Pergamon

Carbonates in CM2 chondrites: Constraints on alteration conditions from oxygen isotopic compositions and petrographic observations

G. K. Benedix,[1,*] L. A. Leshin,[1,2] J. Farquhar,[3,4] T. Jackson,[3] and M. H. Thiemens[3]

[1]Department of Geological Sciences and
[2]Center for Meteorite Studies, Arizona State University, Tempe, AZ 85287-1404, USA
[3]Department of Chemistry, 9500 Gilman Drive, University of California, San Diego, La Jolla, CA 92093, USA
[4]Earth System Science Interdisciplinary Center and Department of Geology, University of Maryland, College Park, MD 20742, USA

Abstract—High-precision measurements of the oxygen isotopic compositions of carbonates (calcite and dolomite) from five CM2 chondrites are presented and put into context of the previously determined mineralogic alteration index (MAI), which places these meteorites into an alteration sequence. The carbonate oxygen isotopic compositions range from +20.0 to +35.7‰ for $\delta^{18}O$, +8.0 to +17.7‰ for $\delta^{17}O$, and −0.7 to −2.7‰ for $\Delta^{17}O$. Carbonate $\Delta^{17}O$ values are inversely correlated with MAI and track the evolution of fluid composition from higher to lower $\Delta^{17}O$ values with increasing alteration on the CM parent body. Similar $\Delta^{17}O$ values for calcite and dolomite fractions from the same splits of the same meteorites indicate that calcite and dolomite in each split precipitated from a single fluid reservoir. However, reversed calcite dolomite fractionations ($\delta^{18}O_{dol} - \delta^{18}O_{cc}$) indicate that the fluid was subject to processes, such as freeze–thaw or evaporation, that fractionated isotopes in a mass-dependent way. Consideration of the carbonate isotopic data in the context of previously proposed models for aqueous alteration of carbonaceous chondrites has provided important insights into both the evolving alteration conditions and the utility of the models themselves. The data as a whole indicate that the isotopic evolution of the fluid was similar to that predicted by the closed-system, two-reservoir models, but that a slightly larger matrix–water fractionation factor may apply. In the context of this model, more altered samples largely reflect greater reaction progress and thus probably indicate more extended times of fluid exposure. Petrographic observations of carbonates reveal a trend of variable carbonate morphology correlated with alteration that is also consistent with changes in the duration of fluid–rock interaction. The data can also be reconciled with fluid-flow models in a restricted region of the parent body, which is consistent with assertions that the different types of carbonaceous chondrites derive from different regions of their parent bodies. In this case, the model results for a 9-km-radius body, and our data place the location of the CM chondrite formation in a 100-m-thick zone 1 km from the surface. The size of this zone could be increased if the model parameters were adjusted. *Copyright © 2003 Elsevier Science Ltd*

1. INTRODUCTION

The formation and subsequent aqueous alteration history of the CM chondrite parent body has been constrained on the basis of the presence of and relationships between various mineral phases found in these meteorites (McSween 1979, 1987; Metzler et al., 1992; Zolensky et al., 1993, 1997; Browning et al., 1996; Clayton and Mayeda, 1984, 1999). Most CM chondrites contain anhydrous minerals (abundant olivine and rare pyroxene) that are found in chondrules, calcium–aluminum inclusions, or as isolated grains. They also contain abundant hydrous phyllosilicates that dominate the meteorite matrix, interspersed between chondrules, calcium–aluminum inclusions, and isolated grains. The anhydrous minerals are thought to have formed at high temperature (i.e., in the nebula), whereas the matrix minerals formed at lower temperatures (Brearley and Jones, 1998, and references therein). Carbonate minerals (primarily calcite, but some aragonite and dolomite) are also present, predominantly in the matrix, along with sulfides (troilite, pentlandite, pyrrhotite, tochilinite, and minor uncharacter-

ized sulfide phases), rare sulfates, and oxides (magnetite) (Fuchs et al., 1973; Bunch and Chang, 1980; Johnson and Prinz, 1993; Riciputi et al., 1994; Brearley and Jones, 1998). There are a few CM chondrites so altered they are classified as CM1 and do not contain any anhydrous minerals (Zolensky et al., 1997)

Browning et al. (1996) extended previous petrographic studies (McSween, 1979, 1987) to derive a quantitative alteration sequence for the CM2 chondrites on the basis of the bulk mineral chemistry of the phyllosilicates in the matrix. The dominant phyllosilicate composition changes during alteration from Mg-serpentine (high Mg/Si, low Fe/Si) to Fe-rich cronstedtite (high Fe/Si, low Mg/Si) (McSween, 1979; Bunch and Chang, 1980; Browning et al., 1996). The mineralogic alteration index (MAI) is a numeric representation of the Fe^{3+}/Si ratio in the phyllosilicate and ranges from 0 to 2, with 2 indicating extensive alteration (see Browning et al., 1996, for a full explanation of how the MAI is determined). This MAI correlates with petrographic features of the meteorites such as the abundance of altered chondrules and isolated anhydrous minerals (unassociated with chondrules). Furthermore, the MAI tracks other whole rock chemical features such as bulk hydrogen content, trapped noble gases, and bulk rock oxygen isotopic compositions. The MAI is a quantitative determination of the relative amount of alteration any given meteorite has

* Author to whom correspondence should be addressed, at Washington University, Department of Earth and Planetary Sciences, Campus Box 1169, One Brookings Drive, St. Louis, MO 63130-4899, USA (benedix@levee.wustl.edu).

experienced and thus places the meteorites in sequence. However, it does not address the fundamental environmental causes of the variation in the degree of alteration. The different alteration indices could, for example, represent variations in temperature, duration of fluid–rock interaction, variations in fluid–rock ratio, or some combination of these effects.

