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Oxygen-isotopic compositions of low-FeO relicts in high-FeO host chondrules in Acfer 094, a type 3.0 carbonaceous chondrite closely related to CM

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Abstract—With one exception, the low-FeO relict olivine grains within high-FeO porphyritic chondrules in the type 3.0 Acfer 094 carbonaceous chondrite have $\Delta^{17}\text{O}$ ($= \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$) values that are substantially more negative than those of the high-FeO olivine host materials. These results are similar to observations made earlier on chondrules in CO3.0 chondrites and are consistent with two independent models: (1) Nebular solids evolved from low-FeO, low- $\Delta^{17}\text{O}$ compositions towards high-FeO, more positive $\Delta^{17}\text{O}$ compositions; and (2) the range of compositions resulted from the mixing of two independently formed components. The two models predict different trajectories on a $\Delta^{17}\text{O}$ vs. log Fe/Mg (olivine) diagram, but our sample set has too few values at intermediate Fe/Mg ratios to yield a definitive answer.

Published data showing that Acfer 094 has higher volatile contents than CO chondrites suggest a closer link to CM chondrites. This is consistent with the high modal matrix abundance in Acfer 094 (49 vol.%). Acfer 094 may be an unaltered CM chondrite or an exceptionally matrix-rich CO chondrite. Chondrules in Acfer 094 and in CO and CM carbonaceous chondrites appear to sample the same population. Textural differences between Acfer 094 and CM chondrites are largely attributable to the high degree of hydrothermal alteration that the CM chondrites experienced in an asteroidal setting. Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

It is widely accepted that chondrules formed by the flash melting of precursor solids (e.g., Hewins, 1996). Because most chondrules have low permeabilities to hydrous fluids and are thus resistant to alteration, they are well suited to the preservation of the compositional and isotopic record of nebular solids; this is particularly true for chondrules in type 3.0 chondrites that have experienced minimal alteration. In addition, mafic phenocrysts resist alteration better than chondrule mesostases.

Recent studies by Jones et al. (2000) and Wasson et al. (2004) showed that, on average, low-FeO chondrules in CO3.0 chondrites have more negative $\Delta^{17}\text{O}$ values than high-FeO chondrules. Expressed in terms of olivine composition, we followed our recent practice and set the boundary between low-FeO and high-FeO modes at Fa9. Wasson and Rubin (2003) reported that low-FeO relict grains are ubiquitous in high-FeO porphyritic chondrules of the CO3.0 chondrite Yamato 81020, and a study of five of these relict-host sets by Kunihiro et al. (2004) showed that $\Delta^{17}\text{O}$ values in low-FeO relict grains are uniformly more negative than those in the hosts, and generally similar to those in phenocrysts of low-FeO chondrules. In contrast, a high-FeO relict studied by Kunihiro et al. (2004) has a $\Delta^{17}\text{O}$ value marginally higher than that in the host.

The Acfer 094 chondrite is among the most primitive carbonaceous chondrites. It shows no evidence of thermal alteration and minimal evidence of aqueous alteration (Greshake, 1997); it has the highest known content of presolar SiC grains

and the second highest content of presolar diamonds after the CI chondrite Orgueil (Newton et al., 1995). The texture of Acfer 094 is very similar to those in CO3.0 chondrites such as Yamato 81020 (Y81020) and Allan Hills A77307 (ALHA77307), but Spettel et al. (1992) reported high contents in Acfer 094 of the volatile metals Zn and Se, suggesting a classification as a CM chondrite. Because Acfer 094 is uniquely important, because it and Y81020 may belong to different groups of carbonaceous chondrites, and because the statistics of O-isotopic compositions in relict-host pairs is still limited, we have used the UCLA Cameca 1270 ion probe to study five high-FeO chondrules and their enclosed low-FeO relicts in Acfer 094.

2. EXPERIMENTAL PROCEDURES

2.1. Petrographic Techniques

To choose suitable target chondrules for O-isotope analysis we prepared a back-scattered electron (BSE) map of thin section M9324 of Acfer 094 from the Naturhistorisches Museum in Vienna. We superposed a millimeter grid on this map and labeled the horizontal coordinates with letters and the vertical coordinates with numbers. Each millimeter square was subdivided into 25 0.2-mm squares that were labeled with letters. The top row is labeled a, b, c, d, and e; the last square on the bottom right is y. The chondrules were assigned names based on this grid system.

Back-scattered electron images were made with the UCLA LEO-1430VP scanning electron microscope. Preliminary studies of the thin sections were made on a mosaic BSE map with 2- μm resolution. We then examined all $\geq 100\text{-}\mu\text{m}$ -size high-FeO chondrules, looking for objects with large relict grains. We chose five high-FeO chondrules containing relict grains coarse enough ($\geq 20\text{ }\mu\text{m}$ across) to be analyzed optimally with the ion microprobe. In these chondrules we analyzed the olivine by determining the concentration of 10 elements using the UCLA JEOL JXA-8200 electron microprobe with a wavelength-dispersive system. We used natural and synthetic standards, an accelerat-

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ing voltage of 15 keV, a 15-nA sample current, a focused beam, 20-s counting times per element, and ZAF corrections.

Modal abundances of chondrules and matrix in Acfer 094 and two other primitive carbonaceous chondrites were determined by point counting on the BSE mosaic images of thin sections at high magnification on the computer monitor. We counted points at millimeter intervals along the grid lines: CO3.0 Y81020,51-1, 1504 points; M9324 of Acfer 094, 1880 points; CM2 QUE97990,13, 1194 points.

2.2. Ion Microprobe Techniques

Oxygen-isotope measurements were performed by secondary-ion mass spectrometry with the UCLA Cameca IMS-1270 instrument. Analytical details are essentially identical to those described by McKeegan et al. (1998). Briefly, a primary beam consisting of 20 keV Cs⁺ ions was defocused to produce an ion intensity of 0.3 nA on a uniformly illuminated 20- μm -diameter spot. Negative secondary ions corresponding to ¹⁶O⁻, ¹⁷O⁻, and ¹⁸O⁻ were analyzed in a peak-jumping mode at a mass resolution of ~ 7000 (sufficient to quantitatively eliminate all molecular isobaric interferences). A normal-incidence electron gun was used to flood the analysis area with low-energy electrons for charge compensation. One run typically consisted of 20 blocks of three cycles each (3-, 10-, and 5-s integration times on the O-isotope peaks). The ion intensities were determined by pulse counting with an electron multiplier for ¹⁷O⁻ and ¹⁸O⁻; ¹⁶O⁻ ions were collected on a Faraday cup. The ¹⁸O⁻ secondary ion intensity was between 8×10^4 and 1.5×10^5 counts per second. Appropriate corrections were made for detector deadtime.

Olivine data were corrected for instrumental mass fractionation by analyzing San Carlos olivine and assuming (1) a linear mass-fractionation law ($\Delta\delta^{17}\text{O} = 0.52\Delta\delta^{18}\text{O}$) and (2) that its $\delta^{18}\text{O}$ value is +5.25‰ relative to SMOW (Eiler et al., 1995). We did not correct isotopic ratios for the matrix effect, because this bias is still not well defined. Had we used the factor (-0.5‰ for each +10% change in fayalitic content of the olivine) reported by Leshin et al., (1997), it would have increased the differences in $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values within our data set by as much as 1.5‰. The reported uncertainties include both the internal measurement precision on individual analyses and an additional factor representing point-to-point reproducibility estimated from the standard deviation of the mean (in both $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$) for measurements on the San Carlos standard.

