



The oxygen isotopic composition of olivine and pyroxene from CI chondrites

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Abstract—The CI chondrites are taken to represent average solar system material based on the similarity of their elemental compositions to that of the solar photosphere. However, their oxygen isotope geochemistry is dominated by secondary minerals that formed during aqueous alteration on the CI parent body. Precursors to this alteration, namely olivine and pyroxene, are extremely rare in CI chondrites, precluding previous measurements of their oxygen isotopic composition. We report ion microprobe analyses of oxygen isotopes in single olivine and pyroxene grains separated from CI chondrites Orgueil and Ivuna.

The CI chondrite olivine and pyroxene grains most likely represent liberated chondrule phenocrysts, based on petrographic, chemical, and isotopic evidence consistent with crystallization from a melt. The oxygen isotope data form an array that falls nearly along the carbonaceous chondrite ¹⁶O mixing line with $\delta^{18}\text{O}$ values ranging from -9.3‰ to $+12.3\text{‰}$ and $\delta^{17}\text{O}$ from -11.3‰ to $+7.8\text{‰}$, consistent with nebular processes being the source of the oxygen isotopic compositions. The degree of ¹⁶O-enrichment in Orgueil olivines is negatively correlated with FeO content, but the exact nature and timing of the process that introduced this variation remains unknown. The pyroxene oxygen isotopic compositions are similar to those of olivines with >5 mol% fayalite.

The oxygen isotopic analyses of the olivine and pyroxene in CI chondrites have been used to revise previous models for the isotopic evolution of CI materials. Our data require more complete gas-solid equilibration in the nebula and constrain the initial aqueous fluids on the CI parent body to have lower $\Delta^{17}\text{O}$ values than previously postulated. The refined model indicates that the temperature of aqueous activity on the CI parent body was no higher than $\sim 50^\circ\text{C}$, and the fluid:rock ratio was significantly less than previously estimated. Even prior to alteration and formation of secondary minerals, the CI chondrites were the most ¹⁶O-depleted carbonaceous chondrites and thus the solids originally contained in the CI chondrites are the most equilibrated nebular materials represented in the carbonaceous chondrites. The data suggest the oxygen isotopic composition of average solar system to be approximately equivalent to average terrestrial oxygen as recorded in the compositions of terrestrial and lunar basalts. Copyright © 1997 Elsevier Science Ltd

1. INTRODUCTION

Studies of oxygen isotopic compositions of anhydrous, mafic phases such as olivine and pyroxene in carbonaceous chondrites (or analyses of whole chondrules predominantly comprised of these phases) have provided critical insights into the processes that formed materials in the early solar system (for a review of oxygen isotopic studies in meteorites see Clayton, 1993). Because CI chondrites are taken to represent average solar system composition based on the similarity of their elemental abundances to those of the solar photosphere (Anders and Grevesse, 1989), knowledge of the oxygen isotopic compositions of pristine CI materials is an important part of understanding oxygen isotopic reservoirs in the solar system. However, secondary minerals so pervade the CI chondrites that oxygen isotope analysis of olivine and pyroxene in these meteorites has not been accomplished previously.

The extremely low abundance of anhydrous precursors to secondary minerals in CI chondrites is reflected in their whole-rock oxygen isotopic compositions, which lie dis-

tinctly apart from the other carbonaceous chondrites (Clayton, 1993) on an oxygen three-isotopic plot (Fig. 1). While all other whole-rock carbonaceous chondrite samples have oxygen isotopic compositions that lie below the terrestrial fractionation (TF) line along or near the carbonaceous chondrite anhydrous minerals (CCAM[†]) line, the CI chondrites fall slightly above the TF line and away from the CCAM line (Clayton, 1993).

Different mineralogical components of carbonaceous chondrites are out of equilibrium with respect to oxygen isotopes (e.g., Clayton and Mayeda, 1984; Rowe et al., 1994). The best example of this is found in the CM meteorites, which contain ¹⁶O-enriched high-temperature minerals (refractory oxides, olivine, and pyroxene) that fall approximately along the CCAM line, and more ¹⁶O-depleted secondary phases formed by low-temperature processes on the parent body (Clayton and Mayeda, 1984). In the case of CI meteorites, where only the low-temperature secondary phases have been analyzed previously, phyllosilicate and

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† The CCAM line used here is defined as a best-fit to published data from the Chicago group for mineral separates from Allende CAI: $\delta^{17}\text{O} = 0.94 \times \delta^{18}\text{O} - 4.1$ where δ values are expressed in permil (‰) relative to standard mean ocean water (SMOW).

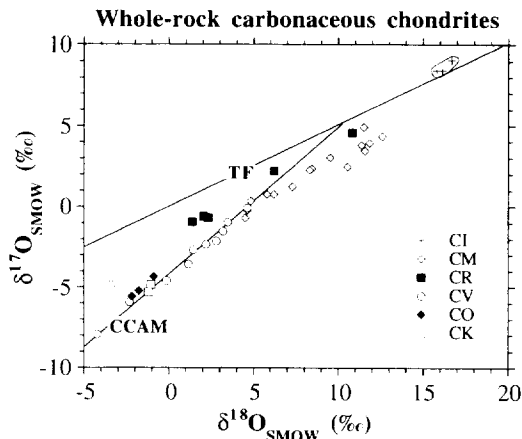


Fig. 1. The oxygen isotopic compositions of whole-rock carbonaceous chondrite samples. The data are from Fig. 5 of Clayton (1993) for all but the CK group, which are from Clayton and Mayeda (1989). The isotopic compositions of the CM, CR, CV, CO, and CK chondrite groups are all significantly different from those of the CI chondrites Orgueil, Ivuna, and Alais. This has been postulated to be the result of almost complete aqueous alteration of the anhydrous minerals in CI chondrites to secondary minerals such as phyllosilicates (Clayton, 1993). The terrestrial fractionation (TF) and carbonaceous chondrite anhydrous minerals (CCAM) lines are shown for reference.

magnetite have been shown to be out of oxygen isotopic equilibrium with each other (Rowe et al., 1994).

Analysis of the oxygen isotopic compositions of the various mineralogical components in the carbonaceous chondrites has allowed constraints to be placed on the origin of, and relationship among, the different minerals. For example, Clayton and Mayeda (1984) and Rowe et al. (1994) have shown that it is possible to produce the entire range of oxygen isotope compositions previously measured in CI and CM mineral separates starting with only two initial oxygen isotope reservoirs. In this model, an ^{16}O -depleted (relative to terrestrial values) nebular gas exchanges oxygen with initially ^{16}O -enriched solids in the solar nebula at high temperature to produce anhydrous minerals that lie along the CCAM line. These anhydrous minerals (as represented in the model by an average anhydrous mineral composition) are then altered to form secondary minerals (e.g., phyllosilicate, magnetite, carbonate) in a water-rich environment on an asteroidal parent body. The relative isotopic compositions of the model water and the secondary minerals have been used to constrain the conditions of alteration (e.g., T, fluid:rock ratio) on the CI and CM parent bodies (Clayton and Mayeda, 1984; Rowe et al., 1994). For the CI model, however, the composition of the anhydrous precursors to the parent body alteration, which reflect the extent of nebular gas-solid interaction, was assumed to be the same as for the CM calculations, because CI olivine and pyroxene data were not available.

Presented here are the first oxygen isotopic analyses of olivine and pyroxene grains from CI chondrites. The goals of this study are to compare CI mafic silicates to those from other carbonaceous chondrite groups and to use the isotopic compositions of these minerals to constrain the nature of the

physical processes that have affected CI chondrite materials, both in the nebula and on the CI parent body.