Previous studies indicate that the carbonates in CM chondrites formed by precipitation from aqueous fluids (Kerridge and Bunch, 1979; Bunch and Chang, 1980; Barber, 1981; Fredriksson and Kerridge, 1988; Brearley et al., 1999), and the composition of the carbonate minerals is interpreted to reflect the composition and/or evolution of these fluids (e.g., Johnson and Prinz, 1993; Riciputi et al., 1994). From minor element data (Fe partitioning), Johnson and Prinz (1993) concluded that calcite compositions are consistent with formation at low temperature, in agreement with the temperature inference from oxygen isotope analyses of CM components (Clayton and Mayeda, 1984, 1999). Ion microprobe measurements of trace elements led Riciputi et al. (1994) to suggest that dolomite and calcite precipitated from different fluids (i.e., they did not form in equilibrium with each other). This conclusion was based upon the higher Fe-, Mg-, and Mn-to-Ca ratios, and on the mean Sr content of dolomite relative to calcite. These studies also concluded that carbonate and phyllosilicate formation was coeval.

The oxygen isotopic composition of carbonate minerals therefore can provide a snapshot of the fluid from which they precipitated. In solution, the bicarbonate species rapidly exchanges oxygen with water, but once crystallized, oxygen isotope exchange rates in carbonates are slow (Farver, 1994). Therefore, detailed studies of the oxygen isotopic composition of carbonates can provide additional insights into evolution and chemistry of the fluid as aqueous alteration proceeds on the CM parent body. Clayton and Mayeda (1984) reported the first three-oxygen isotopic measurement of carbonate in Murchison ($\delta^{18}O = 35.1‰$, $\delta^{17}O = 16.7‰$, $\Delta^{17}O = -1.6‰$; uncertainty of $\sim\pm 0.1‰$). This measurement was used to argue that carbonate and phyllosilicate equilibrated with the same fluid and at the same temperature, ~ 0 to $25°C$, and to constrain the water:rock ratio during the alteration to be between 0.35 and 0.6 (Clayton and Mayeda, 1984, 1999). Grady et al. (1988) measured oxygen ($\delta^{18}O$ only) and carbon isotopic compositions of carbonates from several groups of meteorites that included 25 Antarctic and non-Antarctic CM chondrites. They showed that the CM carbonates have variable $\delta^{18}O$ values, which they concluded to be weakly correlated with the extent of alteration as determined by McSween (1979) but are not correlated with the MAI determined by Browning et al. (1996) (within Murchison, Grady et al., 1988, found that $\delta^{18}O$ spans a 10‰ range from $\sim +26$ to $\sim +35‰$).

We present a petrographic and isotopic study of carbonates from CM2 chondrites that span the Browning et al. (1996) alteration sequence. We report high-precision three-isotope oxygen isotopic compositions of carbonates from five CM2 chondrites and petrographic observations of the carbonates with this alteration sequence in mind. The data presented allow constraints to be placed on the nature of fluid:rock interaction and the environment under which the CM alteration sequence was produced.

2. SAMPLES AND TECHNIQUES

Carbonates from samples of CM2 chondrites Murchison, Murray, Nogoya, Cold Bokkeveld (both bulk material and polished thin sections from Arizona State University), and Mighei (bulk material from Smithsonian) were analyzed for oxygen isotopes, and polished thin sections of all samples except Mighei were studied to determine the petrographic setting of the carbonates. Samples of these meteorites were used in the determination of the quantitative alteration sequence of Browning et al. (1996), and they span the entire sequence from least (Murchison) to most altered (Cold Bokkeveld). In addition, all of these meteorites are falls, which minimizes interaction of the meteorite with the terrestrial environment. We note that Murchison is not the least altered CM2—Kivesvaara (Zolensky, personal communication) likely is—but Murchison is the least altered of the meteorites in the study of Browning et al. (1996) and in this study.

Traditional optical microscopy techniques are hampered by the fine-grained nature of the phyllosilicate matrix, which is opaque in transmitted light (except in thin sections polished to less than the usual 30-μm thickness). Elemental X-ray maps of entire thin sections, acquired at a resolution of 9 μm per pixel on the ASU JEOL JXA-8600 electron microprobe (EPMA) at 15 kV and 10 nA, were used to identify calcite and dolomite. High-resolution back-scattered electron images of selected single grains of calcite and dolomite were obtained on a JEOL JSM-840 scanning electron microscope at 15 kV and between 6- and 9-nA beam current. Mineral identification was made with qualitative EDS analysis.

