-bearing clast A of PCA91241,10.

	$\delta^{18}\text{O} \pm 1\sigma^a$ (‰)	$\delta^{17}\text{O} \pm 1\sigma^a$ (‰)	$\Delta^{17}\text{O} \pm 1\sigma^a$ (‰)
Oct '98			
m3mt, 1 <sup>b</sup>	-12.6 ± 1.2	-3.0 ± 0.9	+3.6 ± 0.8
m3mt, 2 <sup>b</sup>	-14.9 ± 1.3	-5.0 ± 1.0	+2.8 ± 0.9
m3mt, 3	-12.8 ± 1.6	-3.4 ± 1.2	+3.3 ± 1.0
Mean <sup>c</sup>	-13.5 ± 0.7	-3.8 ± 0.6	+3.2 ± 0.4 <sup>e</sup>
m1mt, 1	-13.7 ± 1.6	-3.3 ± 1.4	+3.8 ± 1.2
May '99			
m3mt, 1a <sup>d</sup>	-11.9 ± 0.8	-2.7 ± 0.8	+3.5 ± 0.9
m3mt, 2a <sup>d</sup>	-11.4 ± 0.7	-3.4 ± 0.8	+2.5 ± 0.8
m3mt, 3a <sup>d</sup>	-15.1 ± 1.2	-5.1 ± 0.9	+2.8 ± 1.1
m3mt, 4	-10.9 ± 0.7	-1.4 ± 0.6	+4.3 ± 0.6
Mean <sup>c</sup>	-11.8 ± 0.4	-2.7 ± 0.3	+3.4 ± 0.8 <sup>e</sup>
m1mt, 1a <sup>d</sup>	-9.4 ± 0.8	-1.1 ± 0.7	+3.8 ± 0.7

<sup>a</sup> Error includes the uncertainty in the mass fractionation correction, but not in the composition of the standard.

<sup>b</sup> Mean weighted by the variance of two analyses in this spot.

<sup>c</sup> Mean weighted by the variance.

<sup>d</sup> Analyses in the same pit as October 1998.

<sup>e</sup> SD calculated from listed values.

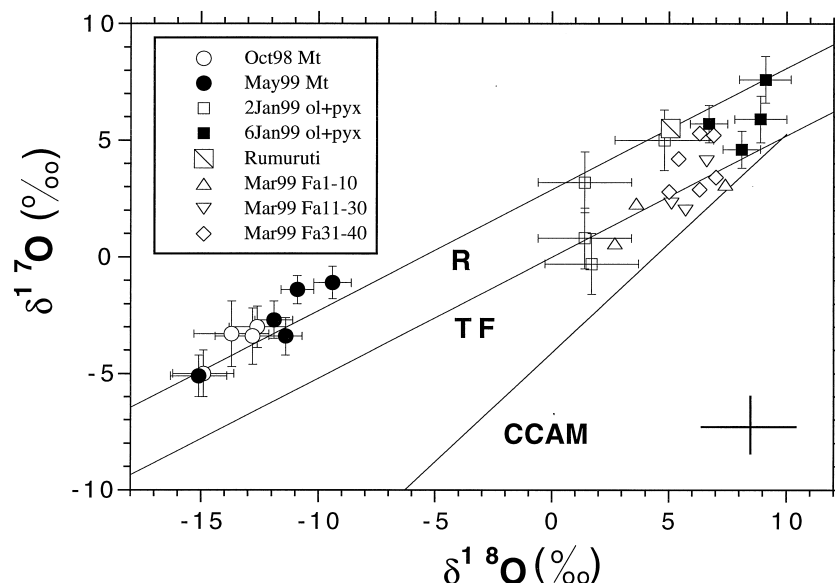


Fig. 6.  $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$  plot of R magnetite, olivine, and pyroxene data. Triangles and diamonds represent March 99 olivine and pyroxene data divided into three olivine compositional ranges. The slashed square represents Rumuruti, the only RC fall (Schulze et al., 1994). Error bars show  $1\sigma$  uncertainties; a representative  $1\sigma$  error bar is shown on the lower right for the Mar 99 data (see Table 5). Also shown are the terrestrial fractionation line (TF), the carbonaceous chondrite anhydrous mineral line (CCAM), and the "R" line (a slope 0.52 line with  $\Delta^{17}\text{O} = +2.9$ ). All values relative to SMOW (Fahey et al., 1987).

inside a Type I POP chondrule were analyzed. There is again evidence of correlated systematic errors in  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  in these silicates (Fig. 6). The large difference in  $\delta^{18}\text{O}$  between the two sessions is associated with a large instrumental mass fractionation (ca. 8‰ of the standard) in the January 2, 1999 session (hence, there are larger uncertainties in  $\delta^{18}\text{O}$  for this session); despite the large errors in  $\delta^{18}\text{O}$ , uncertainties in  $\Delta^{17}\text{O}$  are  $< 1\%$ . This is well illustrated by pyroxene grain c17px; the difference in  $\delta^{18}\text{O}$  between the two analytical sessions is very large ( $+1.4 \pm 2.0\%$  and  $+9.1 \pm 1.1\%$ ), yet the  $\Delta^{17}\text{O}$  values are similar ( $+2.5 \pm 0.6\%$  and  $+2.9 \pm 0.9\%$ ).

In clast A, the  $\Delta^{17}\text{O}$  values of olivine and pyroxene grains in the POP chondrule are more positive (ca.  $+2.5\%$ ) than those in the four other (isolated) olivine grains ( $-1$  to  $+1\%$ ), two of which are chondrule fragments, and the other two probably also. The weighted mean  $\Delta^{17}\text{O}$  for these four isolated olivine grains is  $-0.1 \pm 0.3\%$  (both analytical sessions). The weighted mean  $\Delta^{17}\text{O}$  of olivine and pyroxene in the POP chondrule is  $+2.5 \pm 0.3\%$  (both analytical sessions), similar to but resolvably lower than the mean magnetite value. Magnetite and high- $\Delta^{17}\text{O}$  olivine differ in  $\delta^{18}\text{O}$  by ca. 15‰; as discussed in more detail below, this is consistent with low-temperature equilibrium partitioning between these phases (Clayton and Kieffer, 1991). The  $\Delta^{17}\text{O}$  values of the POP chondrule silicates are slightly lower than Rumuruti whole rock ( $\Delta^{17}\text{O} = +2.9\%$ ).