2. METHODS

Olivine and pyroxene grains were separated from ~1.5 grams of the Orgueil meteorite (Muséum National D'Histoire Naturelle, Paris; sample #235). An additional two pyroxene grains from Ivuna (the type meteorite for the CI group) were provided by J. Goswami. Aliquots of Orgueil were crushed gently in a new porcelain mortar and the debris rinsed into a glass beaker containing a 3% solution of Na-metaphosphate. The sample was ultrasonically cleaned in this solution for 1 h to remove fine-grained clay minerals that could have been adhering to larger silicate crystals. Grains larger than 60 μm and 30 μm were separated by filtration, and material with density $>2.96 \text{ g/cm}^3$ was concentrated using heavy liquids. Olivine and pyroxene candidates (i.e., clear grains) were handpicked from these separates, mounted in epoxy along with oxygen isotope standards, and polished using diamond paste. Consistent with previous work (Kerridge and Macdougall, 1976), most of the clear grains were carbonates. Mafic silicates were identified by energy-dispersive X-ray analysis.

The major-element compositions of twenty-one olivine and nine pyroxene grains (including the two Ivuna pyroxenes mentioned above), and one olivine-pyroxene aggregate were determined with the UCLA CAMECA Camebax-microbeam electron microprobe using crystal spectrometers and a sample current of 13 nA at 15 keV. At least three points were analyzed on every grain. Analysis times were 20 sec; PAP corrections were applied to the data.

Oxygen isotopic compositions of fourteen Orgueil olivines, three Orgueil pyroxenes, and two Ivuna pyroxenes were measured with the UCLA CAMECA ims 1270 ion microprobe. Grain mounts were coated with ~350 Å of Au. Negative secondary ions were sputtered by a ~1 nA Cs^+ primary beam defocused to a ~25–30 μm diameter spot. In some cases a field aperture was inserted into the secondary ion beam path to restrict the analysis area to the central 10–15 μm of the sputtered crater. A normal-incidence electron gun was utilized to flood the analysis area with low energy electrons for charge compensation (Slodzian, 1980). Secondary ions with initial kinetic energies of ~95–120 eV were measured at a mass resolving power ($M/\Delta M$) of ~6100, sufficient to completely eliminate hydride interferences (Fig. 2). Each measurement comprised fifty cycles of counting ^{16}O for 1 sec, ^{17}O for 15 s, and ^{18}O for 10 s. Secondary ions were counted with an electron multiplier (EM), and analyses were corrected for deadtime (typically 22 ns; measured during each analysis session). The EM pulse height distribution was monitored routinely and the EM gain adjusted to keep the peak of the distribution at a constant level since changes in the EM gain can cause drift in the magnitude of the instrumental mass fractionation and can also lead to inaccuracy in the deadtime correction.

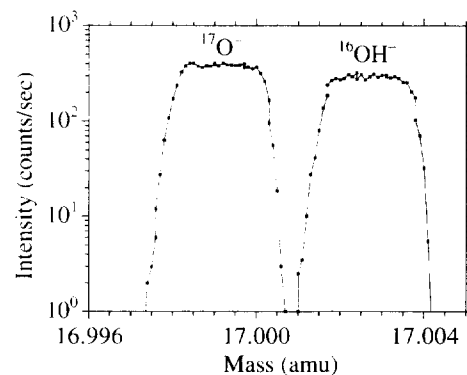


Fig. 2. High-resolution mass spectrum in the mass 17 region for an olivine grain from Orgueil. The molecular ion interference from $^{16}\text{OH}^-$ is well separated from the $^{17}\text{O}^-$ peak at a mass resolving power of ~6100.

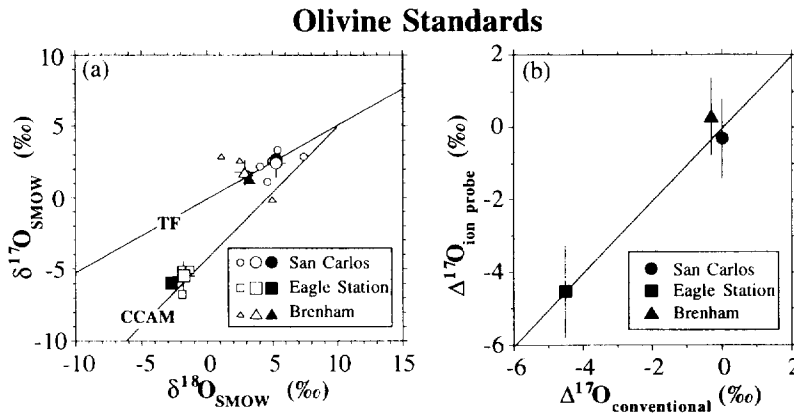


Fig. 3. Demonstration of the accuracy of oxygen isotopic analyses in silicates with the UCLA CAMECA ims 1270 ion microprobe. We analyzed olivines separated from two pallasites (Brenham and Eagle Station) whose oxygen isotopic compositions had been previously determined by conventional fluorination on mineral separates (Clayton and Mayeda, 1996) along with our San Carlos terrestrial olivine standard. (a) Individual analyses of the olivines are plotted as small open symbols (shown without error bars for clarity). The large open symbols show the weighted mean (with standard error reflecting propagation of analytical uncertainties as discussed in the text) of the individual analyses, and these should be compared to the filled symbols which represent the previously published compositions (Clayton and Mayeda, 1996; Eiler et al., 1995). The data were corrected for instrumental mass fractionation as discussed in the text. (b) The mean isotopic values, expressed as $\Delta^{17}\text{O}$ (with standard error), measured by ion probe compared to those determined by conventional gas-phase mass spectrometry. The ion probe data are consistent with conventional values at the 1σ level.

An analysis session typically consisted of one day of analyses; the data were collected during two 3–4 day-long periods three months apart. For each analysis session the olivine data were corrected for instrumental mass fractionation by using the known $\delta^{18}\text{O}$ value for San Carlos olivine (+5.25‰; Eiler et al., 1995) and pyroxene data were corrected in a similar fashion using a diopside standard (GP101 with $\delta^{18}\text{O} = +8.25\%$; Mathey and Macpherson, 1993) and assuming a linear mass fractionation law (with $^{17}\text{O}/^{16}\text{O}_{\text{SMOW}}$ from Fahey et al., 1987). The instrumental fractionation correction determined from the San Carlos olivine data ranged from -7.7% /amu to -32.4% /amu among the different sessions but was constant to within about 1% /amu during a single analysis session. The large variation in the correction factor was due to different instrumental conditions between analysis sessions and can be traced predominantly to the presence or absence of a field aperture in the secondary beam and to the performance of the EM.

An additional correction to account for changes in instrumental mass discrimination due to deviations of FeO-content of some of the CI olivine grains from that of the standard (the so-called matrix effect) was included in the data reduction procedure. This correction was calibrated by measurement of San Carlos olivine and nearly pure fayalite of known $\delta^{18}\text{O}$. The correction amounts to $\sim 0.5\%$ for each 10% change in fayalite content of the olivine ($\text{Fa} = \text{molar FeO}/(\text{MgO} + \text{FeO})$) and, for the range of olivine compositions analyzed, resulted in shifts of $< 1\%$ from the values produced by correcting only to San Carlos. No such matrix effect correction was made for the CI pyroxene grains. Uncertainties on individual analyses reflect both the internal measurement precision and an additional factor introduced by the scatter of the San Carlos olivine measurements during a given analysis session (represented in the error calculation by the standard deviation of the San Carlos measurements, typically 1.25–1.50‰ in $\delta^{18}\text{O}$ for an analysis session). Uncertainties in the deadtime and the true $\delta^{18}\text{O}$ values of the standards are not included in the error estimate, but they would have a negligible effect on the overall uncertainty.