Carbonates from Murchison (four splits), Murray (two splits), Mighei (one split), Nogoya (two splits), and Cold Bokkeveld (one split) were analyzed for $\delta^{18}O$ and $\delta^{17}O$ at the University of California–San Diego by means of methods described previously (Farquhar et al., 1998; Farquhar and Thiemens, 2000). Variable amounts (from ~ 350 to ~ 1050 mg; Table 1) of whole rock were crushed with a percussion mortar and consisted of unsieved micron- to millimeter-sized material. Replicate analyses of Murray and Nogoya represent separate splits rather than replicates of a homogenized sample. For Murchison, two of the splits (Murchison-A and Murchison-B) are from a single homogenized sample, and the third and fourth splits were from separate bulk samples. CO_2 from carbonates was liberated following the methods of previous workers (McCrea, 1950; Rosenbaum and Sheppard, 1986; Al-Aasm et al., 1990). The crushed sample was loaded into a side-arm reaction vessel along with 10 mL of 100% H_3PO_4 ($\rho = 1.896$ g/cm³). The reaction vessels were attached to an extraction line and outgassed overnight. They were then placed in a bath at 25°C for 1 h, after which the acid was introduced to the sample. The reactions were carried out at 25°C for 18 to 24 h to extract CO_2 from calcite. The acidified whole rock sample was further allowed to react for 1 h at 100°C to extract CO_2 from the dolomitic carbonates. On the basis of the experimental results of Rosenbaum and Sheppard (1986) and Al-Aasm et al. (1990), calcite will completely react after ~ 24 h at 25°C, whereas only $\sim 15\%$ of the dolomite is reacted at that temperature in that amount of time. Evolved CO_2 was purified (i.e., separated from H_2S) by gas chromatography with a Varian 3600 gas chromatograph equipped with an 8-foot-long, 1/8-inch-diameter, packed

Table 1. Results of CM chondrite acid dissolution experiments.

Sample	MAI	Amount reacted (mg)	CO_2 Yield ($\mu g/g$)	$\delta^{18}O^a$ (‰)	$\delta^{17}O^a$ (‰)	$\Delta^{17}O$ (‰)
Calcite (25° acidification)						
Murchison-A	0.43	475	398	26.6	13.2	−0.67
Murchison-B	0.43	420	513	29.2	14.5	−0.72
Murchison-C	0.43	895	2099	35.7	17.7	−0.88
Murchison-D	0.43	998	1618	32.5	15.9	−1.02
Murray-A	0.57	1050	1848	35.3	17.5	−0.87
Murray-B	0.57	565	896	35.2	17.6	−0.72
Mighei	0.77	490	2326	29.7	14.1	−1.38
Nogoya-A	0.97	1035	1683	28.1	12.8	−1.85
Nogoya-B	0.97	675	2040	20.0	8.0	−2.44
Nogoya-B[b]		675	280	21.0	8.8	−2.16
C. Bokkeveld	1.03	360	2004	28.3	13.1	−1.65
Dolomite (100° acidification)						
Murchison-C		See above	516	31.3	15.5	−0.80
Murray-A		See above	1056	33.8	16.6	−0.99
Murray-B		See above	607	31.3	15.6	−0.70
Mighei		See above	1491	27.6	13.0	−1.39
Nogoya-A		See above	952	25.2	11.3	−1.84
Nogoya-B		See above	932	19.7	7.6	−2.69
C. Bokkeveld		See above	1124	25.9	12.0	−1.51

[a] Relative to SMOW.
[b] These compositions reflect acid reaction at 22°C overnight after extraction of 25°C reaction.

Alltech Hayesep Q column with a He carrier flow of 40 mL/min (Farquhar et al., 1998, 2002). CO_2 yields were determined by measuring the amount of CO_2 gas released with a calibrated volume and capacitance manometer.

To measure both $\delta^{17}O$ and $\delta^{18}O$ accurately, it is necessary to analyze O_2. CO_2 was transferred to a Ni reaction tube along with 1000 times excess amount of precooked (120 min at 800°C) BrF_5. The mixture was reacted for 45 h at 800°C (Bhattacharya and Thiemens, 1989). O_2, NF_3, and CF_4 were separated in a U-Trap filled with molecular sieve 13× (60/80 mesh) at −116.5°C for 70 min. The samples were then frozen with liquid He to the inlet of a Finnigan MAT 251 for analysis of m/e^- 32, 33, and 34 to determine $\delta^{18}O$ and $\delta^{17}O$. Isotopic compositions are reported relative to standard mean ocean water (SMOW) assuming the fractionation factors of Rosenbaum and Sheppard (1986). The fractionation factor for ^{17}O ($^{17}\alpha$) was assumed to be equal to the fractionation factor for ^{18}O ($^{18}\alpha$) raised to the power of 0.52. On the basis of analysis of standards, analytical uncertainties on individual analyses are estimated to be ±0.4‰ for $\delta^{18}O$, ±0.2‰ for $\delta^{17}O$ values and ±0.05‰ for $\Delta^{17}O$. $\Delta^{17}O$ is the offset in $^{17}O/^{16}O$ from a reference fractionation line (Miller, 2002). In other words, it is the difference in $^{17}O/^{16}O$ from one slope-1/2 line to another slope-1/2 line. We calculate it by the following equation:

$$\Delta^{17}O = \delta^{17}O - 1000 \times [(1 + \delta^{18}O/1000)^{0.5247} - 1] \quad (1)$$

where 0.5247 is the slope of the terrestrial fractionation line recently published by Miller (2002).

3. RESULTS

3.1. Petrographic Observations

Several authors have discussed the petrographic occurrences of calcite and dolomite in CM chondrites (e.g., Fuchs et al.,

1973; Bunch and Chang, 1980; Johnson and Prinz, 1993; Brearley, 1998). We briefly describe here the dominant petrographic characteristics of the carbonates concentrating on describing trends of the occurrence with increasing MAI. Figure 1 illustrates the progressive change in crystal morphology and petrographic association with increasing alteration index.