#### 4.2. Unequilibrated and Equilibrated Olivine from PCA91241,14 and Equilibrated Olivine from an R5 Clast in PCA91002,29

Olivine O-isotope data are listed in Tables 4 and 5 and plotted in Fig. 6. We determined the O-isotopic composition of

olivines having compositions from Fa<sub>1-40</sub> located inside and outside an unequilibrated clast (clast B in PCA91241,14) and an equilibrated R5 clast (clast C in PCA91002,29; Table 5). All  $\Delta^{17}\text{O}$  values are  $\leq +2.0\%$ , i.e., less than R whole-rock values; however, the uncertainties in the analysis of individual spots were large,  $\pm 1.1$  to  $1.6\%$ . The highest  $\Delta^{17}\text{O}$  value was found in clast C in which olivine compositions are Fa<sub>39</sub>; the mean of three spots is  $+1.7 \pm 0.7\%$ . In contrast,  $\Delta^{17}\text{O}$  in olivine in isolated grain g8ol1, which also has a Fa<sub>39-40</sub> composition is only  $-0.4 \pm 1.1\%$ , among the lowest values found.

The higher values of  $\Delta^{17}\text{O}$  for olivine in clast C, as compared to low-FeO olivines in PCA91241,14 and isolated low-FeO olivines in the magnetite-bearing clast A of PCA91241,10 are consistent with the idea that equilibrated RC material should have  $\Delta^{17}\text{O}$  values similar to whole-rock oxygen-isotope measurements. However, the R5 values are ca. 1‰ lower than the whole-rock value. As discussed below, this implies incomplete equilibration of O isotopes within coarse R5 materials and (mass-balance arguments require) the existence of an RC component with  $\Delta^{17}\text{O} \gg 2.9\%$ .

An interesting example is the partially equilibrated chondrule shown in Figure 3; the exteriors of all grains have high FeO contents, and high FeO contents are also present along cracks in the interiors of the olivines. There appears to be no correlation between  $\delta^{18}\text{O}$  or  $\Delta^{17}\text{O}$  and chemical zoning in this chondrule; the  $\Delta^{17}\text{O}$  values of two olivine core analyses (c5ol1,1:  $+0.7 \pm 1.2$ ; c5ol1,3:  $-0.4 \pm 1.3\%$ ) bracket that of an olivine near the chondrule rim (c5ol2:  $+0.2 \pm 1.3$ ). The range of  $\delta^{18}\text{O}$  values in one unequilibrated isolated olivine grain (g7ol; Fa<sub>5</sub>) is  $+2.7 \pm 2.3\%$  to  $+7.4 \pm 2.0\%$ . This is also the total range observed in the thin section. The  $\Delta^{17}\text{O}$  values of

Table 4. Oxygen isotopic composition of olivine and low-Ca pyroxene in a POP chondrule and in other grains in the PCA91241,10 magnetite-bearing clast A.

	Im spot core Rim			$\delta^{18}\text{O} \pm 1\sigma^b$ (‰)	$\delta^{17}\text{O} \pm 1\sigma^b$ (‰)	$\Delta^{17}\text{O} \pm 1\sigma^b$ (‰)
	(mol% Fa or Fs) <sup>a</sup>					
2 Jan 99*						
<i>POP chondrule</i>						
c18px <sup>c</sup>	Fs7			4.8 ± 2.1	5.0 ± 1.3	2.5 ± 0.6
c17px <sup>c</sup>	Fs5	5	5	1.4 ± 2.0	3.2 ± 1.3	2.5 ± 0.6
<i>Other grains</i>						
c21ol <sup>d</sup>	20	16	24	1.4 ± 2.0	0.8 ± 1.3	0.1 ± 0.6
g35ol <sup>d</sup>	20	20	36	1.7 ± 2.0	-0.3 ± 1.3	-1.2 ± 0.5
6 Jan 99						
<i>POP chondrule</i>						
c18ol <sup>d,e</sup>	10	6	21	6.7 ± 0.8	5.7 ± 0.8	2.2 ± 0.7
c17pxa <sup>c,f</sup>	Fs7			9.1 ± 1.1	7.6 ± 1.0	2.9 ± 0.9
<i>Other grains</i>						
c20ol <sup>d</sup>	20	16	24	8.9 ± 1.1	5.9 ± 1.0	1.3 ± 0.9
g25ol <sup>d,e</sup>	25	21	40	8.1 ± 0.8	4.6 ± 0.8	0.4 ± 0.7

\* 2 Jan 99 data on the standard showed a large mass-dependent range in fractionations, but a normal, small range in  $\Delta^{17}\text{O}$ . See text for discussion.

<sup>a</sup> Fa = FeO/(FeO + MgO), Fs = FeO/(FeO + MgO + CaO), both in mol%.

<sup>b</sup> Error includes uncertainty in mass fractionation correction, but not in the composition of the standard.

<sup>c</sup> Instrumental mass fractionation for the pyroxenes was calibrated by using San Carlos olivine (Fa<sub>11</sub>), and thus includes a minor instrumental mass bias between pyroxene and olivine (McKeegan et al., 1998; Shearer et al., 1999).

<sup>e</sup> Mean weighted by the variance of two successive analyses.

<sup>f</sup> Analysis in the same pit as c17px (2 Jan 99).

mafic silicates in PCA91241,14 range from  $-0.8 \pm 1.2\text{‰}$  to  $+0.7 \pm 1.2\text{‰}$ . The  $\Delta^{17}\text{O}$  value of these olivines are similar to that found for olivine grains (excluding the POP chondrule) in clast A of PCA91241,10 ( $\Delta^{17}\text{O} = -1.2 \pm 0.5$  to  $+1.3 \pm 0.9\text{‰}$ ).

## 5. DISCUSSION

### 5.1. Incomplete O-isotopic Exchange in RC Olivine and Pyroxene

Fluorination studies have yielded whole-rock  $\delta^{18}\text{O}$  values for the RC (Weisberg et al., 1991; Bischoff et al., 1994; Schulze et al., 1994; Kallemeyn et al., 1996; Jäckel et al., 1996; Bischoff et al., 1998) that—with the exception of the weathered hot-desert find Hughes 030 ( $+7.5\text{‰}$ )—range from  $+4$  to  $+6\text{‰}$  (Fig. 6). The extreme  $\delta^{18}\text{O}$  in Hughes 030 probably reflects contamination by terrestrial oxides (Bischoff et al., 1998).

RC whole-rock  $\Delta^{17}\text{O}$  values less than Rumuruti ( $+2.9\text{‰}$ ) have also been ascribed to terrestrial alteration (Kallemeyn et al., 1996). However, the amount of terrestrial oxides is probably too low to explain the  $\Delta^{17}\text{O}$  of  $+0.6\text{‰}$  observed by Weisberg et al. (1991) with fluorination techniques, in an unequilibrated (olivine: Fa<sub>17-39</sub>) Carlisle Lakes chondrule. In three equilibrated chondrules (olivine: Fa<sub>38</sub>) from ALH85151 they also determined  $\Delta^{17}\text{O}$  values ( $+2.5$  to  $+3.0\text{‰}$ ) near the mean *R* value of  $+2.9\text{‰}$ .