3. RESULTS

3.1. Petrographic Studies

The chondrules shown in Figure 1 are all type II porphyritic-olivine chondrules dominated by bright angular high-FeO phenocrysts. Two or more olivine grains in each chondrule show dark centers that consist of low-FeO olivine. As discussed by various authors (e.g., Jones, 1992; Wasson and Rubin, 2003), these low-FeO olivine cores appear to be grain fragments derived from earlier generations of chondrules. The surrounding “host” overgrowths of high-FeO olivine grew from melts having much higher FeO/(FeO + MgO) ratios relative to those parental to the low-FeO relicts.

In Table 1 we list olivine compositions of hosts and relicts in the five chondrules. The values in the relicts range from 0.4 to 2.2 mol% Fa; host compositions are typically in the range of 25–40 mol% Fa. We will discuss the chondrules in alphanumeric order, with the exception of H5b, which is discussed last.

Chondrule A4q (Fig. 1a) is a 220 \times 440- μm -size chondrule fragment. It contains one coarse (150 \times 170 μm) olivine grain that includes a large (80 \times 100 μm) low-FeO (Fa0.4) relict and a 17–40- μm -thick high-FeO (Fa27–29) overgrowth. The narrowest overgrowth region on the large grain is $\sim 17 \mu\text{m}$, located just to the right of the 12 o'clock position, but there is no adjacent mesostasis preserved. Chondrule fragment A4q

also contains numerous smaller high-FeO olivine grains (5–40 μm in size), two of which contain low-FeO relicts (not shown). Some patches of feldspathic mesostasis occur between adjacent olivine phenocrysts.

Chondrule D4j (Fig. 1b) is a large (1070 \times 1150 μm), seemingly intact, chondrule containing many angular olivine phenocrysts that may have formed in previous chondrule generations. High-FeO (Fa31–37) olivine phenocrysts range in size from 180 \times 250 μm down to $\sim 5 \mu\text{m}$. Dark relict cores (F \bar{a} 0.5) are clearly present in eight of the phenocrysts; a few others also appear to preserve cores from earlier generations of chondrules, but some of these tend to be more ferroan (e.g., Fa14). Inspection of more detailed images shows the narrowest overgrowth regions (in a cluster of relict bearing grains near the 9 o'clock position) to be ~ 4 – $5 \mu\text{m}$. The chondrule also contains a feldspathic mesostasis that includes Ca-pyroxene crystallites.

Chondrule J8u (Fig. 1c) is a seemingly intact, 400 \times 470- μm -size, irregular-ellipsoidal chondrule with a bright rim that consists mainly of terrestrial weathering products. High-FeO olivine (Fa24–30) phenocrysts range in size from 130 μm down to $\sim 3 \mu\text{m}$. The three largest phenocrysts have prominent low-FeO relict cores (Fa0.6–1.5); relicts are also clearly recognizable in six other phenocrysts. The thinnest overgrowth layers are $\sim 2 \mu\text{m}$ thick. The chondrule has a feldspathic mesostasis containing Ca-pyroxene crystallites.

Chondrule M7f (Fig. 1d) is a 180 \times 200- μm -size chondrule fragment consisting of high-FeO olivine phenocrysts (Fa32–38) that range in size from 80 \times 170 μm down to $\sim 3 \mu\text{m}$. The largest phenocryst consists almost entirely of a low-FeO relict (Fa0.7); three other phenocrysts also host low-FeO relicts (Fa1.6). The thinnest overgrowth on the large olivine that is adjacent to mesostasis is $\sim 4 \mu\text{m}$ across. The chondrule contains abundant (~ 20 vol%) feldspathic mesostasis free of Ca-pyroxene crystallites.

Chondrule H5b (Fig. 1e) is a large (310 \times 420 μm) irregular chondrule fragment containing several low-FeO relicts (Fa2–3). FeO-rich olivine phenocrysts (Fa36–40) range in size from 110 \times 120 μm down to $\sim 5 \mu\text{m}$. The ion probe point on a lobate low-FeO relict core (Fa2.2) occurs near the center of the chondrule and is surrounded by a ~ 3 - μm -thick high-FeO overgrowth. The largest grain on the bottom left of the image has a dark center (Fa17.8) and a high-FeO rim; we suspect that the core is relict but normal igneous zoning of the phenocryst cannot be excluded. Patches of feldspathic mesostasis occur between adjacent olivine phenocrysts.

3.2. Oxygen-Isotope Analyses

We analyzed three points in each of the five chondrules. The results are listed in Table 2 and shown graphically in Figure 2. The analyzed spots are indicated by ellipses on Figure 1. For convenience, olivine Fa contents from Table 1 are repeated in Table 2.

Two reference lines are shown on Figure 2: the terrestrial-fractionation (TF) line and the carbonaceous–chondrite–anhydrous minerals (CCAM) line (Clayton et al., 1977). The slope of the former is 0.52, the latter 0.94. $\Delta^{17}\text{O}$ values of the host phenocrysts are relatively uniform and range from -4.3 ‰ to -1.3 ‰ (in J8u).