3.1.1. Murchison (MAI = 0.43)

The primary carbonate is calcite, which dominantly occurs as isolated, inclusion-free, subhedral to subrounded, 20- to 50-μm grains dispersed throughout matrix (Fig. 1a). These isolated grains are occasionally rimmed by PCP material (which comprises a fine-grained mixture of tochilinite and cronstedtite). Whether rimmed or not, calcite typically exhibits sharp boundaries with the surrounding material. Other morphologies of calcite, although very rare, include veins within chondrules and isolated in the matrix, and small aggregates of calcite crystals. We have not observed dolomite in any Murchison section studied to date. This contrasts with the observed release of CO_2 from what is most plausibly dolomite in the oxygen isotopic extractions (see results below). The lack of identification of individual dolomite grains in the Murchison sections is probably a sampling artifact implying the size of the dolomite grains are below the resolution limit (~9 μm/pixel) of the EPMA maps we utilized to locate single grains for petrographic study.

3.1.2. Murray (MAI = 0.57)

Calcite in Murray exhibits very similar features to calcite in Murchison, consistent with the similarity in MAI of these two meteorites. Grains are, however, often surrounded by very thin (~1 μm) rings of alteration material, which appear bright in backscattered electron images. Rims of this type, but slightly larger (~10 μm in width), were described by Browning and
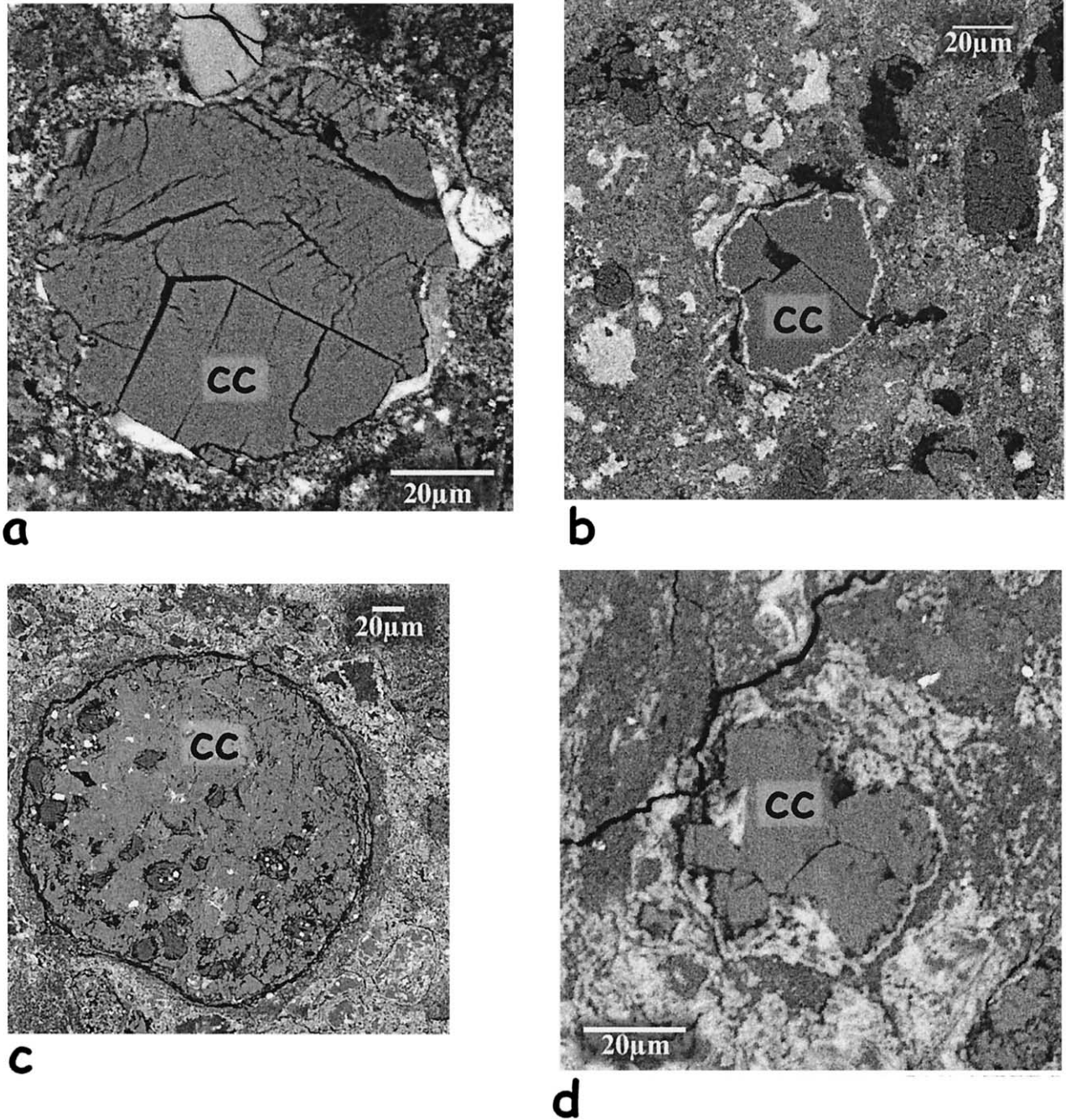
Fig. 1. Back-scattered electron images comparing carbonate morphology in four CM2 chondrites in order of increasing MAI (Browning et al., 1996). (a) Typical morphology of calcite (cc) found in several thin sections of Murchison, which has an MAI of 0.43. The calcite generally exhibits a sharp contact with the surrounding materials. (b) Calcite (gray) in Murray (MAI = 0.57) with a rim of highly reflective material. This morphology is more common in Murray than Murchison, but Murray also contains abundant carbonate with sharp contacts with surrounding material. (c) Morphology of calcite in Nogoya (MAI = 0.97) showing occurrence as replacement product of a chondrule. The darker gray grains are remnant primary chondrule minerals. (d) Calcite morphology in Cold Bokkeveld, the most altered in the sequence, with an MAI of 1.03. The calcite in this meteorite usually exhibits irregular contacts with the surrounding altered material.