Olivine and pyroxene in the PCA91241,10 magnetite-bearing clast (clast A) show a range of  $\Delta^{17}\text{O}$  values (Table 4). In the POP chondrule shown in Fig. 1,  $\Delta^{17}\text{O}$  is  $+2.2$  to  $+2.9\text{‰}$ , whereas olivine and pyroxene grains outside this chondrule have  $\Delta^{17}\text{O}$  ranging from  $-1.2$  to  $+1.3$ . The relatively high  $\Delta^{17}\text{O}$  in the POP chondrule might suggest exchange with the same fluid that was involved in magnetite formation. However,

the  $\Delta^{17}\text{O}$  values of the POP silicates are lower (by ca. 1‰) than the magnetite values, and  $\Delta^{17}\text{O}$  values in the isolated grains from clast A differ by a still greater amount. Thus it appears that, after formation of this unequilibrated breccia clast, exchange between mafic silicates and the fluid responsible for magnetite formation was limited or even negligible.

The  $\Delta^{17}\text{O}$  values determined in the March 1999 run for chondrule olivine and isolated olivine grains from PCA91241,14 (Table 5, Fig. 6) are quite low ( $-1.0 \pm 1.2$  to  $+0.7 \pm 1.4$ ), even lower than the value of  $+0.6\text{‰}$  in the unequilibrated chondrule from Carlisle Lakes (Weisberg et al., 1991). Our data overlap the lower part of the OC chondrule range (Clayton et al., 1991). Fluorination studies of three equilibrated chondrules from ALH85151 yielded  $\Delta^{17}\text{O}$  values of  $+3.03$ ,  $+2.83$ , and  $+2.54\text{‰}$ , similar to whole-rock  $\Delta^{17}\text{O}$  values (Weisberg et al., 1991) and considerably higher than our ion-probe results. Because there is extensive overlap in the scatter fields and there are high uncertainties in our ion-probe  $\Delta^{17}\text{O}$  values, we doubt that the apparent difference between our mean composition in PCA olivine and the somewhat higher values in OC chondrules is significant.

Relevant to the discussion of O-isotope equilibration are the oxygen-isotopic analyses of three olivine grains (perhaps part of the same chondrule from the R5 clast in PCA91002,29 (Table 5). The mean  $\Delta^{17}\text{O}$  of these three grains is  $+1.7 \pm 0.7\text{‰}$ , higher than we observed in isolated grains and chondrules of PCA91241,14 but lower than R whole-rock values ( $\Delta^{17}\text{O}$  ca.  $+2.9$ ). That these clasts, equilibrated in terms of Fe and Mg, are lower in  $\Delta^{17}\text{O}$  than the whole-rock samples indicates that  $\Delta^{17}\text{O}$  was not uniform within the RC parent body, and (as noted above) requires additional materials having  $\Delta^{17}\text{O} > +3\text{‰}$ . This is consistent with similar evidence from OC (Bridges et al., 1999). It has also been shown from equil-



Table 5. Oxygen isotopic composition of olivine in PCA91241,14 and R5 clast in PCA91002,29 measured in Mar 1999.

Sample <sup>a</sup>	Im spot core Rim			$\delta^{18}\text{O} \pm 1\sigma^b$ O <sup>c</sup> (‰)	$\delta^{17}\text{O} \pm 1\sigma^b$ O <sup>c</sup> (‰)	$\Delta^{17}\text{O} \pm 1\sigma^b$ O <sup>c</sup> (‰)
	(mol% Fa or Fs) <sup>a</sup>					
<i>Isolated grains</i>						
g7ol1, 2 <sup>d</sup>	5	5	66	$2.7 \pm 2.3$	$0.6 \pm 1.3$	$-0.8 \pm 1.4$
g7ol1, 3 <sup>d</sup>	5	5	66	$7.4 \pm 2.0$	$3.1 \pm 1.2$	$-0.8 \pm 1.2$
g9ol2	40			$7.0 \pm 2.2$	$3.4 \pm 1.3$	$-0.2 \pm 1.3$
g8ol1	39			$6.3 \pm 2.0$	$2.9 \pm 1.2$	$-0.4 \pm 1.1$
g6ol1	21	21	40	$5.7 \pm 2.0$	$2.0 \pm 1.2$	$-1.0 \pm 1.2$
<i>Chondrule grains (clast B)</i>						
c50l1, 1 <sup>d</sup>	17			$6.6 \pm 2.1$	$4.1 \pm 1.2$	$0.7 \pm 1.2$
c5ol1, 3 <sup>d</sup>	13			$5.1 \pm 2.3$	$2.3 \pm 1.2$	$-0.4 \pm 1.3$
c5ol2	34	33	42	$5.0 \pm 2.3$	$2.8 \pm 1.3$	$0.2 \pm 1.3$
c4px1	26			$5.7 \pm 2.2$	$3.7 \pm 1.4$	$0.7 \pm 1.4$
PCA91002,29						
<i>R5 clast (clast C)</i>						
elo11	39			$6.3 \pm 2.4$	$5.3 \pm 1.5$	$2.0 \pm 1.6$
e3ol1	39			$5.4 \pm 2.5$	$4.2 \pm 1.2$	$1.4 \pm 1.4$
e4ol1	39			$6.9 \pm 2.1$	$5.2 \pm 1.2$	$1.6 \pm 1.2$
<i>Chondrule</i>						
e3ol1	1			$3.6 \pm 2.2$	$2.3 \pm 1.2$	$0.4 \pm 1.3$

<sup>a</sup> Analyses have been corrected for matrix effects due to different FeO contents of olivine (0.7% every 10 mol% fayalite was used; see text).

<sup>b</sup> Fa = FeO/(FeO + MgO); Fs = FeO/(FeO + MgO + CaO), both in mol%.

<sup>c</sup> Error includes uncertainty in mass fractionation correction, but not in composition of standard.

<sup>d</sup> Separate analytical spots on the same olivine grain.

ibrated OC studies that O diffuses very slowly in silica polymorphs during metamorphism (e.g., Bridges et al., 1995). Although, we cannot rule out the possibility that the R5 clast is xenolithic (i.e., that it originated on another RC parent body or another part of the RC body, one that suffered a somewhat different degree of aqueous alteration) this seems unlikely in view of the commonality of R5 clasts in RC breccias.