Because this work represents the first measurements of oxygen isotopes in silicate samples with the ims 1270 ion microprobe, in order to illustrate the reliability of the technique, we present the results of analysis of two pallasite olivines previously studied for oxygen isotopes. Large, chemically homogeneous olivine grains were separated from Brenham, a main group pallasite, and Eagle Station, an anomalous pallasite (Clayton and Mayeda, 1996), and

mounted in epoxy together with San Carlos in a manner analogous to the CI olivine grains. The data, corrected for instrumental mass fractionation using the known $\delta^{18}\text{O}$ value of San Carlos olivine and accounting for the varying Fa contents of the olivines, are shown in Fig. 3. In Fig. 3a, the small open symbols represent individual ion probe analyses (1σ errors of approximately $\pm 1.5\%$ in each isotope ratio, including all propagated analytical uncertainties discussed above, are not plotted for the sake of clarity), the large open symbols represent weighted means of the individual analyses and filled symbols represent previously measured values for the olivines (by conventional fluorination in the case of the pallasite olivines, Clayton and Mayeda, 1996; and by laser fluorination in the case of San Carlos olivine, Eiler et al., 1995). Figure 3b shows a comparison of our mean measured values of $\Delta^{17}\text{O}$ ($=\delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$) to the values determined previously. These data demonstrate that our ion microprobe measurements of oxygen isotopes in olivine are accurate at the permil level.

3. RESULTS

3.1. Petrography and Mineral Chemistry

Mafic minerals separated from Orgueil include olivine ($\text{Fa}_{0.5-26}$), low-Ca pyroxene ($\text{Fs}_{6-10}\text{Wo}_{0-3}$), and high-Ca pyroxene ($\text{Fs}_5\text{Wo}_{41-44}$), and generally are similar to previously studied olivine and pyroxene grains from CI chondrites (Kerridge and Maccougall, 1976; Reid et al., 1970). The grains range in maximum dimension from 50 to 375 μm ; most are anhedral although a few appear to have retained one or two crystal faces. Several grains contain 2–5- μm -diameter spherical blebs of metallic Fe-Ni, and some contain silicate melt inclusions complete with shrinkage bubbles (e.g., Fig. 4). Representative major element analyses of olivine and pyroxene are reported in Table 1.

Most Orgueil olivine grains are normally zoned; Fa contents at grain edges are 8–40% higher than in grain centers (e.g., grain 3–2: $\text{Fa}_{8.4}$ vs. $\text{Fa}_{7.8}$; grain 4–10: $\text{Fa}_{13.6}$ vs. $\text{Fa}_{9.7}$; grain 4–75: $\text{Fa}_{21.3}$ vs. $\text{Fa}_{19.0}$). This degree of zoning is similar



Fig. 4. Transmitted light photomicrograph of Orgueil olivine grain 2–28, which has been mounted in epoxy and polished. The maximum grain diameter is $\sim 250 \mu\text{m}$. The photograph was taken before oxygen isotopic analysis and is focused below the polished surface of the grain at a level where a glass inclusion with shrinkage bubble is visible near the bottom edge of the grain (marked by an arrow). McSween (1977) used similar features in isolated grains from other carbonaceous chondrites to argue that the isolated grains formed in chondrules.

to that measured for olivine phenocrysts in porphyritic olivine chondrules in other chondrites (e.g., Jones and Scott, 1989; Scott and Taylor, 1983). One separated Orgueil grain is a polycrystalline aggregate consisting of olivine and low-Ca pyroxene (Table 1).

Figure 5 shows a plot of CaO vs. Fa content for Orgueil olivines from this study. Although the dataset is somewhat limited, our separated CI olivine grains show similar (though not as well-defined) trends to those observed by Kerridge and Macdougall (1976) and are consistent with their observation that the low-FeO ($\leq 1 \text{ mol}\%$ Fa) olivines in Orgueil vary significantly in CaO content, whereas olivines with higher Fa content show a positive correlation between CaO and Fa (see Fig. 4 of Kerridge and Macdougall, 1976). This trend is also similar to a correlation observed in olivines from chondrules in CM, CO, CV, and type-3 ordinary chondrites (McSween, 1977; Scott and Taylor, 1983). Orgueil olivines differ from olivine in CM, CO, and CV chondrules in that some of them fill the gap between the FeO-poor (type I

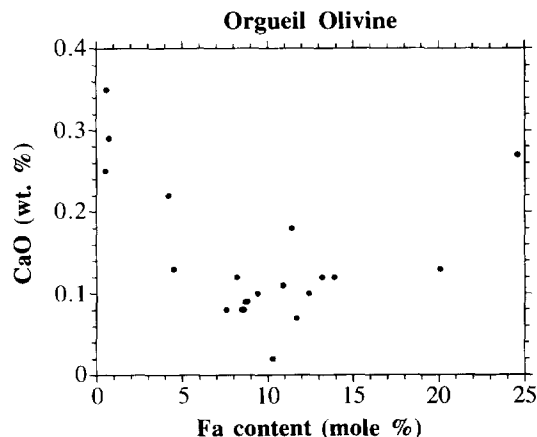


Fig. 5. Variation of CaO and Fa content in olivines from Orgueil as measured by electron microprobe. Each point represents the average of three or four analyses on each of twenty-one separated olivine grains. The data are consistent with observed trends in previously studied CI olivines (Kerridge and Macdougall, 1976) and olivine phenocrysts from porphyritic chondrules in other chondrite groups (McSween, 1977; Scott and Taylor, 1983).

chondrule) and FeO-rich (type II chondrule) fields; in this way they are more similar to olivine from chondrules in type-3 ordinary chondrites (e.g., LL3.0 Semarkona; Scott and Taylor, 1983). The CI olivines show no correlation of FeO with MnO, consistent with observations by McSween (1977) that olivines from carbonaceous chondrite chondrules with $< 12 \text{ wt}\%$ FeO show no correlation of FeO with MnO. We do not have enough grains to determine if a correlation exists in the higher FeO region where McSween (1977) did observe a correlation of FeO with MnO.

3.2. Oxygen Isotopes

Oxygen isotopic analyses of the CI olivine and pyroxene grains are summarized in Table 2 and Fig. 6. In cases where two oxygen isotope analyses were performed in the same spot, the weighted mean of the two values is plotted in Fig. 6. The $\delta^{18}\text{O}$ values of the fourteen olivines analyzed range from $-9.3 \pm 1.7\text{‰}$ to $+12.3 \pm 1.4\text{‰}$ (all errors are 1σ) and the $\delta^{17}\text{O}$ values range from $-11.3 \pm 2.2\text{‰}$ to $+7.8$