Bourcier (1998) and are probably a fine-grained mixture of tochilinite and Fe-rich phyllosilicates. The alteration material occurs at the edges, but still within, the calcite grains (Fig. 1b) in Murray.

3.1.3. Nogoya (MAI = 0.97)

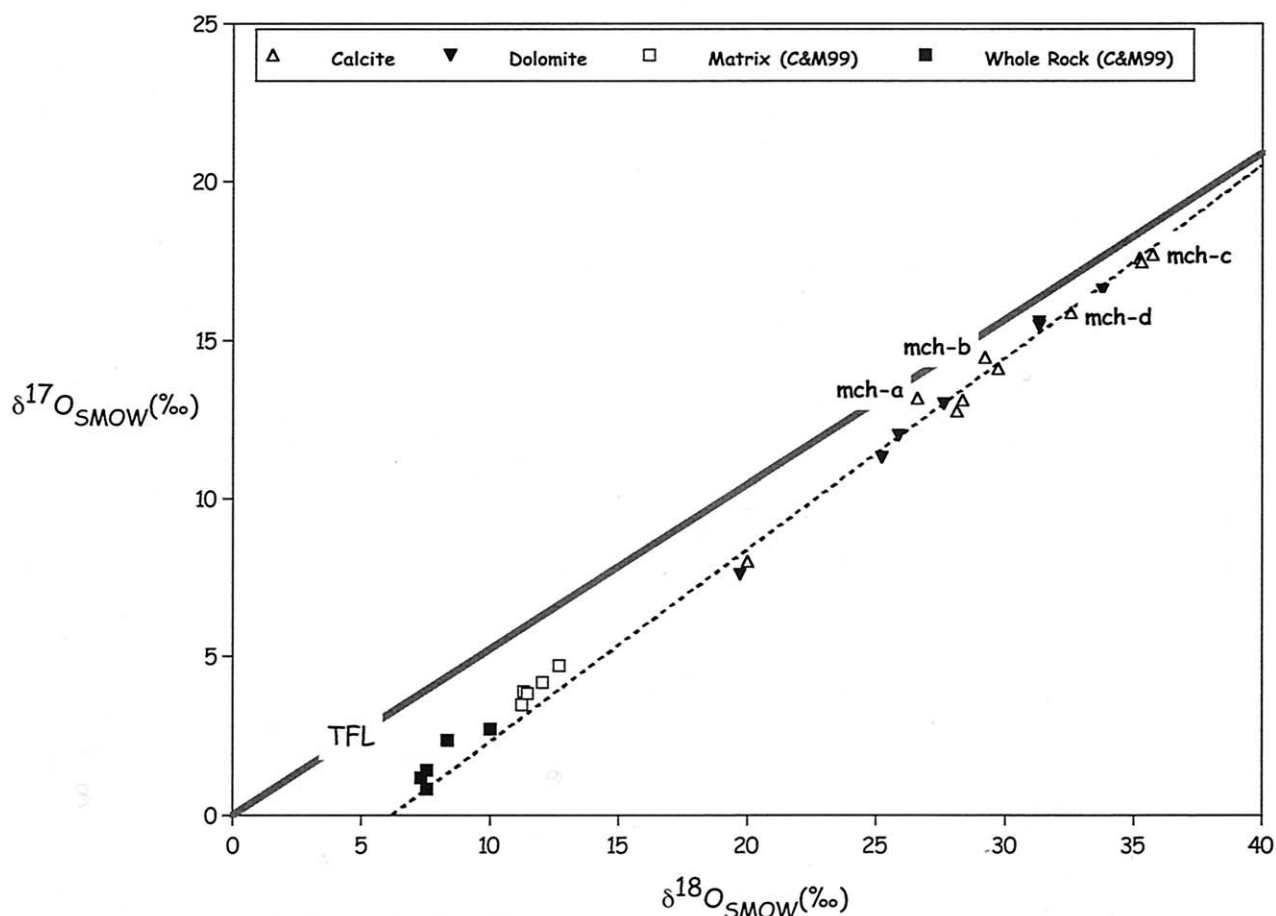Calcite is found almost exclusively in the form of replacement products of chondrules, occurring as rounded aggregates

Fig. 2. Traditional three-isotope plot of $\delta^{17}O$ vs. $\delta^{18}O$ relative to SMOW illustrating the relationship between new CM2 carbonate analyses (calcite = open triangles; dolomite = solid triangles), and whole rock (solid squares) and matrix analyses (open squares) from Clayton and Mayeda (1999) for the same meteorites. The terrestrial fractionation line (TFL) is shown for reference. The carbonates are heavier than matrix and whole rock and span a wider range in $\delta^{18}O$ than the other mineral components. The range in $\delta^{18}O$ of carbonates in a single meteorite is illustrated by the labeled carbonate points, showing the four analyses of calcite in Murchison (Table 1). The linear regression line (dashed), which has a slope of 0.611, illustrates the non-mass-dependent nature of the oxygen isotopic composition of the calcite.

(Fig. 1c). These aggregates sometimes contain small sulfide inclusions and/or small, unaltered core minerals of olivine and pyroxene. In one instance, a vein of calcite in contact with an aggregate is observed. Isolated, inclusion-free grains in the matrix are rare.