The range of  $\Delta^{17}\text{O}$  values observed by us confirms and extends the observations of Weisberg et al. (1991) on separated

chondrules (Fig. 7). We did not analyze equilibrated chondrules, although we did analyze high-Fa and presumably Fe-Mg equilibrated isolated olivine grains (g8ol and g9ol; Table 5). These grains had low  $\Delta^{17}\text{O}$  values, similar to nearby low-Fa olivine grains (Table 5) that are presumably of chondrule origin. The equilibrated olivine in the R5 clast is lower in  $\Delta^{17}\text{O}$  (mean  $\Delta^{17}\text{O}$ :  $+1.7 \pm 0.7\text{‰}$ ) than R whole rocks, although marginally within  $2\sigma$  error. The analyzed unequilibrated chondrule from the magnetite-bearing clast is similar in

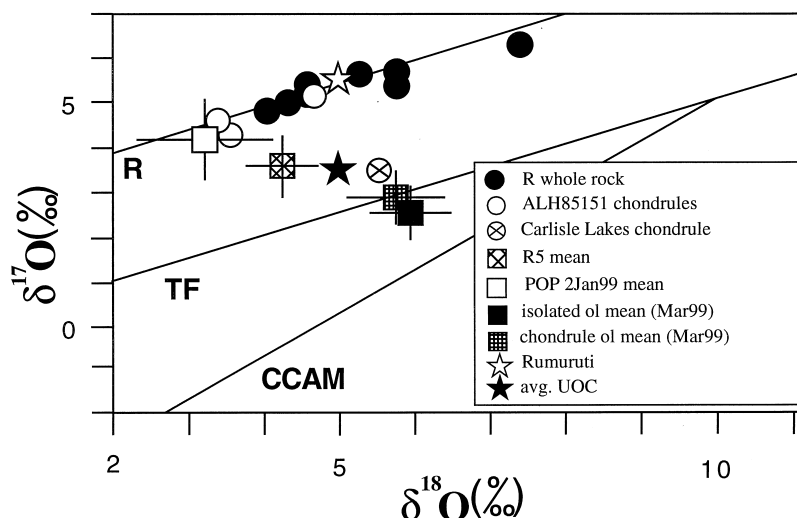


Fig. 7.  $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$  plot of mean R components, R whole rocks, and R chondrules. Squares are results from this study. Closed circles represent R whole rocks (references in text). Open circles are separated chondrules (Weisberg et al., 1991). The open star represents Rumuruti, the only RC fall. Closed star represents the average unequilibrated ordinary chondrite oxygen (Clayton et al., 1991). Also shown are the R, TF, and CCAM lines. All values relative to SMOW.

$\Delta^{17}\text{O}$  (Table 4) to the equilibrated ALH85151 chondrules of Weisberg et al. (1991) and the R whole rocks. It appears that the PCA RC consists of materials with variable  $\Delta^{17}\text{O}$  and that the  $\Delta^{17}\text{O}$  values are not related in simple fashion to the formation of high-Fa olivine. These data show that Fe/Mg exchange can occur in olivine or pyroxene without equilibrating the O. The fact that PCA91002-PCA91241 is a breccia hinders drawing more detailed conclusions about the relationship between O-isotope and cation equilibration.

The low  $\Delta^{17}\text{O}$  values of some chondrule mafic silicates are similar to those observed in chondrules from unequilibrated ordinary chondrites (Clayton et al., 1991). This opens the possibility that the R chondrules are derived from the same basic nebular components as those agglomerated to form ordinary chondrites. This idea is explored in more detail below.

## 5.2. Magnetite and Other High $\Delta^{17}\text{O}$ Components in RC

Our magnetite data were obtained on the only known RC magnetite-bearing assemblage, an unequilibrated clast in PCA91241,10 (Fig. 1). Our  $\delta^{18}\text{O}$  values for the two large magnetite grains ( $-9.4$  to  $-15.1\text{‰}$ ) are the lightest yet reported for meteoritic magnetite. The range in  $\Delta^{17}\text{O}$  ( $+2.2$  to  $+4.3\text{‰}$ ) is large and  $\Delta^{17}\text{O}$  is positively correlated with  $\delta^{18}\text{O}$ . The mean values of  $\Delta^{17}\text{O}$  for the large grain measured for the first and second sessions are in agreement,  $+3.2 \pm 0.4\text{‰}$  and  $+3.4 \pm 0.8\text{‰}$ , respectively, for a combined mean of  $+3.3\text{‰}$ . This mean is, at most, marginally higher than the whole-rock  $\Delta^{17}\text{O}$  value for Rumuruti ( $+2.9\text{‰}$ ). The common interpretation is that magnetite formed by the oxidation of metal during aqueous alteration on an asteroid. If, before magnetite formed, some O-isotope exchange occurred between the oxidant and the RC silicates, the initial  $\Delta^{17}\text{O}$  of the  $\text{H}_2\text{O}$  could have been higher than that in the magnetite.

A regression line through the magnetite data yields a slope of 0.72, greater than the expected mass fractionation slope of 0.52. Choi et al. (1998) found a similar slope in their study of magnetite grains from the LL3.0 ordinary chondrite Semarkona. Choi et al. also observed a large range (ca. 13‰) in  $\delta^{18}\text{O}$  that they interpreted to indicate formation from a limited aqueous reservoir, most likely in an asteroidal setting. Our  $\delta^{18}\text{O}$  range is smaller (ca. 4‰) and offset from that of Choi et al.; our highest  $\delta^{18}\text{O}$  value is 6.6‰ lower than the lowest Semarkona magnetite. Choi et al. observed much of their total range in a single magnetite grain, and much of our observed range is present in the large grain m3mt.

If the PCA magnetite formed from an aqueous fluid, and if the magnetite with the highest  $\delta^{18}\text{O}$  ( $-9\text{‰}$ ) formed first, then the initial fluid must have had a  $\delta^{18}\text{O}$  of ca. 0‰, assuming equilibrium fractionation between magnetite and  $\text{H}_2\text{O}$  (l); the interphase fractionation factor,  $\Delta^{18}\text{O}(\text{magnetite}-\text{H}_2\text{O})$  is ca.  $-10\text{‰}$  at temperatures around 300 K (Clayton and Kieffer, 1991). Because  $\Delta^{18}\text{O}(\text{magnetite}-\text{H}_2\text{O})$  is so large and negative, if magnetite were the only phase forming, the composition of the fluid would evolve towards more positive  $\delta^{18}\text{O}$  values. As discussed below, the simultaneous formation of phyllosilicates can push the evolution in the opposite direction.

## 5.3. Comparison of Oxygen-Isotopic Compositions of Magnetite and Olivine in LL3 Semarkona and R chondrites

As stated in the Introduction, we embarked on this study with the idea that the RC magnetite might preserve very high  $\Delta^{17}\text{O}$  values, similar to or higher than those in the LL3 magnetite studied by Choi et al. (1998). Instead, we found much lower  $\Delta^{17}\text{O}$  values. However, when we plotted our data together with those from Choi et al., we found that, although the  $\delta^{18}\text{O}$  values in the PCA magnetite are much lower than those in the Semarkona magnetite, the PCA and Semarkona data have similar slopes (ca. 0.7) and, within the experimental scatter, could be segments of the same linear array (Fig. 8).