Table 1. Selected electron microprobe analyses of separated mafic silicates[†] from Orgueil

| grain no. | 4-49 | 2-45 | 3-2 | | 3-61* | | 3-20 | 1-37 |
|--------------------------------|-------------------|--------------------|-------------------|-------------------|--------------------|-------------------------------------|--------------------------------------|--------------------------------------|
| phase | olivine | olivine | olivine (core) | olivine (rim) | olivine | low-Ca pyroxene | high-Ca pyroxene | high-Ca pyroxene |
| oxide wt. % | | | | | | | | |
| SiO ₂ | 43.6 | 39.8 | 41.9 | 41.7 | 41.2 | 58.6 | 55.0 | 55.6 |
| MgO | 55.9 | 37.6 | 49.8 | 50.1 | 48.6 | 33.1 | 17.6 | 18.7 |
| Cr ₂ O ₃ | 0.42 | 0.32 | 0.49 | 0.64 | 0.08 | 0.61 | 1.7 | 1.4 |
| CaO | 0.25 | 0.29 | 0.08 | 0.15 | 0.03 | 1.1 | 21.6 | 19.6 |
| Al ₂ O ₃ | 0.12 | bd | bd | bd | bd | 0.44 | 2.2 | 1.7 |
| MnO | 0.08 | 0.40 | 0.51 | 0.52 | 0.57 | 0.51 | 0.38 | 0.35 |
| FeO | 0.50 | 23.0 | 7.5 | 8.2 | 10.0 | 6.4 | 3.1 | 3.2 |
| total | 100.97 | 101.41 | 100.28 | 101.31 | 100.48 | 100.76 | 101.58 | 100.55 |
| end member | Fa _{0.5} | Fa _{25.6} | Fa _{7.8} | Fa _{8.4} | Fa _{10.4} | Fs _{9.6} Wo _{2.1} | Fs _{4.9} Wo _{44.5} | Fs _{5.2} Wo _{40.7} |

[†]Analyses are of grain cores unless otherwise indicated

*This grain is an aggregate of olivine and low-Ca pyroxene

bd = below detection limit of 0.03 wt. %

Table 2. Oxygen isotopic compositions of olivine and pyroxene from Orgueil and Ivuna

| ORGUEIL OLIVINES | | | |
|-------------------|-------------------------|-----------------------|-----------------------|
| Grain no. | Fa content [†] | $\delta^{18}\text{O}$ | $\delta^{17}\text{O}$ |
| 1-12 | 8.5 | 3.8 ± 1.9 | 0.2 ± 2.5 |
| 1-12 | 8.5 | 4.1 ± 1.9 | 1.5 ± 2.5 |
| weighted mean | | 3.9 ± 1.4 | 0.9 ± 1.7 |
| 1-50 | 8.6 | 7.6 ± 1.8 | 3.3 ± 2.5 |
| 2-3 | 13.2 | 7.6 ± 1.9 | 4.4 ± 2.5 |
| 2-3 | 13.2 | 5.8 ± 2.0 | 3.8 ± 2.4 |
| weighted mean | | 6.8 ± 1.4 | 4.1 ± 1.7 |
| 2-7 | 12.4 | 6.4 ± 1.9 | 3.8 ± 2.1 |
| 2-7 | 12.4 | 5.7 ± 2.1 | 2.3 ± 2.1 |
| weighted mean | | 6.1 ± 1.4 | 3.1 ± 1.5 |
| 2-28 | 7.6 | 5.3 ± 1.8 | 2.5 ± 2.2 |
| 2-28 | 7.6 | 5.5 ± 1.8 | -1.6 ± 2.5 |
| weighted mean | | 5.4 ± 1.3 | 0.7 ± 1.7 |
| 2-31 | 9.4 | 1.9 ± 1.8 | 2.9 ± 2.3 |
| 2-31 | 9.4 | 4.9 ± 1.8 | 2.5 ± 2.4 |
| weighted mean | | 3.4 ± 1.3 | 2.7 ± 1.7 |
| 2-45 | 24.6 | 11.7 ± 2.0 | 6.5 ± 2.3 |
| 2-45 | 24.6 | 12.8 ± 1.9 | 7.0 ± 2.5 |
| weighted mean | | 12.3 ± 1.4 | 6.7 ± 1.7 |
| 3-2 | 8.2 | 7.0 ± 1.6 | 8.2 ± 2.4 |
| 3-2 | 8.2 | 7.1 ± 1.8 | 5.4 ± 2.1 |
| weighted mean | | 7.0 ± 1.2 | 6.7 ± 1.6 |
| 3-55 | 14.0 | 7.0 ± 1.8 | 4.2 ± 2.3 |
| 4-10 | 11.0 | 5.4 ± 1.7 | 2.4 ± 2.1 |
| 4-48 | 4.2 | -4.4 ± 1.8 | -5.9 ± 2.3 |
| 4-49 | 0.5 | -7.3 ± 1.8 | -7.0 ± 2.3 |
| 4-75 | 20.0 | 8.2 ± 1.7 | 7.8 ± 2.3 |
| 4-97 | 0.6 | -9.3 ± 1.7 | -11.3 ± 2.2 |
| ORGUEIL PYROXENES | | | |
| Grain no. | mineral* | $\delta^{18}\text{O}$ | $\delta^{17}\text{O}$ |
| 1-37 | HCpx | 9.9 ± 2.0 | 3.4 ± 2.5 |
| 2-5 | HCpx | 7.9 ± 1.9 | 4.6 ± 2.4 |
| 3-20 | HCpx | 7.5 ± 1.7 | 2.9 ± 2.3 |
| IVUNA PYROXENES | | | |
| Grain no. | mineral* | $\delta^{18}\text{O}$ | $\delta^{17}\text{O}$ |
| 1-1 | LCpx | 3.5 ± 2.0 | 2.3 ± 2.3 |
| 1-2 | HCpx | 9.4 ± 1.9 | 2.0 ± 2.6 |

δ values reported in ‰ relative to SMOW; errors are 1σ
[†]Average of 3-4 electron probe analyses on each grain.
 Fa content = mole % FeO/(FeO + MgO)
 *HCpx = high-calcium pyroxene (diopside),
 LCpx = low-Ca pyroxene

$\pm 2.3\%$. The $\delta^{18}\text{O}$ values of five pyroxene grains range from $+3.5 \pm 2.0\%$ to $+9.9 \pm 2.0\%$ and the $\delta^{17}\text{O}$ values range from $+2.0 \pm 2.6\%$ to $+4.6 \pm 2.4\%$. The data may be summarized as follows: (1) Similar to anhydrous silicate minerals from other carbonaceous chondrites, the CI olivine and pyroxene grains form an array that falls nearly along the CCAM line. (2) The CI anhydrous silicates are distinct from those in Murchison and other carbonaceous chondrites (Clayton, 1993) in that their isotopic compositions extend up to and above the TF line. (3) Taken as a group, the CI pyroxene grains have oxygen isotopic compositions indistinguishable from the majority of the olivine grains. (4) The olivine grains show a striking correlation of ^{16}O -enrichment with fayalite content (Fig. 7).

4. DISCUSSION

4.1. Chondrule Origin of CI Olivine and Pyroxene

The origin(s) of isolated olivine grains in carbonaceous chondrites has been the subject of considerable debate with

certain authors invoking formation of at least some grains by condensation processes in the nebula (e.g., Steele, 1986; Weinbruch et al., 1993) and others favoring an origin as remnants from fragmented chondrules (e.g., Jones, 1992; McSween, 1977; Richardson and McSween, 1978; Steele, 1988). In the case of CI meteorites, the only chondrite group without chondrules, the uncertainties regarding the relative importance of direct condensation from a nebular gas vs. processing through a chondrule melt are exacerbated by the rarity of mafic silicates which limits petrographic observations. Nevertheless, chemical, isotopic, and petrographic data obtained on individual isolated mafic silicate grains in this study provide constraints on the origin of these materials.