3.1.4. Cold Bokkeveld (MAI = 1.03).

Calcite occurs as isolated grains surrounded by PCP material (Fig. 1d). Boundaries between calcite and surrounding altered material show evidence of resorption in the form of needles of altered material invading calcite grains. This was also reported for calcite in Murray (Bunch and Chang, 1980) but is much more common in Cold Bokkeveld. Veins of inclusion-filled calcite are more common in Cold Bokkeveld than in the other meteorites studied.

Several important results are obtained from the petrographic observations. (1) The dominant carbonate is calcite. Dolomite is rare. This observation is also apparent from the CO_2 yields (Table 1) from the acid extractions of the bulk samples, and

consistent with previous observations (Bunch and Chang, 1980; Johnson and Prinz, 1993; Brearley, 1998). (2) There is general trend in carbonate morphology with alteration index. The least altered meteorite contains carbonates with the dominant textural feature of sharp boundaries with the surrounding material. With increasing alteration index, the carbonate morphology indicates evidence for increasing resorption of the carbonate into PCP or phyllosilicate material, redistribution of carbonates, and veining. (3) The interspersed morphologies of the carbonate and phyllosilicate across the alteration sequence are consistent with coformation of these phases during alteration, in agreement with previous studies (Bunch and Chang, 1980; Johnson and Prinz, 1993; Riciputi et al., 1994).

3.2. Oxygen Isotopic Compositions

Data are presented in Table 1 and in Figure 2. The CO_2 yields were variable both among splits of the same sample and among different samples and do not show a distinctive corre-
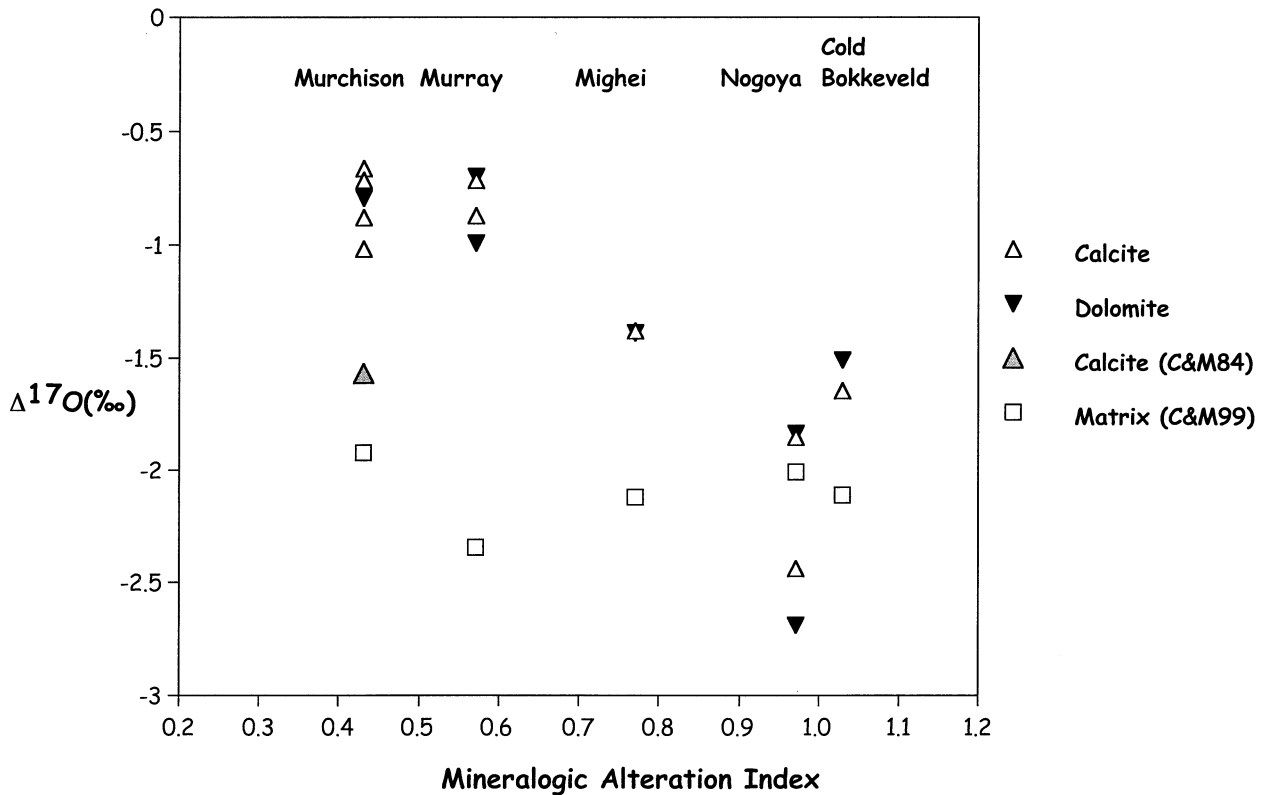
Fig. 3. $\Delta^{17}O$ vs. MAI (after Browning et al., 1996) for carbonates from five CM2 chondrites (shown on plot). Calcite and dolomite are shown as triangles. Original calcite (grey triangle); C&M84) and matrix (squares; C&M99) oxygen isotopic analyses of Clayton and Mayeda (1984, 1999) are also shown. There is a distinct trend of $\Delta^{17}O$ of carbonates becoming more negative with increasing MAI, indicative of evolution of the fluid from which the carbonates precipitated.

lation with MAI. However, in general, the more altered samples contain more carbonate and thus released higher amounts of CO_2 upon acidification. CO_2 from the calcite fraction is significantly higher than from the dolomite fraction (Table 1) in all cases.