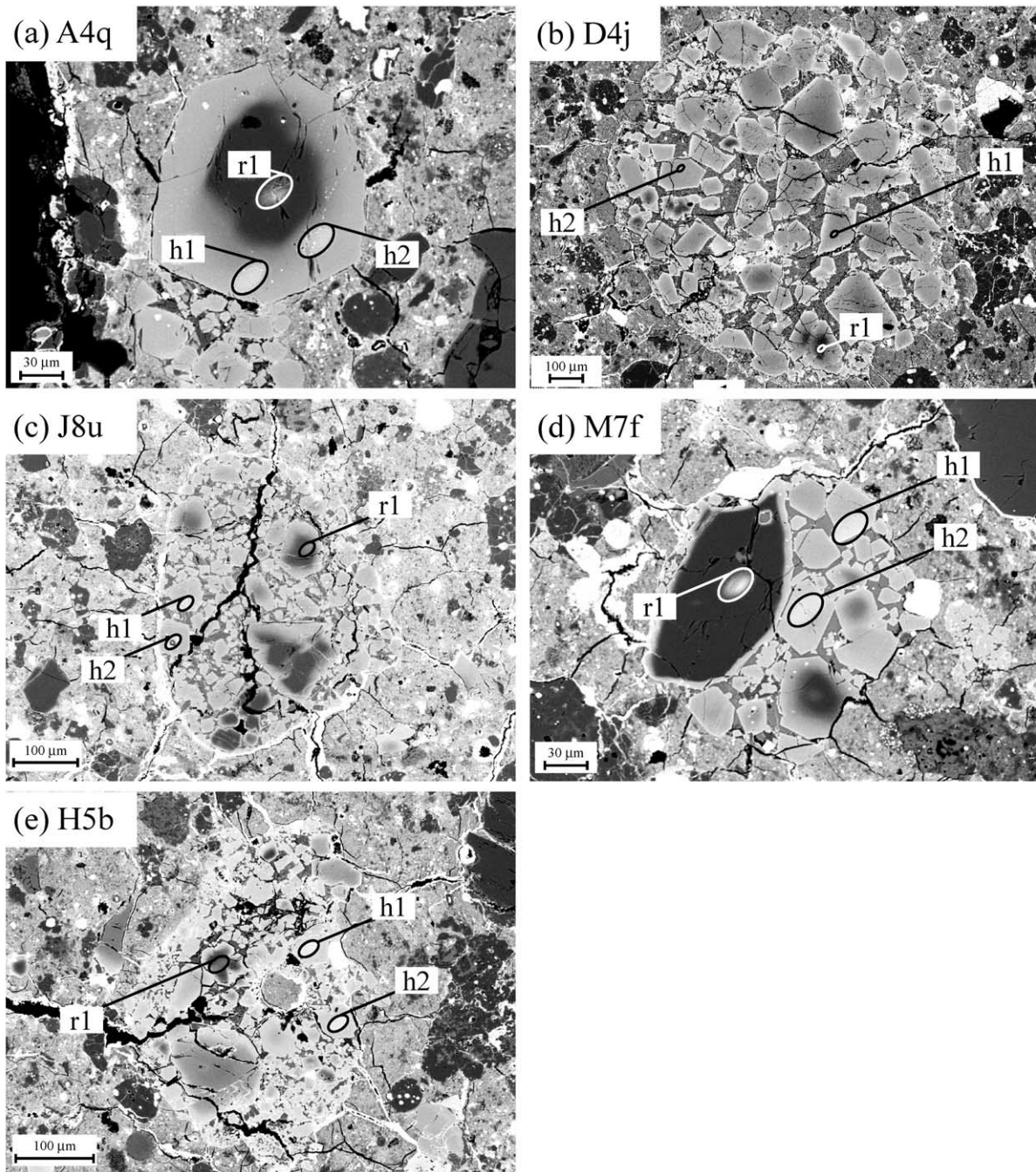


Fig. 1. In these BSE images of the investigated high-FeO (type II) porphyritic olivine chondrules in Acfer 094, the low-FeO relicts are much darker than the surrounding host chondrule. Bright lines reflect pervasive weathering along cracks (Acfer 094 is weathering grade W3). Labeled ellipses show the locations of ion-probe spots. As discussed in the text, sample names are assigned based on a rectangular grid superposed on the BSE image of the thin section.

With one exception, the $\Delta^{17}\text{O}$ values of the relict grains also show a modest range (from -7.7‰ up to -5.2‰). The exception is the analyzed relict in chondrule H5b. It has a positive $\Delta^{17}\text{O}$ value (but is within 1σ of the TF line) and an unusually high $\delta^{17}\text{O}$ value of $+1.2\text{‰}$ which is 1.3‰ higher than the next highest value (on D4j host 1).

All points plot on or above the CCAM line in Figure 2. The same effect has been observed in the study of Y81020

by Kunihiro et al. (2004) and Pack et al. (2004); 11 points are above the CCAM line, seven touch the line, and two are below the line. Although this could reflect a faulty standardization, we think that the data are probably correct. Had we employed the Leshin et al. (1997) correction for the matrix effect, the phenocryst points with the highest Fa values would move to the right along a mass fractionation line about the distance indicated by our error bars; only a single

Table 1. Mean olivine compositions (wt%) in grains studied by ion microprobe (columns on left) and in other grains (left columns) in the same chondrules.

| | imp* relicts | overgrowth on r1 | imp phenocrysts | | other rel.* | other ph.* |
|--------------------------------|-----------------|------------------|-----------------|-------|-------------|------------|
| A4q | r1 | h1 | h2 | | | |
| no. of points | 1 | 3 | 3 | | 1 | 1 |
| SiO ₂ | 42.4 | 37.7 | 37.5 | | 40.3 | 36.7 |
| TiO ₂ | 0.06 | <0.04 | <0.04 | | <0.04 | <0.04 |
| Cr ₂ O ₃ | 0.07 | 0.32 | 0.20 | | 0.22 | 0.22 |
| FeO | 0.39 | 24.4 | 25.8 | | 9.5 | 30.9 |
| MnO | <0.04 | 0.23 | 0.26 | | 0.10 | 0.34 |
| MgO | 56.2 | 36.9 | 36.0 | | 49.1 | 32.0 |
| CaO | 0.58 | 0.32 | 0.35 | | 0.24 | 0.52 |
| Fa (mol%) | 0.38 | 27.1 | 28.7 | | 9.8 | 35.1 |
| D4j | r1 | | h1 | h2 | | |
| no. of points | 1 | | 3 | 4 | 1 | 4 |
| SiO ₂ | 42.3 | | 37.4 | 36.9 | 41.8 | 36.7 |
| TiO ₂ | 0.08 | | <0.04 | <0.04 | 0.14 | <0.04 |
| Cr ₂ O ₃ | 0.07 | | 0.34 | 0.35 | <0.04 | 0.36 |
| FeO | 0.55 | | 28.0 | 30.2 | 3.2 | 31.3 |
| MnO | <0.04 | | 0.26 | 0.29 | <0.04 | 0.33 |
| MgO | 56.2 | | 34.7 | 32.5 | 54.5 | 31.3 |
| CaO | 0.67 | | 0.13 | 0.16 | 0.50 | 0.19 |
| Fa (mol%) | 0.54 | | 31.2 | 34.2 | 3.2 | 36.7 |
| J8u | r1 | | h1 | h2 | | |
| no. of points | 2 | | 4 | 4 | 2 | 2 |
| SiO ₂ | 41.6 | 38.0 | 38.3 | 38.1 | 42.1 | 37.9 |
| TiO ₂ | 0.06 | <0.04 | <0.04 | <0.04 | 0.05 | <0.04 |
| Cr ₂ O ₃ | 0.34 | 0.35 | 0.44 | 0.44 | 0.23 | 0.31 |
| FeO | 1.5 | 24.2 | 23.6 | 22.4 | 0.58 | 26.6 |
| MnO | 0.11 | 0.30 | 0.25 | 0.26 | 0.05 | 0.29 |
| MgO | 55.1 | 37.5 | 38.0 | 38.9 | 56.1 | 35.4 |
| CaO | 0.31 | 0.30 | 0.27 | 0.27 | 0.50 | 0.40 |
| Fa (mol%) | 1.5 | 26.6 | 25.8 | 24.4 | 0.57 | 29.6 |
| M7f | r1 | | h1 | h2 | | |
| no. of points | 3 | | 3 | 3 | 2 | 2 |
| SiO ₂ | 42.4 | 37.1 | 37.2 | 36.9 | 41.8 | 36.2 |
| TiO ₂ | 0.11 | <0.04 | <0.04 | <0.04 | 0.05 | <0.04 |
| Cr ₂ O ₃ | 0.26 | 0.29 | 0.27 | 0.24 | 0.36 | 0.40 |
| FeO | 0.73 | 29.7 | 28.9 | 30.6 | 1.6 | 33.1 |
| MnO | 0.05 | 0.33 | 0.27 | 0.31 | 0.06 | 0.33 |
| MgO | 56.2 | 33.0 | 33.6 | 32.1 | 55.8 | 29.8 |
| CaO | 0.35 | 0.55 | 0.40 | 0.47 | 0.29 | 0.54 |
| Fa (mol%) | 0.72 | 33.6 | 32.5 | 34.9 | 1.6 | 38.4 |
| H5b | r1 | | h1 | h2 | | |
| no. of points | 1 | | 5 | 4 | 2 | 2 |
| SiO ₂ | 41.6 | 35.8 | 36.4 | 36.7 | 42.0 | 36.1 |
| TiO ₂ | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 |
| Cr ₂ O ₃ | 0.43 | 0.18 | 0.18 | 0.22 | 0.28 | 0.13 |
| FeO | 2.2 | 34.2 | 33.5 | 31.8 | 3.4 | 34.0 |
| MnO | <0.04 | 0.32 | 0.30 | 0.29 | 0.08 | 0.29 |
| MgO | 55.2 | 28.8 | 30.0 | 31.4 | 55.1 | 29.1 |
| CaO | 0.27 | 0.59 | 0.48 | 0.47 | 0.21 | 0.50 |
| Fa (mol%) | 2.2 | 40.0 | 38.5 | 36.3 | 3.3 | 39.6 |