Choi et al. (1998) found that LL3 magnetite and olivine were not in equilibrium;  $\Delta^{17}\text{O}$  in magnetite was higher by ca. 4‰ (Fig. 6) than whole-rock silicates. In contrast,  $\Delta^{17}\text{O}$  values in RC mafic silicates are only marginally lower than those of magnetite. Choi et al. showed that the Semarkona trend with slope ca. 0.72 could be modeled by simultaneous formation of magnetite and phyllosilicates with minor exchange of O between the fluid and chondrule silicates. They interpreted the very large range in  $\delta^{18}\text{O}$  to indicate that, during the formation of the magnetite, 90% of the  $\text{H}_2\text{O}$  was consumed. If the oxidant  $\text{H}_2\text{O}$  in the RC parent body had the same original composition as that in the LL parent body, then the oxygen isotopic composition of the magnetite in the PCA clast would reflect formation after that reservoir had been highly altered, partly by forming phyllosilicates which moved  $\delta^{18}\text{O}$  to lower values, and by O exchange with silicates, which moved  $\Delta^{17}\text{O}$  to lower values.

Another interesting link to OC O-isotope reservoirs is the fact that a similar slope (0.71; the full equation is  $\delta^{17}\text{O} = 0.707 - \delta^{18}\text{O} + 0.367$ ), is obtained for an array of silica-rich samples studied by fluorination techniques by Bridges et al. (1995) (cristobalite-bearing clasts in LL Parnallee and L Farmington) and Bridges et al. (1999) (feldspar/glass separates from unequilibrated OC). The fluorination-determined  $\Delta^{17}\text{O}$  values of the feldspar-glass separates and cristobalite-bearing clasts from unequilibrated OC are commonly high, up to  $+3.1\text{‰}$  (Bridges et al., 1995, 1999);  $\Delta^{17}\text{O}$  values in these silica-rich materials can be interpreted to be mixtures of original (nebular) mineral O and new O added from an aqueous (or vapor according to Bridges et al., 1995) phase with  $\Delta^{17}\text{O} \geq 3\text{‰}$ . This array and the LL3-magnetite array are essentially parallel, consistent with formation in equilibrium with the same aqueous reservoir. The offset in  $\delta^{18}\text{O}$  between the two phases at constant  $\Delta^{17}\text{O}$  would then correspond to  $\Delta^{18}\text{O}_{(\text{silica-magnetite} [\text{sl-mt}])}$ , a quantity that varies with temperature. Because the silica-feldspar-glass contains O that is inherited from precursor oxides we obtain a better estimate of the difference at higher  $\Delta^{17}\text{O}$  corresponding to a larger fraction of O from the aqueous phase. At  $\Delta^{17}\text{O} = +5\text{‰}$  the difference is 23‰, consistent with formation around 300 K (Clayton and Kieffer, 1991).

## 5.4. Implications of Oxygen-Isotopic Systematics for the Aqueous Alteration on the R and LL Chondrite Parent Bodies

There are several properties that link the RCs and the clan of ordinary chondrites (OC): (a) similar refractory lithophile

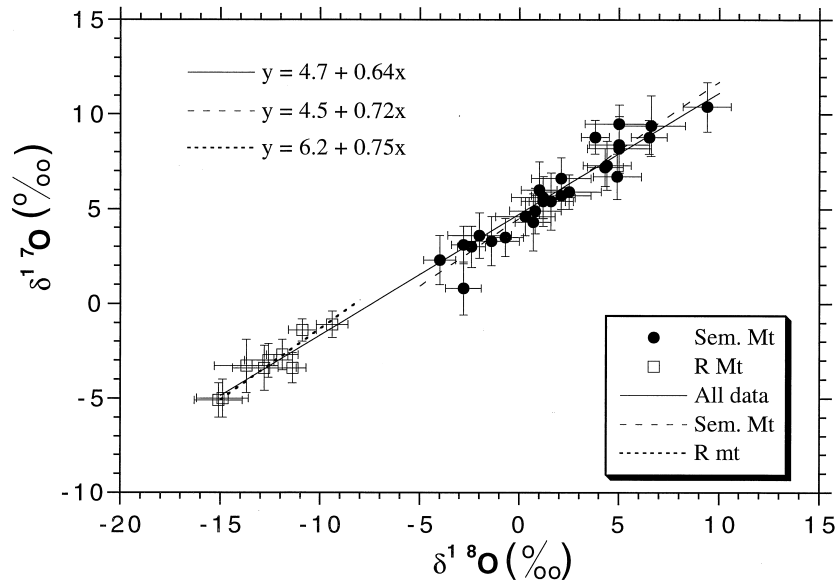


Fig. 8.  $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$  plot showing R magnetite (open squares) from this study and OC (Semarkona, Ngawi) magnetite (closed circles) data of Choi et al. (1998). Linear fits to the combined data set (solid line), to Semarkona magnetite (dashed line), and to RC magnetite (dotted line) have slopes of 0.64, 0.72, and 0.75, respectively. Within the uncertainties the RC and OC arrays could be segments of a single array. All values relative to SMOW.

abundances (Kallemeyn et al., 1996); (b) similar chondrule sizes and textures (Kallemeyn et al., 1996); and (c) similar chondrule  $O$ -isotopic compositions (Clayton et al., 1991; Weisberg et al., 1991). Relative to OC, the properties that resolve these two clans are: ( $\alpha$ ) the higher R whole-rock  $\Delta^{17}\text{O}$  values (Clayton et al., 1991; Weisberg et al., 1991); ( $\beta$ ) the higher abundances in RC of moderately volatile elements such as S, Ga, Se, and Zn (Kallemeyn et al., 1996); ( $\gamma$ ) the higher matrix/chondrule ratio in RC (ca. 0.9 vs. 0.14 in OC) (Rubin and Kallemeyn, 1989; Weisberg et al., 1991; Bischoff, 2000); ( $\delta$ ) the higher FeO content in the silicates and lower metallic Fe-Ni contents in RC (Kallemeyn et al., 1996), particularly when the comparison is made with OC having similar common siderophile abundances (RC common siderophile abundances are higher than those in L chondrites and ca. 0.90 to 0.95 $\times$  those in H chondrites).

Chondrites formed by the mechanical agglomeration of nebular components (i.e., chondrules, fine-grained "matrix," metal, refractory "inclusions," etc.). As discussed above, in RC these components seem to have been similar in their properties (although not in their relative abundances) to those in ordinary chondrites. It has been suggested that differences in elemental composition between the OC groups and the fact that, on several compositional diagrams, the OC seem to define a "continuous-fractionation sequence" (Wasson, 1972), can be understood in terms of minor nebular mechanical fractionations associated with differences in grain-size distributions of the nebular components.