The $\delta^{18}O$ of calcite ranges from +20.0‰ in Nogoya to +35.7‰ in Murchison, and $\delta^{17}O$ ranges from +8.0‰ in Nogoya to +17.7‰ in Murchison. Similar ranges in $\delta^{18}O$ (+19.7‰ to +33.8‰) and $\delta^{17}O$ (+7.6‰ to +16.6‰) are found for dolomite. Carbonate $\Delta^{17}O$ values range from −0.67‰ to −2.69‰. Calcite and dolomite from the same splits have identical $\Delta^{17}O$ values within uncertainties.

The $\delta^{18}O$ values are consistent with the range of previous measurements for these same meteorites (Clayton and Mayeda, 1984; Grady et al., 1988; Brearley et al., 1999). Previous high-precision (conventional) analyses of $\delta^{17}O$ in chondrite carbonates are limited to a single analysis of calcite from Murchison with $\delta^{18}O$ = +35.1‰ and $\delta^{17}O$ = +16.7‰ (Clayton and Mayeda, 1984). The $\Delta^{17}O$ value for this analysis (−1.6‰; Clayton and Mayeda, 1984) is different from our analyses (Table 1) of four splits of Murchison (−0.67 to −1.02‰) by almost 1‰, outside the analytical uncertainty of either study. Although such large $\Delta^{17}O$ heterogeneity is not indicated by our multiple split analyses, it is possible that different samples could show such heterogeneity.

The most important observations from the isotopic data are

as follows. (1) The $\delta^{18}O$ values of the carbonates are variable both within a single meteorite (Fig. 2) and among the different CM meteorites analyzed in this study. The $\delta^{18}O$ values do not correlate significantly with MAI, in agreement with the Grady et al. (1988) data; however, there is a general trend of decreasing $\delta^{18}O$ with increasing MAI. (2) The variation in $\Delta^{17}O$ values is much greater between different CM chondrites than among different splits of the same meteorite. Further, $\Delta^{17}O$ values show a distinct inverse correlation with MAI (Fig. 3) such that meteorites with high MAI (i.e., more altered) have lower $\Delta^{17}O$ values. (3) With one exception (Nogoya-B), $\Delta^{17}O$ values of calcite and dolomite extractions from the same splits are identical at the 0.1‰ level. (4) Isotopic fractionation between dolomite and calcite ($\delta^{18}O_{dol} - \delta^{18}O_{cc}$) is negative in all cases and ranges from −1.5 to −4.5‰. (5) Utilizing matrix analyses from Clayton and Mayeda (1999), our data indicate that $\Delta^{17}O$ values of carbonates are distinct from those of the bulk matrix (Fig. 3).

4. DISCUSSION

The goal of this study was to investigate the relationship between the oxygen isotopic composition of the fluid on the CM parent body (as recorded by carbonates) and the extent of alteration of CM2 meteorites (as indicated by the MAI), and to constrain the environment that produced the alteration. The

~2‰ variation of $\Delta^{17}O$ of carbonates, anticorrelated with MAI (Fig. 3), supports the hypothesis that the different CM2 meteorites preserve a record of evolving environmental conditions consistent with alteration sequence determined for the meteorites (e.g., Browning et al., 1996; Clayton and Mayeda, 1999). In this section, we discuss the implications of the new oxygen isotopic data for understanding the conditions of aqueous alteration on the CM parent body and the isotopic evolution of the fluids responsible for the alteration.

The variable $\Delta^{17}O$ of carbonate within a single meteorite and the different $\Delta^{17}O$ for carbonate relative to other CM phases reinforces the conclusion that the compositions of different mineral phases of carbonaceous chondrites cannot be explained by simple isotopic equilibrium during alteration (Clayton and Mayeda, 1999). With the possible exception of Nogoya, the $\Delta^{17}O$ values of carbonate preclude mass-dependent equilibrium between carbonate and matrix. This interpretation is different from Clayton and Mayeda (1984) who argued that carbonate and matrix oxygen isotopic compositions in Murchison were within error of mass-dependence, and bears on the use of carbonate-matrix fractionations as paleothermometers. On the basis of isotopic fractionations between calcite and matrix in Murchison (i.e., the value of $\delta^{18}O_{cc}$ to $\delta^{18}O_{matrix}$), Clayton and Mayeda (1984) concluded that the alteration of Murchison took place at a temperature between 0°C and 25°C. Our observation that carbonate and matrix have different $\Delta^{17}O$ values makes this interpretation invalid in a strict sense. However, a similar assessment of mineral fractionation that uses the $\delta^{18}O$ of calcite and matrix from Nogoya (which do have similar $\Delta^{17}O$ and thus are more likely to have reached equilibrium) yields a similar estimate of the temperature conditions (by use of fractionation factors from Wenner and Taylor, 1971; Savin and Lee, 1988; Zheng, 1993), and thus we do not argue for a different interpretation of alteration temperature. In other words, although the difference between the carbonate and phyllosilicate $\Delta^{17}O$ values for Murchison indicate nonequilibrium conditions and an exact temperature of alteration for Murchison cannot therefore be derived, the data from Nogoya indicate that CM alteration temperatures are consistent with the 0 to 25°C values previously discussed (Clayton and Mayeda, 1984).