* Abbreviations: imp, ion microprobe; rel., relict; ph., phenocryst.

phenocryst (in J8u) would cross the CCAM line. Clayton et al. (1983) noted that chondrules plot above the CCAM line, and Young and Russell (1998), Ash and Young (2000), and Young et al. (2000) noted that many of the high- $\delta^{18}\text{O}$ samples included in the CCAM regression had suffered aqueous alteration that moved them along a fractionation line toward higher $\delta^{18}\text{O}$ values. Because the samples preserving low $\Delta^{17}\text{O}$ values ($< -20\text{‰}$) had not been affected by aqueous alteration, the alteration of the samples with high $\Delta^{17}\text{O}$ values lowered the slope of the CCAM line.

4. THE CLASSIFICATION OF ACFER 094

There is no doubt that the proper petrographic type for Acfer 094 is 3.0. This class is reserved for meteorites that show negligible evidence of aqueous alteration (which would, if present, result in a classification of <3) and negligible evidence of thermal alteration (which would, if present, require a classification >3.0). There is some serpentine and ferrihydrite in the matrix of Acfer 094 (Greshake, 1997) but otherwise only minimal evidence of aqueous alteration. The evidence for minimal thermal alteration is also strong: There is abundant glass in

Table 2. Oxygen isotopic analyses of chondrules from Acfer 094. Data are relative to the SMOW standard; errors are 1 σ based on the standard

| Chondrule | $\delta^{17}\text{O} \text{‰} \pm 1\sigma \text{‰}$ | $\delta^{18}\text{O} \text{‰} \pm 1\sigma \text{‰}$ | $\Delta^{17}\text{O} \text{‰} \pm 1\sigma \text{‰}$ | Fa % |
|------------|---|---|---|------|
| A4q | | | | |
| relict 1 | -14.2 ± 1.2 | -13.1 ± 1.1 | -7.3 ± 1.3 | 0.38 |
| host 1 | -3.5 ± 1.5 | -2.2 ± 1.0 | -2.3 ± 1.5 | 27 |
| host 2 | -5.4 ± 1.3 | -6.5 ± 1.1 | -2.0 ± 1.2 | 29 |
| D4j | | | | |
| relict 1 | -15.9 ± 1.6 | -15.7 ± 1.2 | -7.7 ± 1.5 | 0.54 |
| host 1 | -0.1 ± 1.5 | 2.4 ± 1.2 | -1.4 ± 1.4 | 31 |
| host 2 | -2.2 ± 1.4 | 0.0 ± 1.0 | -2.2 ± 1.5 | 34 |
| J8u | | | | |
| relict 1 | -10.3 ± 1.2 | -8.1 ± 1.1 | -6.1 ± 1.3 | 0.90 |
| host 1 | -2.8 ± 1.5 | 1.6 ± 1.0 | -3.6 ± 1.4 | 26 |
| host 2 | -7.2 ± 1.2 | -5.6 ± 1.0 | -4.3 ± 1.2 | 24 |
| M7f | | | | |
| relict 1 | -8.9 ± 1.4 | -7.2 ± 0.9 | -5.2 ± 1.5 | 0.75 |
| host 1 | -2.1 ± 1.6 | 1.5 ± 1.1 | -2.9 ± 1.5 | 32 |
| host 2 | -1.7 ± 1.5 | -0.7 ± 1.2 | -1.3 ± 1.4 | 35 |
| H5b | | | | |
| relict 1 | 1.2 ± 1.2 | 0.6 ± 0.9 | 0.9 ± 1.3 | 2.2 |
| host 1 | -2.5 ± 1.4 | 0.5 ± 1.2 | -2.7 ± 1.4 | 38 |
| host 2 | -1.4 ± 1.7 | 1.7 ± 1.2 | -2.3 ± 1.8 | 36 |

the chondrules, and the bulk meteorite contains the highest known content of presolar SiC grains and the second highest content of presolar diamonds (Newton et al., 1995). As noted by Huss and Lewis (1995), the latter are inversely correlated with evidence of thermal metamorphism. Acfer 094 is the first chondrite shown to contain micrometer-size presolar silicates (Nagashima et al., 2004).

The chondrules in Acfer 094 closely resemble those in CO3.0 Y81020 and in a CM2 chondrite that has experienced only minor aqueous alteration (QUE97990). Acfer 094 chondrules range in apparent diameter from 50 to 1140 μm with a mean of $230 \pm 150 \mu\text{m}$ ($n = 100$); those in Y81020 range from 40 to 910 μm with a mean of $210 \pm 110 \mu\text{m}$ ($n = 100$); and those in QUE97990 range from 45 to 890 μm with a mean of $190 \pm 140 \mu\text{m}$ ($n = 100$). Among 144 randomly selected porphyritic chondrules in Acfer 094, $\sim 80\%$ are low-FeO (type I) and $\sim 20\%$ are high-FeO (type II). Among randomly selected porphyritic chondrules in both Y81020 ($n = 149$) and QUE97990 ($n = 137$), $\sim 75\%$ are low-FeO and $\sim 25\%$ are high-FeO. Among the type I porphyritic chondrules in Acfer 094 and Y81020, respectively, $\sim 75\%$ and $\sim 70\%$ are non-spherical objects with aspect ratios ≥ 1.20 (this study; Rubin and Wasson, 2005). The similarities in all of these values suggest that, although pervasive alteration has veiled some CM chondrule features, the chondrules in Acfer 094 and in CO and CM chondrites are samples from the same population, produced in a limited region of time/space in the solar nebula.

The key remaining question is whether Acfer 094 is best designated a CM or CO chondrite, or as an ungrouped carbonaceous chondrite. Until now, aqueous alteration has been part of the definition of CM chondrites, but there seems to be little doubt that this alteration occurred in an asteroidal setting (e.g., McSween, 1979), and it is likely that the nebular precursor solids of CM chondrites showed no more alteration than did those of Acfer 094 (or Y81020).