It is likely that most of the olivine and pyroxene grains analyzed in this work represent chondrule phenocrysts that have been freed from their parent chondrules by extensive aqueous alteration on the CI asteroid. This conclusion is most strongly supported by the observation of melt inclusions in several olivines (such as the grain shown in Fig. 4) which are essentially identical to those used by McSween (1977)

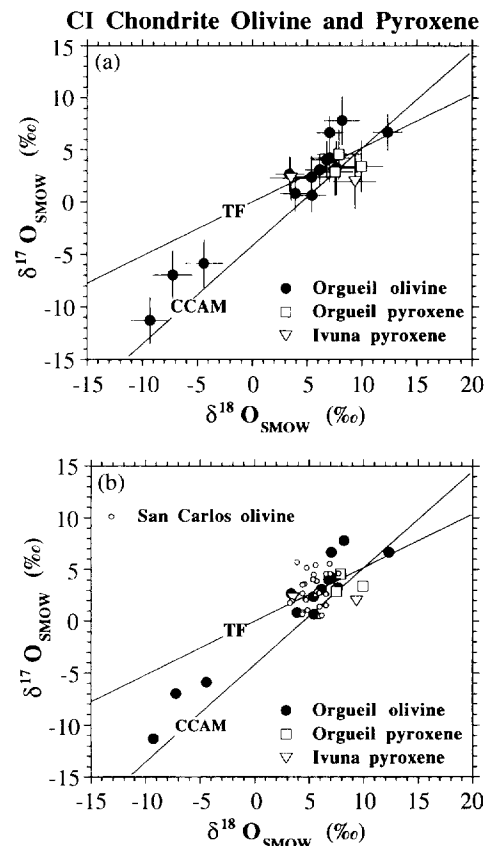


Fig. 6. (a) Three-isotope diagram showing the oxygen isotopic compositions of olivine and pyroxene from CI chondrites. Uncertainties (1σ) reflect the measurement precision and an uncertainty introduced by the instrumental mass fractionation correction (see text for discussion). In cases where two analyses were performed in a single spot (Table 2) the weighted mean with standard error is plotted. (b) The same olivine and pyroxene analyses, shown without error bars, to facilitate comparison to the San Carlos olivine standards analyzed interspersed with the CI grains. The TF and CCAM lines are shown for reference.

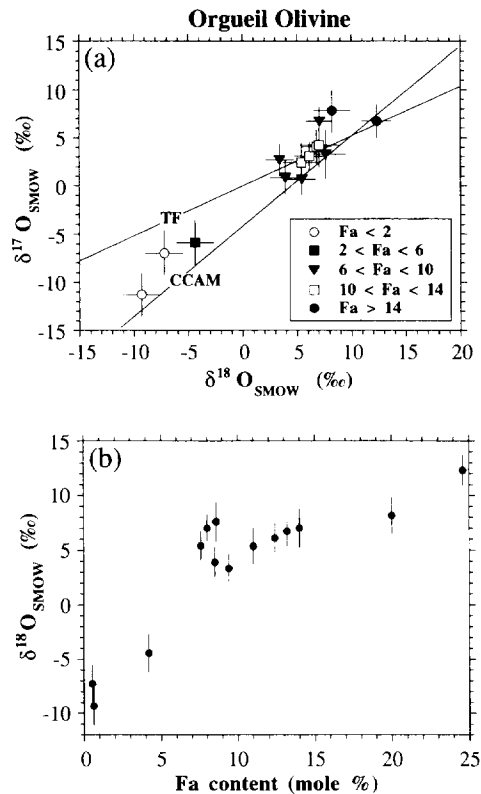


Fig. 7. The variation of oxygen isotopic compositions with FeO-content for olivine from Orgueil expressed (a) on a three-isotope diagram and (b) as $\delta^{18}\text{O}$ vs. Fa content. In (a), olivine with different FeO-contents (expressed as % fayalite) are shown with the different symbols as described in the legend. The most forsteritic olivines are the most ^{16}O -enriched while the more fayalitic olivines are the most ^{16}O -depleted.

to argue for a chondrule origin of isolated grains in other carbonaceous chondrites. In addition, several lines of evidence are consistent with the interpretation that CI olivine and pyroxene grains crystallized from igneous melts, including: (1) the occurrence of normal igneous zoning in most grains, (2) the variation of CaO with Fa (Fig. 5) which is similar to that observed in chondrule olivines from other chondrite groups (McSween, 1977; Scott and Taylor, 1983), and (3) the existence of an olivine-pyroxene aggregate with major element chemistry similar to that of co-existing olivine and pyroxene phenocrysts in chondrules from the Semarkona LL3.0 chondrite (Jones, 1994). Moreover, most condensation models predict that condensate particles would be micrometers or less in size (Blum and Munch, 1993), far smaller than the grains separated from Orgueil in the present study, which range from 18 to 370 μm in diameter. Finally, as discussed below, the oxygen isotopic data are also most consistent with a chondrule origin of the olivine and pyroxene grains. Some of the individual lines of evidence outlined above are not uniquely diagnostic of a chondrule origin for the grains. For example, condensates might also be expected to become less refractory-element enriched from core to rim, a pattern that may be indistinguishable from normal igneous zoning. However, all the evidence presented here is at least

consistent with the interpretation that the olivine and pyroxene grains are derived from chondrules, and some of the evidence (e.g., the presence of melt inclusions, the large size of the grains) is clearly inconsistent with a condensation origin.

The conclusion that the grains studied here most plausibly are derived from fragmented chondrules does not necessarily mean that all CI olivine and pyroxene grains were formed from chondrule melts, nor does it require that CI meteorites contained abundant chondrules prior to alteration. However, the simplest interpretation is that all of the large olivine and pyroxene grains in CI meteorites were formed in chondrules that were subsequently partly altered and disaggregated on the CI parent body. The occurrence of porphyritic chondrules in CM meteorites wherein the mesostasis has been completely transformed into phyllosilicates (Richardson and McSween, 1978) may be considered evidence of the early stages of this same process on the CM parent body.

4.2. Oxygen Isotopes

Rowe et al. (1994) found that CI phyllosilicates have $\Delta^{17}\text{O} = 0.0 \pm 0.3\text{‰}$. The similarity of this $\Delta^{17}\text{O}$ value to those of most of the olivine and pyroxene grains studied here suggests the possibility that some of the olivine and pyroxene grains could have acquired their isotopic composition by diffusive exchange with ^{16}O -depleted fluids during the same low-temperature event responsible for the formation of the secondary phases. However, laboratory measurements of oxygen self-diffusion rates in olivine and pyroxene (Farver, 1989; Ryerson et al., 1989) show that the degree of this exchange would be insignificant for any reasonable time-temperature history of aqueous activity on the CI parent body. For example, even at 200°C it would take a 5- μm olivine or pyroxene grain a time roughly twice the age of the solar system to equilibrate oxygen isotopes with the fluid (considering only exchange by volume diffusion). Thus, the isotopic signature of the olivine and pyroxene is not the result of low-temperature exchange but represents the initial isotopic composition of some of the anhydrous precursors to the secondary minerals in the CI chondrites.

Anhydrous, primary minerals in other carbonaceous chondrites such as those found in refractory inclusions (CAI), typically form arrays on an oxygen three-isotope plot that fall along the slope ~ 1 CCAM line (Clayton et al., 1977), and chondrules typically fall slightly above but nearly along this line (Clayton et al., 1983; Weisberg et al., 1993). The line reflects mixing between a relatively ^{16}O -enriched reservoir and an ^{16}O -depleted one (Clayton, 1993). While the origins, exact isotopic compositions, physical states, and precise nature of the interaction of the two endmembers remain unresolved, it is generally agreed that the mixing process that resulted in the distribution of oxygen isotopic anomalies preserved in carbonaceous chondrite anhydrous minerals took place in a nebular setting (Clayton, 1993). That the oxygen isotopic compositions of CI olivine and pyroxene grains distribute approximately along the CCAM line (but slightly above it, similar to chondrules) from near its intersection with the TF line to values $\sim 15\text{‰}$ more ^{16}O -enriched than terrestrial samples implies that these minerals also ac-

quired their oxygen isotopic signatures in a nebular environment.