In Figure 9 the elemental compositions of individual RC (Kallemeyn et al., 1996) are compared with mean compositions of H, L, and LL chondrites. Lithophile abundance ratios are plotted in Figure 9a, those of siderophiles and chalcophiles in Figure 9b; on each of these diagrams the elements are plotted in order of volatility increasing to the right, except rare earth

elements that are plotted in order of increasing atomic number. To minimize the scatter, the R, L, and LL abundances are normalized to H-chondrite abundances. On Figure 9a we see that RC abundances of the refractory lithophiles (Al, Sc, Ca, and the rare earth elements) are ca. 5 to 6% higher than those in OC. Abundances of the moderately volatile lithophiles Mn and Na are also ca. 5% higher in RC than in OC; K data scatter, probably reflecting a high sensitivity to weathering effects (Kallemeyn et al., 1996). In Figure 9b RC abundance ratios of refractory siderophiles (Os, Ir, Ru) are ca. 0.87 and, after allowance for weathering effects, abundance ratios of common siderophiles are ca. 0.95 those in H chondrites. Note that L and LL chondrite abundance ratios of refractory siderophiles are also appreciably lower than those of the common siderophiles.

The largest difference between R and H chondrites is found in the five most volatile elements (all dominantly siderophile or chalcophile), As, Ga, Sb, Se, and Zn whose abundance ratios increase from ca. 1.12 for As to ca. 3.3 for Zn. With the exception of a reversal between Ga and Sb, abundance ratios of these five elements increase with decreasing condensation temperature (Wasson, 1985).

The three links between RC and OC are fundamental in the sense that all can be directly attributed to nebular components. It is widely recognized that both  $O$ -isotopic compositions (Clayton et al., 1991; Clayton and Mayeda, 1999) and the distribution of chondrule textures in ordinary chondrites are very different from those in carbonaceous chondrites (Grossman et al., 1988; Rubin, 2000). In RC the  $O$ -isotopic compositions of the chondrules and the relative abundances of different (porphyritic and nonporphyritic) textural types are similar to those in OC, suggesting formation at the same nebular location/time. It also is widely accepted that chondrite clans recognized on the basis of petrographic texture tend to have similar whole-rock refractory lithophile abundances (e.g., in the

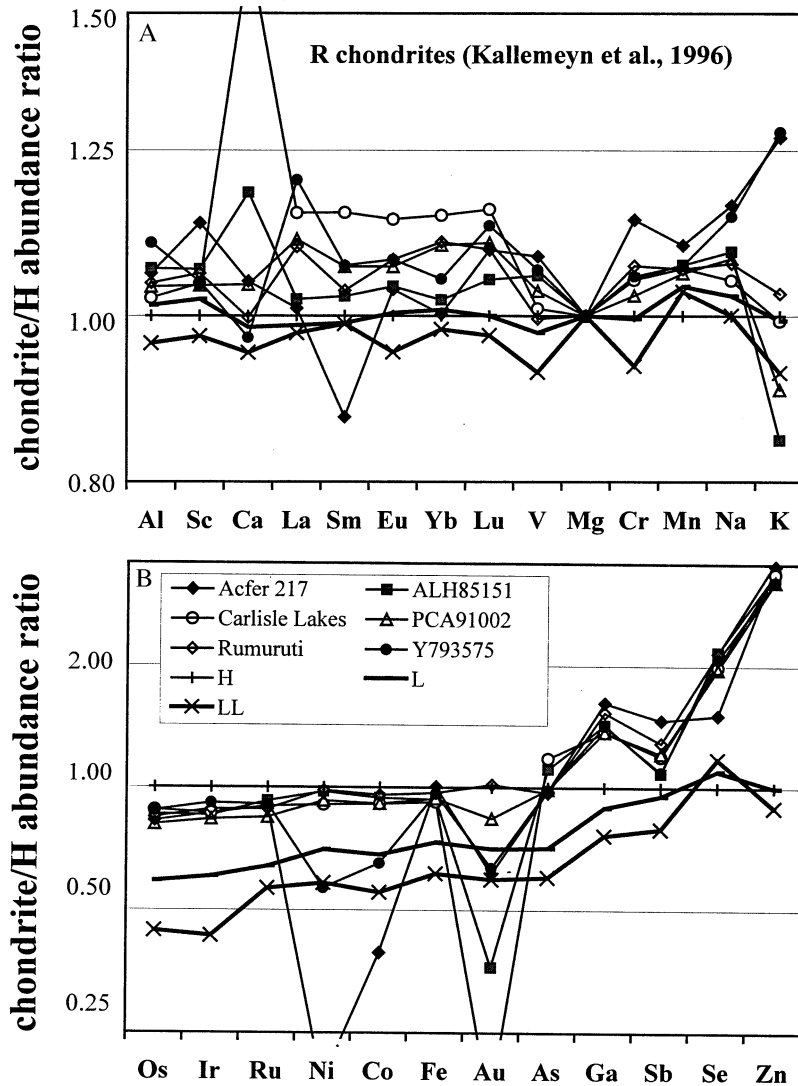


Fig. 9. Elemental abundances in R chondrites (Kallemeyn et al., 1996) normalized to Mg and mean H chondrites (Kallemeyn et al., 1989): (a) lithophile abundances, (b) siderophile and chalcophile abundances, both plotted in order of decreasing condensation temperature. Shown for reference are the abundances in L and LL chondrites. Refractory lithophile element (Al-Lu) abundances are flat and ca. 6% higher in RC than in OC. Refractory and common siderophile elements (Os-Fe) abundances are intermediate between H and L abundances. Volatile siderophile and chalcophile element (As-Zn) abundances increase with decreasing condensation temperature. Au shows variable depletions attributed to weathering.

OC or the CM-CO clans) that are inferred to have formed at similar location/times.

We therefore suggest that a fruitful approach to understanding the formation of the RC is to examine the processes that could have created RC from the same nebular components recognized in primitive OC such as Semarkona. For discussion purposes we make the common assumption that chondrites formed by agglomeration of nebular components that had settled to the midplane, and that these materials settled with roughly similar efficiencies with the exception of fine matrix, which may have incompletely settled to the midplane. In other words, we will examine whether OC materials, similar to highly unequilibrated H chondrites (but slightly lower in metal, i.e., the composition displaced towards L chondrites) but hav-

ing a substantially higher fraction of fine matrix would resemble RC.