The high diamond and SiC contents of Acfer 094 favor a CM classification, as do the high contents of the volatile metals Zn

and Se reported by Spettel et al. (1992). Newton et al. (1995) reported that Acfer 094 has a N content similar to those in CM chondrites, 5–10 \times higher than those in CO chondrites. The bulk $\delta^{15}\text{N}$ value is about +50‰, similar to the highest values observed in CM chondrites such as Murchison (Kerridge, 1985) and higher than those in CO chondrites of type 3.2 and higher. The high matrix modal abundance of Acfer 094 (49 vol%) and the high matrix/(chondrule+coarse silicate) ratio (1.2) are appreciably higher than those in the Y81020 CO3.0 chondrite (26 vol% and 0.50, respectively; this study). The Acfer 094 data more closely resemble those of CM2 QUE97990 (50 vol.% and 1.8, respectively; this study). The CM results are not exactly comparable because the “matrix” category for CM chondrites includes fine-grained alteration products. The alteration process in CM chondrites has also diminished the modal abundance of chondrules.

The chief doubt about designating Acfer 094 an unaltered CM chondrite seems to be the low bulk C content, ~ 1.5 – $2\times$ lower than the lowest measured in a CM chondrite (Newton et al., 1995). However, the strength of this conclusion is limited by the small (<1 mg) sample masses analyzed by Newton et al. (1995) and the large (factor of 3) range reported in CM-chondrite C contents (e.g., Kerridge, 1985).

We conclude that the most reasonable classification of Acfer 094 is “anomalous CM” or the more radical “anomalous CM-CO” (a designation that conveys more information).

5. DISCUSSION

5.1. Petrographic Evidence Regarding the Formation of High-FeO Chondrules Containing Low-FeO Relict Grains

Wasson and Rubin (2003) reported that >90% of the high-FeO porphyritic-olivine chondrules in CO3.0 Y81020 and ALHA77307 contain low-FeO olivine relicts. The high-FeO overgrowths on these relicts that are adjacent to patches of

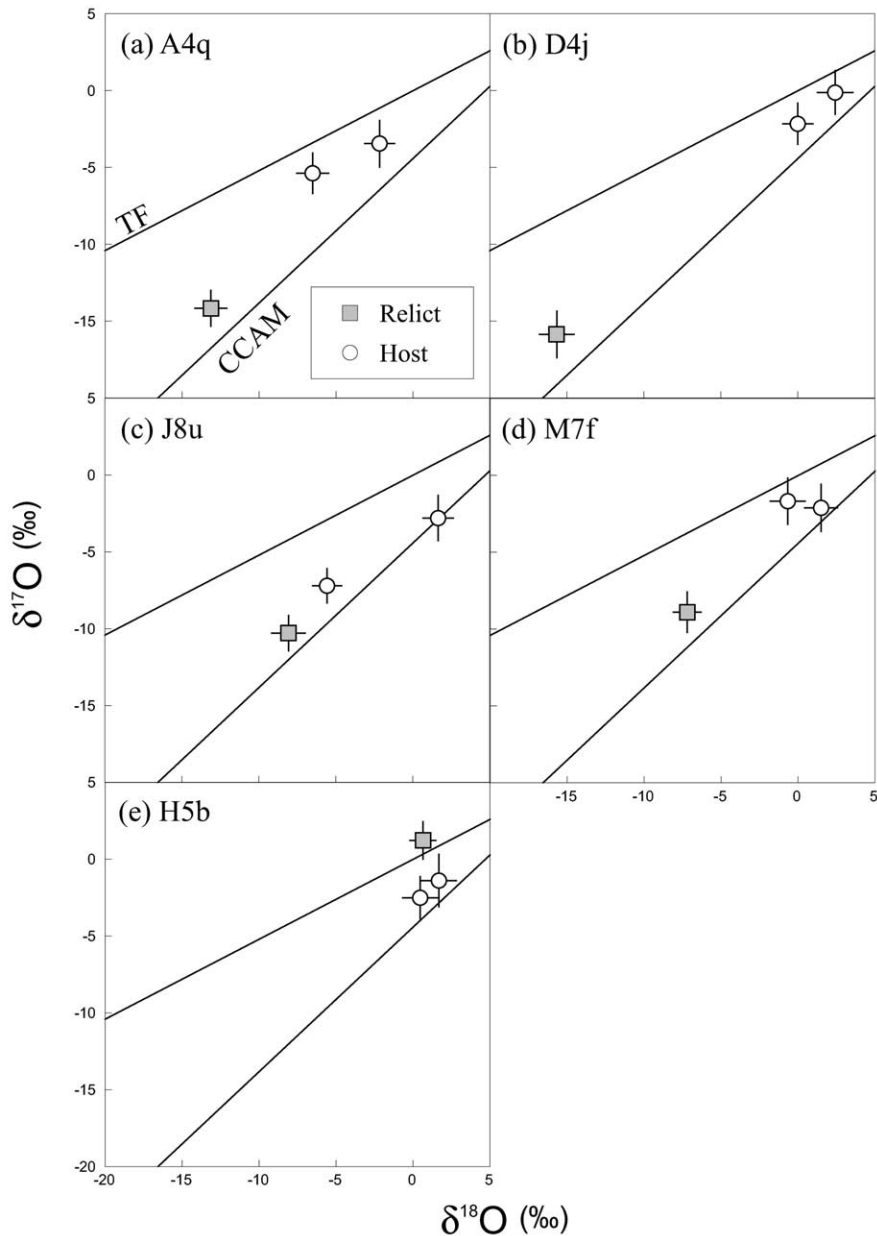


Fig. 2. Plot of $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ for Acfer 094 chondrules; individual values are shown for one low-FeO relict and two high-FeO olivine phenocrysts in five high-FeO chondrules. With the exception of chondrule H5b, the relicts are more ^{16}O -rich than the phenocrysts from the same chondrule. The terrestrial fractionation (TF) and carbonaceous-chondrite-anhydrous-mineral (CCAM) lines are shown for reference.

mesostasis were found to be thin, on the order of $5\ \mu\text{m}$. Although there are some expected effects relating to a tiny mismatch in lattice spacing between low-FeO and high-FeO olivines, Wasson and Rubin (2003) argued that these played only a minor role and that overgrowths provide an accurate measure of the amount of olivine growth that followed the last melting event experienced by these chondrules. This, in turn, implies that the large high-FeO olivine phenocrysts also grew $\sim 5\ \mu\text{m}$ on a side following the final melting events and thus that their central regions are also relicts.

A preliminary survey of the relative abundance of low-

FeO relicts and the thicknesses of overgrowth layers in Acfer 094 indicates that parameters are similar to those observed in Y81020. We examined ~ 200 high-FeO porphyritic olivine and porphyritic olivine-pyroxene chondrules having dimensions $\geq 100\ \mu\text{m}$ in Acfer 094 and found low-FeO phenocrysts in $\sim 80\%$ of these. Because the BSE image of the thin section shows only the surface of a thin plane through chondrules, it is likely that relicts are also present above or below this plane in most of the chondrules in which no relicts were observed. It seems likely that such relicts are present in $>90\%$ of high-FeO chondrules in Acfer 094.