Whereas the observation that some CI olivines and pyroxenes are ^{16}O -enriched and fall approximately along the CCAM line implies that these phases are similar to those in other carbonaceous chondrites, most of the grains studied have oxygen isotopic compositions that plot near the TF line, and thus are more ^{16}O -depleted than olivine, pyroxene, and CAI minerals in other carbonaceous chondrites. This can be seen by comparing our data to previous ion probe analyses of chondrule and isolated olivine from CV3 Allende (Choi et al., 1997; Hervig and Steele, 1992; Saxton et al., 1995; Weinbruch et al., 1993), conventional oxygen isotopic analyses of olivine and pyroxene mineral concentrates from CM2 Murchison (Clayton and Mayeda, 1984) and CR2 Renazzo (Weisberg et al., 1993), as well as separated chondrules from Allende (Clayton et al., 1983; Rubin et al., 1990) and other carbonaceous chondrites (summarized by Weisberg et al., 1993).

As shown in Fig. 7, the degree of ^{16}O -enrichment in the olivine grains is negatively correlated with their Fa content such that the most ^{16}O -depleted grains, which plot near or slightly above the TF line, are the most FeO-rich. This result is consistent with previous data which showed a similar general trend for isolated olivine grains from Allende (Hervig and Steele, 1992; Weinbruch et al., 1993) and a correlation of bulk chondrule ^{16}O -enrichments with FeO content (Clayton et al., 1983; McSween, 1985a; Rubin et al., 1990). However, although the data available for direct comparison to our suite of grains are limited, it appears that in CI meteorites both forsterite and the more FeO-rich olivines are more ^{16}O -depleted (i.e., further up the CCAM line) than olivines of comparable Fa content in Allende (Hervig and Steele, 1992; Weinbruch et al., 1993). The FeO-rich CI olivine grains are also more ^{16}O -depleted than the most FeO-rich (type II) whole CV chondrules (Clayton et al., 1983; McSween, 1985a).

Weinbruch et al. (1993) interpreted the correlation of oxygen isotopic compositions with FeO content between the cores and rims of isolated olivine grains in Allende as reflecting condensation processes in the solar nebula. The Allende grains studied by Weinbruch et al. (1993) are quite different from the grains in this study in that they exhibit dramatically FeO-enriched, narrow rims rather than normal igneous zoning. As discussed above, it appears likely that the olivine and pyroxene grains studied here formed in chondrules. The coincidence of the pyroxene oxygen isotopic compositions with the majority of the olivine data (Fig. 6) is consistent with this conclusion because little isotopic fractionation between olivine and pyroxene would occur at the high crystallization temperatures of chondrule melts. If the grains originated in chondrules, the correlation of oxygen isotopic composition with the FeO-content of the olivines is probably the result of the same processes that introduced the comparable correlation in whole chondrules in other chondrite groups (Clayton et al., 1983; McSween, 1985a; Rubin et al., 1990; Weisberg et al., 1993).

The correlation of ^{16}O -enrichment with decreasing Fa content is consistent with the hypothesis that the initial solid precursors to chondrules (from which the olivine and pyrox-

ene grains formed) were ^{16}O -enriched. The mixing between this ^{16}O -rich reservoir and a relatively ^{16}O -poor reservoir to produce the array of oxygen isotopic compositions along the CCAM line could have taken place either during the chondrule forming event itself or by evolution of the chondrule precursor materials to higher $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values approximately along the CCAM line before melting. McSween (1985a) suggested that the correlation of ^{16}O -enrichment with Fa content of Allende whole chondrules could be explained by the more FeO-rich chondrules having lower liquidus temperatures, thus facilitating greater exchange with a nebular gas during melting because FeO-rich chondrules could be melted to a higher degree and remain molten longer than FeO-poor chondrules. While some have questioned whether any chondrule would be molten long enough to allow oxygen exchange with a nebular gas (Shirley, 1983), recent experimental studies have shown that the gas-melt isotopic exchange process is rapid enough to permit substantial equilibration in a time frame of minutes even in a dilute (i.e., low H_2O concentration) gas (Yu et al., 1995). An alternative scenario invokes the mixing of two solid components to form chondrule precursors: one component is more refractory, reduced, and ^{16}O -rich and most likely represents earlier nebular condensates, and the other is more oxidized (higher FeO) and ^{16}O -depleted and probably formed later as the nebula was cooling (Rubin et al., 1990). Chondrules of varying FeO content could then represent different mixtures of these two components which were flash melted in the chondrule-forming event. It is not possible with our data to distinguish between these models. Further ion microprobe oxygen isotopic studies, particularly in situ measurements of individual grains within chondrules in unequilibrated meteorites, should allow the formulation of better constraints on the timing and physical nature of this important isotopic mixing event.

Based on the similarity in $\Delta^{17}\text{O}$ values of CI chondrites and SNC meteorites (Clayton and Mayeda, 1983, 1984; Rowe et al., 1994), Brandenburg (1996) argued that CI chondrites are derived from Mars since the SNC meteorites are generally considered to be martian samples (McSween, 1985b). However, the oxygen isotopic compositions of CI olivine and pyroxene preserve isotopic disequilibrium among grains, falling along the CCAM line similar to other carbonaceous chondrite anhydrous minerals, while all SNC igneous minerals are in oxygen isotopic equilibrium with $\Delta^{17}\text{O} = 0.3 \pm 0.1\text{‰}$ (Clayton and Mayeda, 1983). Therefore, our data are wholly inconsistent with the proposed martian origin for CI chondrites.

4.3. Implications for Oxygen Isotopic Evolution of the CI Parent Body

While the exact nature of the nebular processes that produced the array of oxygen isotopic values measured in CI olivines and pyroxenes remains unknown, the isotopic compositions of these grains can be placed within the context of previous models of CI oxygen isotopic evolution. As outlined earlier, Rowe et al. (1994) have attempted to understand the isotopic compositions of secondary phases in CI chondrites using a slight variation on an earlier model put

forth by Clayton and Mayeda (1984) to explain the variation of oxygen isotopes in CM2 Murchison. These models demonstrated that the variation of oxygen isotopic compositions of different mineralogical components in CI and CM meteorites can be produced by multiple interactions of two initial endmembers: a solid component enriched in ^{16}O (with $\delta^{18}\text{O} \approx -40\text{‰}$ and $\delta^{17}\text{O} \approx -41\text{‰}$) and a gaseous component depleted in ^{16}O relative to terrestrial materials (with $\delta^{18}\text{O} \approx +30\text{‰}$ and $\delta^{17}\text{O} \approx +24\text{‰}$). According to the model, these reservoirs partially equilibrated isotopically in a two-stage process. First, high-temperature, incomplete exchange between the ^{16}O -enriched solids (or liquids) and the ^{16}O -depleted gas produced anhydrous minerals which lie approximately along the CCAM mixing line. This high-temperature exchange was followed by interaction of the anhydrous minerals with liquid water at low temperatures, presumably on the CM and CI parent asteroids. The H_2O in the fluid presumably condensed (as either solid or liquid H_2O) from the cooling nebular gas and was incorporated into the CI parent body during its accretion. The low-temperature water-rock interaction produced secondary minerals with isotopic compositions that are related to that of the water through mass-dependent fractionation. The oxygen isotopic composition of the H_2O reservoirs, the fluid:rock ratio, and the approximate temperatures of alteration were estimated from the oxygen isotopic data (Clayton and Mayeda, 1984; Rowe et al., 1994).