Concentrations of the most volatile elements are higher in matrix than in silicate chondrules (Grossman, 1985) or metal-sulfide "chondrules." Alexander (1995) showed this to be true for the alkali elements Cu and Mn. Therefore, it is plausible that the more volatile the element, the higher the matrix/chondrule elemental abundance ratios. Thus, a simple model calling for RC to accrete a much larger fraction of matrix than OC can qualitatively explain the enhanced abundances of the five volatiles As-Zn on the right side of Figure 9b. If, as discussed by Wasson (1988), the low refractory lithophile abundances in OC relative to mean solar (=CI-chondrite) abundances reflect incomplete settling to the nebular midplane

of fine components enriched in these elements, then the same mechanical-fractionation process responsible for the enhanced matrix content can also explain the enhancement (ca. 5%) in refractory lithophiles in RC relative to OC.

It is useful to examine whether mass-balance arguments based on O isotopes are consistent with formation of OC and RC from the same or similar nebular components. The isotopic composition of OC matrix is not well constrained. Clayton et al. (1991) reported  $\Delta^{17}\text{O}$  values ranging from +0.35 to +1.48‰ in 16 OC matrix samples and negative values ranging from -0.44 to -0.67‰ in four other OC samples. Grossman et al. (1987) suggested that xenolithic materials (CM chondrite or similar) might be responsible for the negative values, and all samples probably contained chondrule fragments that, on average, had lower  $\Delta^{17}\text{O}$  than matrix. Therefore, it seems probable that the highest  $\Delta^{17}\text{O}$  values reported by Clayton et al. (1991) provide lower limits on the mean composition of FeO-rich fine matrix; we will conservatively assume a nebular matrix  $\Delta^{17}\text{O}$  of +2 to +3‰, but it could have been much higher, particularly if it contained abundant hydrated silicates. If RCs and H chondrules were similar in composition, the mean O isotopic composition of the chondrules would probably have been slightly lower than bulk H-chondrite values because the latter contain matrix. We will assume a mean chondrule  $\Delta^{17}\text{O}$  of ca. 0.5‰.

Given these assumptions, our prediction would be that, when agglomerated in the nebula, the mean  $\Delta^{17}\text{O}$  of RC materials having roughly equal amounts of chondrules and matrix would have had  $\Delta^{17}\text{O}$  values of +1.2 to +1.7‰, lower than the observed whole-rock values. This implies that the parent body originally contained a third component having  $\Delta^{17}\text{O} \gg 3\%$ . Based primarily on the fact that the PCA and Semarkona magnetite O-isotope arrays are nearly linear and could have formed by the same processes operating on the same components, and also the fact that Bridges et al. (1995, 1999) found that silica-rich inclusions and feldspar/glass separates in OC had elevated  $\Delta^{17}\text{O}$  contents and formed an array with a similar slope, we suggest that this high  $\Delta^{17}\text{O}$  component was the oxidant (probably  $\text{H}_2\text{O}$ ) that converted Fe to  $\text{Fe}_3\text{O}_4$ . Choi et al. (1998) interpreted their Semarkona magnetite results to indicate that the  $\Delta^{17}\text{O}$  of  $\text{H}_2\text{O}$  in the LL parent body was ca. 7‰. Although Bridges et al. (1995) suggested an igneous origin for the silica followed by later exchange with exotic gaseous oxygen, we argue that it is more probable that the silica-rich materials formed by reactions involving the same aqueous fluids responsible for the formation of the magnetite.

If RC olivine and pyroxene (which along with plagioclase are the most abundant coarse phases) compositions were initially similar to those of ordinary chondrites, then what is the carrier of the elevated  $\Delta^{17}\text{O}$  in RC? Coarse magnetite is volumetrically minor and close to the whole rock; thus, it cannot be the main high  $\Delta^{17}\text{O}$  component.

We suggest that the high  $\Delta^{17}\text{O}$  component(s) mainly reside in the matrix. Two possibilities present themselves: (1) there are volumetrically minor phase(s) that have very high  $\Delta^{17}\text{O}$  values; or (2) the carrier phases are ubiquitous, and only slightly elevated in  $\Delta^{17}\text{O}$  compared to RC whole rocks. We suspect that the truth is between these extremes, but nearer to the second. We hypothesize that fine-grained matrix olivine is the ubiquitous carrier phase.

Choi et al. (1998) interpreted the Semarkona (OC) magnetite array to imply that  $\Delta^{17}\text{O}$  in the oxidant was ca. +7‰. If this same oxidant was responsible for raising the RC whole-rock composition from +1.2 to +1.7‰ to +2.9‰, then we can use a mass balance calculation to determine the amount of oxidant O that was added. If the initial  $\Delta^{17}\text{O}$  was +1.2‰ (i.e., nebular matrix  $\Delta^{17}\text{O} = +2\%$ ), the fraction of the final O coming from the oxidant is 29%, and if the initial  $\Delta^{17}\text{O}$  was +1.7‰ (matrix = +3‰), the oxidant contribution is 23%. These fractions would be lower if  $\Delta^{17}\text{O}$  in the oxidant is  $> +7\%$ . Most of the extra O goes into oxidizing Fe to FeO or  $\text{Fe}_2\text{O}_3$ , with minor amounts used to oxidize P, Ni, and some S. Because there are no salt veins or other evidence of flow, we suggest that 23% of the O from  $\text{H}_2\text{O}$  is more plausible than 29%.

## 6. CONCLUSIONS

We measured the oxygen-isotope compositions of olivine, pyroxene, and magnetite in thin sections of the RCs PCA91241 and PCA91002 using an in situ ion-microprobe technique. Two large magnetite grains range in  $\delta^{18}\text{O}$  from -9.4 to -15.1‰, with  $\Delta^{17}\text{O}$  ranging from +2.5 to +4.3‰. Olivine from the same clast did not equilibrate with the magnetite;  $\Delta^{17}\text{O}$  values range from -1.2 to +2.9‰. We infer that magnetite formed by the reaction of metallic Fe with  $\text{H}_2\text{O}$  at temperatures near 300 K, in which case equilibrium isotopic fractionation constrains the aqueous fluid to have  $\delta^{18}\text{O}$  near 0‰.

Studies with the electron microprobe show that, in many cases, chondrule olivines in the PCA samples have rims near  $\text{Fa}_{40}$ , near the value for equilibrated RC, but core compositions are commonly lower (we found values as low as  $\text{Fa}_{1,3}$ ). We observed a range of  $\Delta^{17}\text{O}$  values in RC chondrule silicates, in agreement with fluorination studies by Weisberg et al. (1991); in olivines having  $\text{Fa}_{39-40}$   $\Delta^{17}\text{O}$  was in the range -0.4 to +2.0‰, well below the whole-rock value. This indicates that  $\Delta^{17}\text{O}$  values of mafic (chondrule) silicates were only partially reset during metamorphic processes that equilibrated Fe and Mg. Thus, the  $\Delta^{17}\text{O}$  values in RC chondrule silicates were largely established in the nebula.