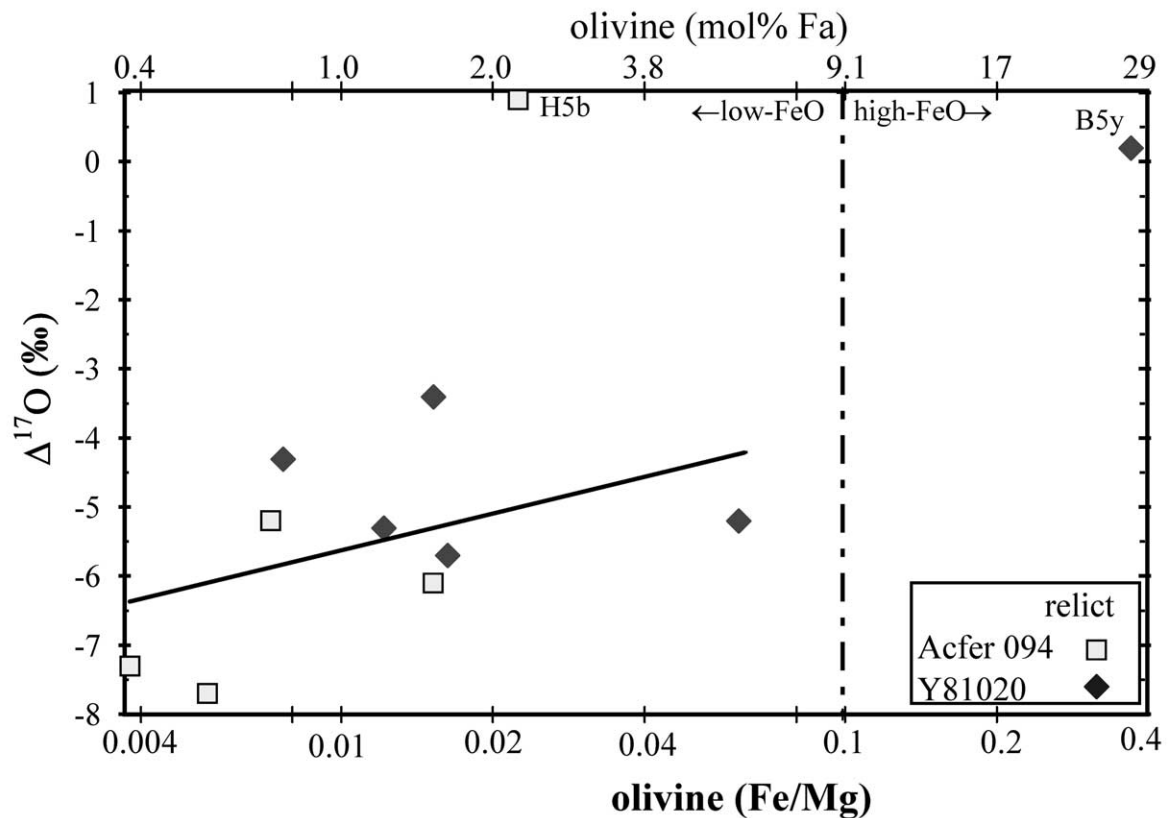


Fig. 3. On a plot of $\Delta^{17}\text{O}$ vs. log olivine Fe/Mg, the data on most relict low-FeO phenocrysts in Acfer 094 (this work) and Yamato 81020 (Kunihiro et al., 2004) show a gradual increase. Acfer 094 relict H5b and Y81020 relict B5y plot at much higher $\Delta^{17}\text{O}$ values than expected from the trend through the remaining points. Typical $\Delta^{17}\text{O}$ errors are $\pm 1.4\text{‰}$ for Acfer 094 data and $\pm 1.0\text{‰}$ for Yamato 81020.

The apparent overgrowth thickness depends on the angle between the plane of the section and the plane tangential to the local surface of the chondrules, with the true thickness only apparent when these two planes are orthogonal. Thus, the true thicknesses are best estimated from the minimum observed thicknesses, providing, of course, that the overgrowth is adjacent to mesostasis that could provide the chemical components necessary for olivine growth.

Wasson and Rubin (2003) listed the minimum Fa contents of ten CO3.0 olivine relicts. These range from 2 to 19 mol% Fa; only three have Fa contents < 9 mol% in the range we define as low FeO. Six relict olivine grains in Y81020 were included in the O-isotope study by Kunihiro et al. (2004); one of these relicts had high FeO (Fa27) and the others ranged from Fa0.8 to Fa5.8, in the low-FeO range.

As stated above, the vast majority of high-FeO porphyritic olivine chondrules in Acfer 094 and Y81020 contain low-FeO olivine relicts. These relicts are surrounded by thin (typically $5 \pm 3 \mu\text{m}$ thick) ferroan olivine overgrowths. The phenocrysts and the overgrowths surrounding the low-FeO relict grains in these chondrules have typical compositions of Fa25–40. The five low-FeO relicts analyzed by ion microprobe in Acfer 094 range from Fa0.38 to Fa2.2, with four of the five having $\text{Fa} \leq 1.5$ (Table 1). The five low-FeO relicts analyzed by ion microprobe in Y81020 (Table 2 of Kunihiro et al., 2004) range from Fa0.76 to Fa5.8; four of the five are $\text{Fa} \leq 1.6$. A closer

look, however, indicates that, whereas three of the five Acfer 094 low-FeO relicts have compositions of $\text{Fa} < 1$, only one of the five Y81020 low-FeO relicts has a composition of $\text{Fa} < 1$. This suggests that the Acfer 094 relicts are slightly less ferroan, but until additional detailed analyses are completed, this inference cannot be confirmed.

5.2. O-Isotopic Compositions in Relict Grains and Host Phenocrysts

By combining our O-isotope data with those published by Kunihiro et al. (2004), we obtain more complete statistics on low-FeO relict grains in high-FeO CO (or CO-related) chondrules but also some possible information about the differences between the two highly primitive chondrites Y81020 and Acfer 094.

In Figure 3 we plot $\Delta^{17}\text{O}$ vs. the olivine composition expressed as Fe/Mg ($= \text{Fa}/[100 - \text{Fa}]$) on a log scale for the combined sets of relict grains studied in Acfer 094 (this work) and Y81020 (Kunihiro et al., 2004). A logarithmic axis is chosen because with decreasing nebular temperature the equilibrium Fe/Mg ratio in silicates increases exponentially, at least until a sizable fraction (perhaps 30%) of the Fe is oxidized. The advantage of Fe/Mg over Fa is that, at higher Fa values, Fe/Mg yields a larger range than Fa. A vertical dash-dot line shows the

location of the boundary (Fa9) we have chosen to separate low-FeO from high-FeO olivine.

We observe a correlation between $\Delta^{17}\text{O}$ and olivine Fe/Mg; the mean $\Delta^{17}\text{O}$ values in Acfer 094 relicts are significantly lower than the Y81020 relicts with their higher Fe/Mg ratios. One Acfer 094 relict (in chondrule H5b) plots far above a trend through the remaining relicts. We will return to this anomalous relict below. For completeness we also plot the high-FeO relict in Y81020 chondrule B5y.