The use of this model for accurately describing CI evolution was limited by the lack of knowledge of the isotopic composition of the anhydrous precursor minerals to the aqueous alteration, and this led previous workers to assume that the composition of average anhydrous silicates in CI meteorites is the same as that of Murchison (Clayton and Mayeda, 1984; Rowe et al., 1994). This assumption effectively fixes the high-temperature interactions, so that the calculated initial and final gas compositions, and hence the initial fluid isotopic composition, were also identical between the Orgueil and Murchison models. Our analyses of CI chondrite anhydrous precursors show that this assumption is not strictly valid because the CI olivines and pyroxenes are more ^{16}O -depleted than similar phases in Murchison (Clayton and Mayeda, 1984).

In Fig. 8 and Table 3 we present a revised model for CI oxygen isotopic evolution incorporating our measured compositions of anhydrous minerals. Clayton and Mayeda (1984) used the average oxygen isotopic composition of their Murchison olivine and pyroxene mineral separates as the anhydrous mineral composition, and we have taken the same approach, averaging the isotopic composition of all grains we have analyzed. This is undoubtedly somewhat of a simplification since: (1) the grains vary in size, but any accounting for size would not change significantly our calculated average of the anhydrous mineral composition, and (2) it is possible that the small percentage of residual anhydrous minerals in the CI meteorites may not accurately represent the proportions of pre-alteration mafic silicates on the CI parent body (e.g., forsterite may have been preferentially destroyed by aqueous alteration). The following model assumes that the compositional variation in the CI anhydrous precursors was similar to that observed in the residual CI

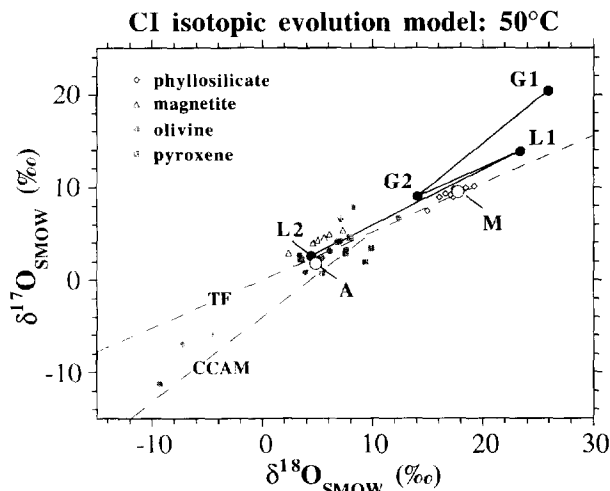


Fig. 8. Revised model for the isotopic evolution of CI chondrite materials (after Clayton and Mayeda, 1984 and Rowe et al., 1994). Data for CI phyllosilicates and magnetite are from Rowe et al. (1994) and olivine and pyroxene data are from this work. Model parameters (L1, L2, etc.) are defined in Table 3. See text for discussion.

olivine and pyroxene analyzed here. Our average CI anhydrous mineral composition ($\delta^{18}\text{O} = +4.8\text{‰}$ and $\delta^{17}\text{O} = +1.8\text{‰}$; point A in Fig. 8) differs by $+4.4\text{‰}$ in $\Delta^{17}\text{O}$ from the value adopted by Rowe et al. (1994; see Table 3 for a comparison of the results of our calculations to previous work) leading to some significant modifications of the environmental conditions inferred for CI alteration.

In the model presented in Fig. 8, the anhydrous minerals at point A are produced by nebular interaction of ^{16}O -enriched solids (or liquids) and the ^{16}O -depleted gas. Next, secondary hydrated minerals which compose the bulk of the Orgueil meteorite are produced from the reaction of fluids (assumed to be liquid H_2O , point L1) with the anhydrous precursor minerals at point A to produce phyllosilicate matrix at point M (taken to be the average of Orgueil matrix values reported by Rowe et al., 1994). According to the model, the difference in isotopic composition between the anhydrous precursors (point A) and the end-product phyllosilicate minerals (point M) is compensated by a change in the fluid isotopic composition (from initial fluid L1 to final fluid L2). The degree to which the fluid evolves in isotopic composition (i.e., the magnitude of the difference between L1 and L2) is constrained by mass balance with the solids and hence depends on the amount of nebular gas that condenses and eventually forms the fluid on the parent body. H_2O is the dominant volatile species at the low temperature of this condensation process, and the fluid:rock ratio (where the amount of fluid is defined to be that which chemically interacts with the rock) is constrained to be less than the assumed solar abundance ratio of oxygen atoms in volatiles to those bound in rock ($<79/21$). The final fluid isotopic composition, by this model, must be in equilibrium with the phyllosilicate matrix minerals and (presumably) also with carbonate, another product of parent-body aqueous alteration. Although the $\Delta^{17}\text{O}$ values of carbonates in Orgueil have not yet been

Table 3. Parameters for oxygen isotopic evolution of CI components

| component | symbol | This study: | | | | Previous studies [#] : | |
|---------------------------------------|-----------------|------------------------------|------------------------------|------------------------------|------------------------------|---------------------------------|------------------------------|
| | | $\delta^{18}\text{O}$ (‰) | $\delta^{17}\text{O}$ (‰) | $\delta^{18}\text{O}$ (‰) | $\delta^{17}\text{O}$ (‰) | $\delta^{18}\text{O}$ (‰) | $\delta^{17}\text{O}$ (‰) |
| initial solids [†] | S | -39.8 | -41.1 | -39.8 | -41.1 | -39.8 | -41.1 |
| anhydrous solids | A | +4.8 | +1.8 | +4.8 | +1.8 | -4.2 | -7.4 |
| phyllosilicate matrix [‡] | M | +17.8 | +9.5 | +17.8 | +9.5 | +17.8 | +9.5 |
| carbonate [‡] | C | +28.0 | +14.8 | +28.0 | +14.8 | +28.0 | +14.8 |
| initial nebular gas | G1 | +24.6 | +19.7 | +25.9 | +20.4 | +30.0 | +24.2 |
| final nebular gas | G2 | +12.8 | +7.8 | +14.1 | +9.0 | +20.6 | +15.2 |
| initial parent body liquid | L1 | +20.7 | +11.9 | +23.4 | +13.9 | +30.3 | +20.2 |
| final parent body liquid [*] | L2 | +9.4 | +5.2 | +4.4 | +2.6 | +14.0 | +7.5 |
| temperature (°C) | T_{eq} | 75 | | 50 | | 150 | |
| fluid:rock ratio | f | 1.15 | | 0.68 | | 3.56 | |

[#] Clayton and Mayeda (1984), Rowe et al. (1994).

[†] Initial solids taken from Murchison spinel separates (Clayton and Mayeda, 1984).

[‡] Average phyllosilicate matrix value calculated from Orgueil matrix compositions reported in Rowe et al. (1994). Average carbonate value estimated from $\delta^{18}\text{O}$ measurements of Clayton (1963) and Grady et al. (1988) and $\delta^{17}\text{O}$ values determined by assuming $\Delta^{17}\text{O}$ equal to average phyllosilicate matrix.