The close similarity in  $\Delta^{17}\text{O}$  of magnetite and R-whole rock oxygen-isotopic measurements suggests that magnetite may have formed from the same fluid responsible for the high  $\Delta^{17}\text{O}$  of R whole-rock samples. The results of this study have parallels with a similar study in Semarkona (Choi et al., 1998). Magnetite in Semarkona also has elevated  $\Delta^{17}\text{O}$  values compared to mafic silicates, but the important differences are that R magnetite has much lower  $\delta^{18}\text{O}$  and is similar in  $\Delta^{17}\text{O}$  to R whole rock. The similarity in  $\Delta^{17}\text{O}$  between RC and OC mafic silicates suggests that these chondritic materials are derived from closely similar nebular components originating in a common oxygen-isotopic reservoir. This contrasts with the view of Bischoff (2000) who inferred a link between the RCs and carbonaceous chondrites.

The lack of highly elevated  $\Delta^{17}\text{O}$  in magnetite (as compared to R whole rocks) and the low  $\Delta^{17}\text{O}$  of mafic silicates (as compared to R whole rocks) indicates that magnetite alone cannot account for the high  $\Delta^{17}\text{O}$  in bulk PCA. We infer that the carrier of elevated  $\Delta^{17}\text{O}$  in the RC is the abundant fine-grained matrix olivine. We suggest that the original source of the high  $\Delta^{17}\text{O}$  was an aqueous fluid with  $\Delta^{17}\text{O}$  ca. +7‰,

similar to that inferred to be responsible for the formation of magnetite in LL3 Semarkona (Choi et al., 1998). No RC samples preserving the composition of this hypothesized high  $\Delta^{17}\text{O}$  fluid phase have been analyzed to date.

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## APPENDIX

### Petrographic Descriptions of Chondrules Analyzed by Ion Microprobe

Clast A in PCA91241,10 contains a POP chondrule (c17,18) with mesostasis ranging in composition (in wt.%) from 40 to 50%  $\text{SiO}_2$ , 25 to 40%  $\text{Al}_2\text{O}_3$ , 5 to 10%  $\text{Na}_2\text{O}$ , and 5 to 8% Cl. These Cl contents are much higher than those of chondrule mesostases in ordinary chondrites

such as LL3.0 Semarkona (e.g., Table C36 of Gooding, 1979); although Gooding (1979) did not analyze for Cl, his totals (which range from 99.2–100.4 wt.%) do not allow more than ca. 1 wt.% Cl as an upper limit. Cl-rich mesostases reported by Bridges et al. (1997) in Chainpur and Parnallee chondrules are most likely formed by aqueous alteration. Low-FeO augite and salite appear to be growing in the mesostasis. Although salite may have formed during aqueous alteration, the augite probably formed during initial chondrule crystallization; augite may have coarsened during subsequent metamorphism. The contact between the POP chondrule (which is at the edge of the clast) and the matrix material outside the clast shows little evidence of reaction, suggesting that most of the alteration in the clast preceded incorporation of the clast into the surrounding host.

The olivine phenocryst (c18ol) analyzed by ion probe from this POP chondrule is zoned from  $Fa_{6-21}$ ; the probe spot is in the  $Fa_{9-12}$  portion of the grain. Compositional zoning profiles are consistent with normal igneous zoning. The two pyroxene grains analyzed in this chondrule are also unequilibrated: c18px ( $Fs_7$ ) is next to olivine c18ol and near the chondrule rim, and c17px ( $Fs_5$ ) is from the center of the chondrule. Both pyroxene grains are unzoned.

Two isolated olivine grains outside the POP chondrule, but within clast A, are partly equilibrated and have somewhat diffuse boundaries with adjacent matrix material in the clast. Olivine g35ol is zoned from a core of  $Fa_{20}$  to rim compositions approaching  $Fa_{40}$ . The ion microprobe spot is from the core region. Another isolated olivine grain (g25ol) has similar Fe/Mg zoning, with a core of  $Fa_{21}$  and a rim of  $Fa_{40}$ . Because these rim compositions are similar to those in equilibrated RC olivine ( $Fa_{38-40}$ ), there appears to have been substantial Fe/Mg exchange between these isolated olivines and olivine in the matrix.

Olivine grains c20ol and c21ol are from a chondrule fragment within clast A; they are both zoned from  $Fa_{16-24}$  and have sharp boundaries with matrix material in the clast. The zoning of these grains is consistent with primary igneous effects.

Clast B in PCA91241,14 contains an unequilibrated PO chondrule (c5) in which three ion microprobe analyses were made. The olivine exhibits significant FeO-enrichment at the grain margins and along cracks (Fig. 3). Olivine grain c5ol2 is zoned from  $Fa_{33}$  in the core to  $Fa_{42}$  at the edge; this value is slightly higher in FeO than the equilibrated RC composition (Fig. 4). C5ol1 is cut by an FeO-rich vein (Fig. 3). Both pieces of this optically continuous olivine were analyzed by ion microprobe. The core of this grain ranges in composition from  $Fa_{12-17}$  (Fig. 4). The high-FeO zones (3 to 5  $\mu\text{m}$  thick) along cracks are consistent with Fe/Mg diffusive exchange at high-surface-energy sites during metamorphism.

The BOP chondrule in clast B is a complex assemblage of ferroan olivine ( $Fa_{36}$ ), low-Ca and high-Ca pyroxene, and feldspathic mesostasis. In a low-Ca pyroxene grain (c4px1) of  $Fs_{27}$  composition that is rimmed by high-Ca pyroxene, the composition of the low-Ca pyroxene analyzed by ion microprobe is approximately that expected if it were in equilibrium with the olivine.

Four isolated olivine grains outside clast B were also analyzed by ion microprobe. Olivines g7ol, g8ol and g9ol are spatially related, but are not mutually equilibrated with respect to Fe/Mg. Olivine g7ol has a thin (ca. 5  $\mu\text{m}$ ), incomplete rim of highly ferroan olivine ( $Fa_{66}$ ) that grades sharply into a forsteritic core (ca.  $Fa_5$ ) over a short distance (<10  $\mu\text{m}$ ; Figs. 4, 5). This high-Fa rim has not equilibrated with the small  $Fa_{40}$  olivine grains in the matrix; it appears to be an overgrowth. Similarly high fayalite values were reported in matrix olivine grains by Bischoff (2000). The two ion probe spots are from the homogeneous forsteritic core. Olivine g8ol is a large and seemingly equilibrated ( $Fa_{39-40}$ ) grain; its contact with matrix is difficult to discern. Olivine g6ol is zoned from  $Fa_{21}$  in the core to  $Fa_{40}$ ; the ion microprobe spot is in the core. Although one edge of this grain has an equilibrated RC composition, another edge exhibits a sharp contact between  $Fa_{21}$  in the grain and  $Fa_{40}$  in adjacent matrix.