Both Jones et al. (2000) and we (Kunihiro et al., 2004; Wasson et al., 2004) noted that among CO chondrules $\Delta^{17}\text{O}$ values in low-FeO chondrules or relicts are lower than those in high-FeO chondrules. As discussed in those papers and by Wasson (2000), these observations seem best understood in terms of a gradual increase in the mean $\Delta^{17}\text{O}$ of nebular solids with time, with most chondrules with low FeO and low $\Delta^{17}\text{O}$ having formed earlier than most of those with high values of these quantities. A recent study by Pack et al. (2004) showed similar trends in a variety of chondritic materials.

To illustrate this model graphically we fitted a least-squares linear trend to the four normal low-FeO relicts in Acfer 094 and the five low-FeO relicts in Y81020 (Fig. 3). We stress that we are not claiming an analytical relationship between $\Delta^{17}\text{O}$ and Fe/Mg; because the nebular processes are complex, we expect a moderate amount of stochastic scatter about the trend line. This line (and a similar one discussed below) attempts to locate the center of a broad trend band, one that may not necessarily be linear. The slope of this regression line is 1.7‰ per factor of ten change in Fe/Mg.

The O-isotopic composition of the high-FeO (Fa18) relict olivine in chondrule B5y of Y81020 is somewhat anomalous (Kunihiro et al., 2004). It plots in the upper right part of Figure 3. Its mean $\Delta^{17}\text{O}$ value of -0.2‰ is higher than the mean value in the host phenocrysts having Fa63 compositions (-2.7‰); the latter are within the range observed in the high-FeO phenocrysts in that study. Kunihiro et al. (2004) suggested that the high $\Delta^{17}\text{O}$ value in the relict was partly related to its high-FeO content (Fa27) but that stochastic sampling variations on a chondrule scale were responsible for the fact that its $\Delta^{17}\text{O}$ value was $\sim 3\text{‰}$ higher than those in other chondrule phenocrysts having similar olivine compositions.

Acfer 094 chondrule H5b proves to be a more extreme exception, one that cannot readily be explained by stochastic sampling of evolving nebular solids. Acfer 094 relict H5b combines a very high $\Delta^{17}\text{O}$ of $+0.9\text{‰}$ with a reduced olivine composition of Fa2.2. Because the H5b $\Delta^{17}\text{O}$ value is so far outside the scatter observed in the other relicts, we cannot confidently state that its compositions are included in the “normal” grain-to-grain variations of nebular particles. We are not able to come up with a simple plausible scenario to account for its composition; additional data are needed to determine how anomalous it is.

Because of the scatter in the data, there are large errors associated with the slope and intercept of the trend line in Figure 3. To attempt to establish the trend line more precisely, in Figure 4 the $\Delta^{17}\text{O}$ values, the log olivine Fe/Mg data, and the relict trend line from Figure 3 are repeated and data are added for the high-FeO phenocrysts in the high-FeO chondrules from the present study and that of Kunihiro et al. (2004). The phenocrysts associated with the anomalous relict in Y81020

chondrule B5y have the highest Fe/Mg ratios. We calculated a new regression line including the data used in the relict regression and all high-FeO phenocrysts except the three in B5y (labeled in Fig. 4). Inclusion of the latter would, however, have had only a minor effect on the placement of the regression line.

The new regression line was calculated giving every phenocryst equal weighting; its locus is shown by short dashes. Given the moderate experimental uncertainties, its position is similar to that of the relict regression line. Its slope is essentially the same, $\sim 1.8\text{‰}$ in $\Delta^{17}\text{O}$ per log unit (i.e., per factor of 10 change in Fe/Mg). As discussed below, this line provides the best estimate of a possible linear evolutionary track of nebular solids in the CO-CM portion of the nebula during the period of chondrule formation.

5.3. Nebular Fractionation of $\Delta^{17}\text{O}$ and Olivine Fe/Mg

In Figure 4 we combine our studies of Acfer 094 and Yamato 81020 chondrules to generate a data set that, when fitted with a linear regression line, yields a slope of 1.7‰ per factor of 10 increase in the Fe/Mg ratio in the analyzed olivine. It is important that the reader recognize that Figure 4 shows rough positive trends both in the low-FeO relicts and in the high-FeO phenocrysts, and that the trend in the relicts would not be recognizable if we plotted all the olivine composition data on a linear scale, because most of the relicts would be crowded together at low Fe/Mg values. Eight of the nine relicts included in the regression have Fa values of 1.6 mol% or less.

We now examine some possible scenarios to account for this roughly linear relationship between $\Delta^{17}\text{O}$ and log Fe/Mg: (1) a mixing of two components, and (2) an incremental process that gradually produces an exponential increase with increasing Fe/Mg. These yield different predictions. The first process would require two independent solid components to have formed at different distances from the Sun and/or at different times. Alternatively, the trend could have resulted from infall into the nebula of distinct batches of presolar matter. The second model can be envisioned as the gradual evolution of nebular solids in the presence of an “evolved” gas having a different O-isotopic composition (solids may also have been introduced together with the gas). The gradual mixing of the first-generation solids with these late-added materials may have resulted from evaporation and recondensation associated with chondrule formation (Wasson, 2000).

The simplest model is a two-component mixing model in which the low-FeO component has an Fe/Mg ratio of 0.004 or lower and the high-FeO component has an Fe/Mg ratio of 1.7 or higher. We used these Fe/Mg values and chose arbitrary values of $\Delta^{17}\text{O}$ (-5.6 and $+0.3\text{‰}$, respectively) to generate a mixing curve that passes through the relict and phenocryst data fields; the mixing curve is shown in Figure 4. The mixing model cannot account for a positive trend in the relict data. However, the positive slope is largely controlled by Y81020 point J3s (Fig. 4). The slope of the mixing curve is not inconsistent with the phenocryst data, particularly if the B5y phenocryst points are excluded.

The incremental process envisaged in the second model can take many forms. A simple version based on the assumption that the low-FeO chondrules formed first is that the mean composition of the original solids (the precursors of the first-