^{*} In this study the final liquid (L2) is assumed to be in isotopic equilibrium with carbonate at indicated T_{eq} . Fractionation factors for calcite-water are from O'Neil et al. (1969). In contrast, Rowe et al. (1994) calculated L2 by assuming equilibrium with Orgueil phyllosilicates and the same L1-L2 trajectory as determined by Clayton and Mayeda (1984) for Murchison. From this composition, and the assumption of carbonate equilibrium, Rowe et al. (1994) calculated a T_{eq} of 150 °C.

measured, under the assumption of equilibrium, a temperature may be derived for the fluid:rock interaction from the known carbonate $\delta^{18}\text{O}$ values (Clayton, 1963; Grady et al., 1988). Given the previously-mentioned assumptions, Clayton and Mayeda (1984) concluded that the aqueous alteration on the CI asteroid took place at $\sim 150^\circ\text{C}$ at nearly the theoretical maximum fluid:rock ratio (corresponding to 80 vol% water).

Taking into account the new constraints from our analysis of CI anhydrous minerals, our calculations show that the isotopic mass balance required by the model cannot be satisfied if the alteration took place at 150°C . Because the final fluid composition (L2) is dependent on the temperature of final equilibration with carbonate, we have evaluated the model at several different (lower) temperatures and find that a self-consistent solution can be obtained only for equilibration temperatures less than $\sim 75^\circ\text{C}$. Once the composition of the final fluid is calculated using the carbonate-water fractionation factors from O'Neil (1969), the initial fluid composition (L1), the fluid:rock ratio, and the final and initial nebular gas compositions (G2 and G1, respectively) are then derived following the methods of Clayton and Mayeda (1984). Table 3 summarizes the results of these calculations for two possible temperatures of carbonate-water equilibration (T_{eq}) and compares the calculated compositions to those previously determined by Clayton and Mayeda (1984) and Rowe et al. (1994).

An additional constraint is provided by the oxygen isotopic values measured for CI magnetite (open triangles, Fig. 8). Rowe et al. (1994) found that magnetites are not in equilibrium with phyllosilicates from the same rock, as reflected in their differing $\Delta^{17}\text{O}$ values (phyllosilicate: $\Delta^{17}\text{O} = 0 \pm 0.3\text{‰}$; magnetite $\Delta^{17}\text{O} = +1.6\text{‰}$ to $+1.8\text{‰}$). They postulated that the magnetite isotopic composition was frozen in by reaction with the fluid during its evolution from L1 to L2. This requires that the $\Delta^{17}\text{O}$ value of the initial fluid reservoir (L1) be higher than those measured for magnetite. At 75°C , the calculated $\Delta^{17}\text{O}$ value of L1 is only $+1.1\text{‰}$ (Table 3) meaning that this temperature (which fixes

the composition of L2) is still too high; a T_{eq} of 50°C increases the equilibrium mass fractionation between L2 and carbonate, driving L2 to isotopically lighter values, which results in a lower fluid:rock ratio and, therefore, an isotopically heavier L1 value. The 50°C L1 composition has a $\Delta^{17}\text{O}$ value of $\sim +1.7\text{‰}$ (Table 3), which is sufficient to form the magnetites from this earliest liquid. Additionally, the fairly constant $\Delta^{17}\text{O}$ values of the magnetite mineral separates follows naturally from the lower slope of the L1-L2 evolution line relative to that presented by Rowe et al. (1994). Finally, for the 50°C case, the magnitude of the mass-dependent fractionation between both magnetite-water and phyllosilicate-water are consistent with those expected based on experimental data (see Rowe et al., 1994 for a discussion).

In summary, consideration of all the secondary mineral oxygen isotopic compositions in conjunction with our new analyses of the precursor materials implies that the aqueous alteration on the CI parent body was not quite as warm and wet as estimated by Clayton and Mayeda (1984) or Rowe et al. (1994). Assuming that carbonate is in isotopic equilibrium with matrix phyllosilicates (we note that this is still to be demonstrated), we find that a reaction temperature of 50°C with a fluid:rock of ~ 0.68 can describe the environmental conditions prevailing during the secondary mineralization on the CI asteroid. These parameters are still slightly warmer (by 50°C) and wetter (by $\sim 20\%$ relative) than those calculated by Clayton and Mayeda (1984) for aqueous alteration of CM materials, which is consistent with the greater extent of alteration in the CI meteorites. The observation that the CI anhydrous minerals are more ^{16}O -depleted than assumed by Rowe et al. (1994) also implies a greater degree of equilibration of the initial solids with the nebular gas. This is reflected in the final gas composition, G2, which has a $\Delta^{17}\text{O} \sim 3\text{‰}$ lower than previously estimated. Finally, the initial composition of the nebular gas, G1, has a slightly lower $\Delta^{17}\text{O}$ value than previously calculated (Clayton and Mayeda, 1984; Rowe et al., 1994) although this composition is dependent on an assumption of the isotopic composition of the initial solids (point S; Table 3).

5. CONCLUSIONS

We have presented the first oxygen isotopic measurements of olivine and pyroxene grains from CI chondrites. The conclusions of this study can be summarized as follows:

- 1) Olivine and pyroxene grains separated from CI chondrites Orgueil and Ivuna most likely represent liberated chondrule phenocrysts, based on the presence of melt inclusions, the similarity of major element compositions to chondrule phenocrysts in unequilibrated meteorites, the large sizes of the grains, the similarities of oxygen isotopic compositions between pyroxene and FeO-bearing olivine, and the observed correlation of oxygen isotopic composition with olivine FeO content.
- 2) The oxygen isotope data form an array that falls nearly along the carbonaceous chondrite anhydrous minerals (CCAM) ^{16}O mixing line with $\delta^{18}\text{O}$ values ranging from -9.3‰ to $+12.3\text{‰}$ and $\delta^{17}\text{O}$ of -11.3‰ to $+7.8\text{‰}$, consistent with nebular processes being the source of the measured oxygen isotopic compositions.
- 3) The ^{16}O -excesses of Orgueil olivines are negatively correlated with fayalite content such that more refractory, forsteritic grains show the largest degree of ^{16}O -enrichment. Further studies are needed to ascertain whether this signature could have been introduced during the chondrule-forming event or reflects compositional evolution of chondrule precursor material.
- 4) The oxygen isotopic analyses of the anhydrous precursor materials in CI chondrites have been used to refine the models of Clayton and Mayeda (1984) and Rowe et al. (1994) for the isotopic evolution of CI materials. Our data fit within the general framework of the models put forth in these works but imply more complete gas-solid equilibration in the nebula and constrain the initial fluids on the CI parent body to have had lower $\Delta^{17}\text{O}$ values than previously postulated. Mass balance and the isotopic composition of magnetite (Rowe et al., 1994) require that the temperature of aqueous alteration on the CI parent body was no more than $\sim 50^\circ\text{C}$ and the fluid:rock ratio was less than previously estimated.
- 5) Finally, our analyses of CI chondrite anhydrous minerals have shown that even prior to alteration and formation of secondary minerals, the CI chondrites were the most ^{16}O -depleted carbonaceous chondrites. In the context of a gas-solid nebular exchange model, the solids that originally composed the CI chondrites represent the most equilibrated nebular materials incorporated into the carbonaceous chondrites and thus, as might be expected from the CI group, most accurately reflect the composition of average solar system oxygen. The data are consistent with this average composition being similar to the oxygen isotopic composition of the bulk silicate Earth as reflected in lunar and terrestrial basalts ($\delta^{18}\text{O} \sim +6\text{‰}$; Kyser, 1986 and references therein).

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