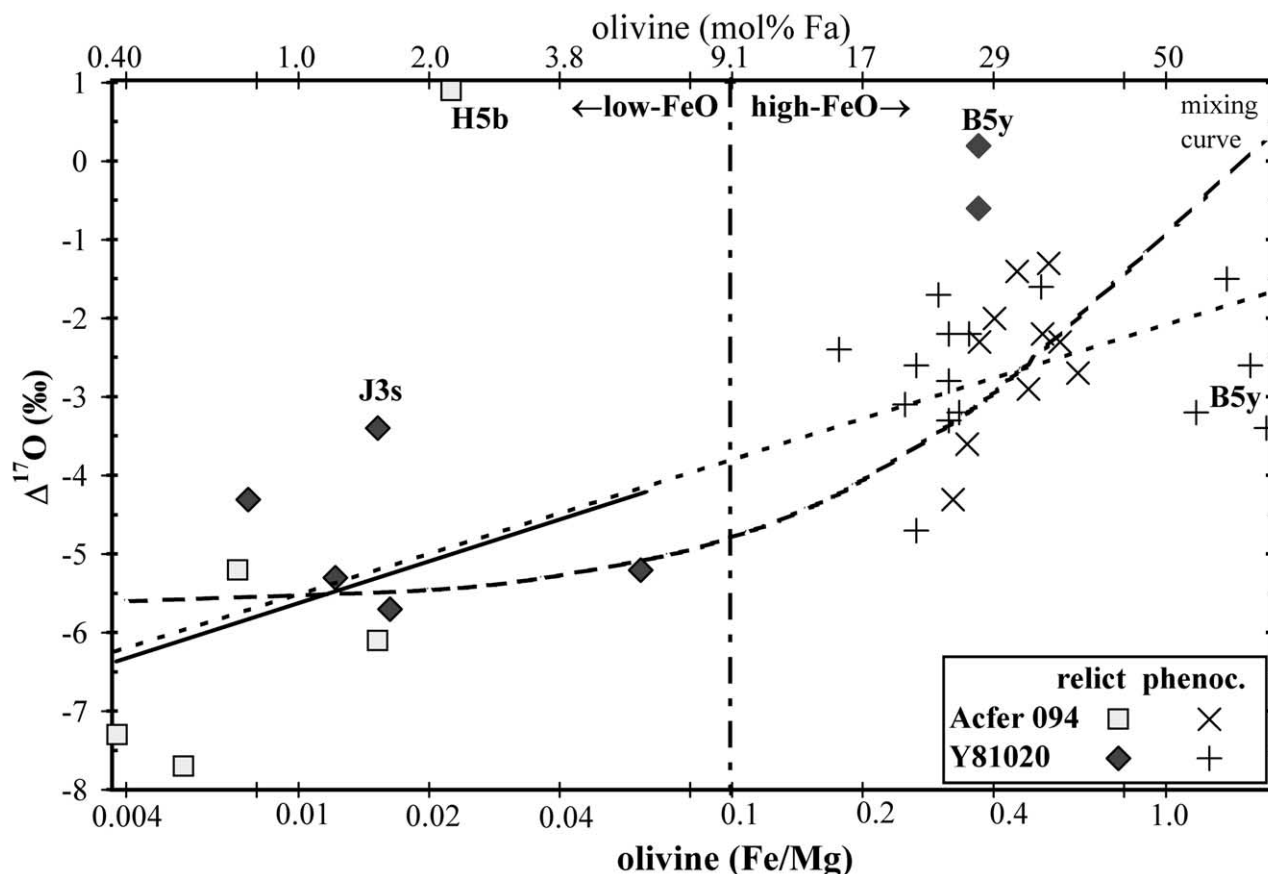


Fig. 4. Plot of $\Delta^{17}\text{O}$ vs. log olivine Fe/Mg. The addition of data on high-FeO phenocrysts to the relict data on a $\Delta^{17}\text{O}$ vs. olivine Fe/Mg diagram yields a regression trend (short dashes) similar to that calculated in Figure 3 but one that is more precisely defined. We excluded the following points from the relict-phenocryst regression: the Acfer 094 H5b relict and Yamato B5y relicts and phenocrysts. Also shown is a curved trend (long dashes) produced by mixing components near the low-FeO end of the relict field and near the high-FeO extreme of the phenocryst field. Typical $\Delta^{17}\text{O}$ errors are $\pm 1.4\text{‰}$ for Acfer 094 data and $\pm 1.0\text{‰}$ for Yamato 81020.

generation chondrules) was near the left end of the regression line segment (e.g., $\Delta^{17}\text{O}$ of -6.3‰ , Fe/Mg = 0.0035 corresponding to Fa0.35) and, as a result of repeated fragmentation, incorporation of minor fractions of a high-FeO components into precursor assemblages, and chondrule melting events, the compositions moved in small compositional jumps toward a composition near an extrapolation of the line segment (perhaps near $\Delta^{17}\text{O} = -1.5\text{‰}$ and Fe/Mg = 2.16 corresponding to Fa 68). Such an incremental process can exactly duplicate the regression line.

The difference between the predictions of these two models is large at intermediate Fe/Mg values, in the range 0.02 to 0.2, a region in which we have only two points. Thus, a goal is to examine the O-isotope compositions of chondrules within this range. In fact, the distribution of mean CO3.0 chondrule olivine compositions is bimodal (e.g., Fig. 6 of Scott and Taylor, 1983), with relatively few Fa values in the corresponding range of Fa2 to Fa16 mol%. Thus, to understand the evolution of olivine more completely, it may be necessary to determine the basis of this compositional bimodality.

Wasson (1996, 2000) noted that flash evaporation of fine materials occurs during chondrule formation and that at low

(<500 K) nebular temperatures this leads to an incremental increase in the FeO content of nebular solids. If the nebular gas has a higher $\Delta^{17}\text{O}$ than the mean solids, this process also leads to a gradual increase in the $\Delta^{17}\text{O}$ of the solids, most apparent in the high-FeO solids. Because we find this model more physically plausible than one involving the independent formation of two distinct solid components, we currently favor the incremental model.

6. SUMMARY

We concur with the observations of Newton et al. (1995) and Greshake (1997) that Acfer 094 shows only minimal evidence of aqueous alteration. Its contents of chondrule glass and presolar grains show it to be highly unequilibrated. The near absence of both aqueous alteration and thermal metamorphic effects confirms that Acfer 094 is a type 3.0 chondrite. Acfer 094 chondrules appear to sample the same population as those in CO and CM chondrites. The high volatile content of Acfer 094 suggests that it is a CM chondrite that avoided aqueous alteration (although the limited data indicating low bulk C argues against this classification). We suggest that the two best clas-

sifications for Acfer 094 are “anomalous member of the CM chondrites” or “anomalous CM-CO chondrite.” The latter conveys more information about this important meteorite.

Our study of O isotopes in low-FeO relict grains and host phenocrysts in high-FeO chondrules in the CM-CO3.0 chondrite Acfer 094 yielded results similar to those obtained by Kunihiro et al. (2004) for CO3.0 Yamato 81020. In four of the five Acfer 094 chondrules, $\Delta^{17}\text{O}$ in the relicts is appreciably lower than in the host phenocrysts. This result is similar to that reported in the Kunihiro et al. (2004) study of low-FeO relicts in high-FeO chondrules in Y81020. On average, $\Delta^{17}\text{O}$ in low-FeO relicts is 3‰–4‰ lower than those in high-FeO phenocrysts in the same chondrules.

The fact that $\Delta^{17}\text{O}$ values correlate with the FeO content of chondrule olivine has been recognized in several previous studies and reviewed by Wasson (2000). We combined our relict and phenocryst data with those of Kunihiro et al. (2004) and prepared plots of $\Delta^{17}\text{O}$ vs. log Fe/Mg of the olivine. We calculated separate correlation lines for the relicts and for the combined set; although the errors are moderate, the line parameters were similar, with slopes of 1.7‰–1.8‰ $\Delta^{17}\text{O}$ per factor of ten increase in Fe/Mg.

Two possible models were considered: (1) a two-component mixing model in which the components had independent origins, and (2) an evolution model in which an initial reservoir (we suggest the precursors of low-FeO chondrules) incrementally evolved to become more oxidized and to have higher $\Delta^{17}\text{O}$ values. Although these models lead to different tracks connecting the low-FeO and high-FeO materials, our data set is insufficient to determine which is better. We find the incremental model more plausible because it fits together with evidence indicating that typical chondrules experienced multiple melting events.

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