In addition to the overall lack of mass dependent equilibrium in the carbonate data, there is also evidence for nonequilibrium conditions on a local scale. Isotopic fractionation between dolomite and calcite (i.e., $\delta^{18}O_{dol} - \delta^{18}O_{cc}$) precipitated in equilibrium at any given temperature is positive (Friedman and O'Neil, 1977). Reversed isotopic fractionations between dolomite and calcite (i.e., negative values of $\delta^{18}O_{dol}$ to $\delta^{18}O_{cc}$) extracted from the same CM chondrite splits are therefore inconsistent with equilibrium coprecipitation of these phases from a single fluid. The similar $\Delta^{17}O$ values of calcite and dolomite extractions from the same splits (Table 1) indicate that that the fluid $\Delta^{17}O$ value did not change during the interval of calcite and dolomite precipitation. To explain the $\delta^{18}O_{dol}$ and $\delta^{18}O_{cc}$ values by a temperature change, calcite and dolomite precipitation temperatures would be required to have differed by 50 to 100°C. Such large temperature swings are inconsistent with previous interpretations (Clayton and Mayeda, 1984; Riciputi et al., 1994) of the alteration conditions. We cannot rule out that postalteration brecciation of these meteorites may be the cause of small scale nonequilibrium

fractionations (i.e., physical juxtaposition of nongenetically related minerals). However, we suggest that the reversed $\delta^{18}O_{dol}$ and $\delta^{18}O_{cc}$ fractionations more likely reflect a process that generated mass-dependent changes in the $\delta^{18}O$ value of the fluid phase. Possibilities for a process that could cause mass-dependent variability in the $\delta^{18}O$ value include partial freezing/thawing or evaporation of the fluid.

The CM carbonate data can be used to constrain the evolution of the isotopic composition of the altering fluid on the CM parent body during the time that carbonates were forming. Because the carbonates precipitate directly from the fluid, where fluid–bicarbonate oxygen exchange is rapid, the carbonate mineral grains provide a snapshot of the fluid composition on the CM parent body at the time carbonates crystallized (or recrystallized). In addition, oxygen diffusivity measurements indicate that once crystallized, isotopic exchange of carbonate grains is extremely slow relative to the timescale likely for asteroidal aqueous activity, especially at the very low temperatures of carbonate precipitation. For example, recent determinations of oxygen self-diffusion in calcite indicate that oxygen diffusivity is less than approximately 10^{-18} cm^2/s for temperatures above 400°C (Farver 1994; Riciputi et al., 1994). Although no data exist on diffusion rates at low temperatures, for a grain radius of 20 μm, the timescale for diffusional resetting is 4×10^7 yr for a conservatively extrapolated diffusivity. The carbonate, in effect, freezes in the oxygen isotopic composition of the fluid from which it precipitated as a result of the slow diffusivity of oxygen in the carbonate grain after formation.

The data presented here document the evolution of the fluid on the CM parent body from higher toward lower $\Delta^{17}O$ values with increasing alteration. This observation is consistent with interpretations that posit initial water on the CM chondrite parent body that is ^{16}O poor compared with the anhydrous precursors to alteration (Clayton and Mayeda, 1984, 1999; Young, 2001). In detail, the carbonate data require that the initial $\Delta^{17}O$ value of the fluid was $\geq -0.6‰$, the highest value observed in the carbonates. Analyses of sulfates in CM chondrites suggest an even higher fluid initial $\Delta^{17}O$ value of $\sim +1.2‰$ (Airieau et al., 2001).

4.1. Implications from Models of Asteroidal Alteration

Interpretations of isotopic data from complex systems such as those being sampled in this work are model dependent. Two generalized types of models have been previously proposed to describe the isotopic consequences of aqueous alteration of carbonaceous chondrite materials: a closed-system, two-reservoir interaction model from Clayton and Mayeda (1984, 1999), and a fluid-flow model of Young and coworkers (Young et al., 1999; Young, 2001). The data presented here can be used both to provide consistency checks on these models and to extract constraints on environmental conditions within the context of each model.

On the basis of petrographic observations and oxygen isotope data for anhydrous minerals, whole rock, matrix, magnetite, and carbonate fractions from the CM chondrites, Clayton and Mayeda (Clayton and Mayeda, 1984, 1999; Rowe et al., 1994) devised a closed system model designed to: (1) place constraints on the composition of protosolar gas (liquid) and solid reservoirs and (2) understand how these reservoirs could

have interacted in planetesimals to produce the isotopic and mineralogic variations observed in the meteorite record. This model indicated that the isotopic compositions and abundance of hydrated phases could be related by reaction between a precursor fluid (aqueous) reservoir with positive $\delta^{18}O$ and $\Delta^{17}O$ and an anhydrous rock with negative $\delta^{18}O$ and $\Delta^{17}O$ (Clayton and Mayeda, 1984, 1999; Rowe et al., 1994; Leshin et al., 1997). The CM carbonate data can be assessed in the context of this model by calculating the composition of the fluid from which the carbonate precipitated by using the fractionation factor between water and calcite at 0 to 25°C. By use of this approach, we find that the water composition evolves along a trajectory that is subparallel to, but offset from the Clayton and Mayeda (1999) model water. The offset derives from the choice of the serpentine–water fractionation factor, a proxy for the phyllosilicate matrix–water fractionation, which Clayton and Mayeda (1984, 1999) took to be 12‰ (from Wenner and Taylor, 1971). The model water derived from the carbonate data for that temperature range yields a value of ~16 to 20‰ for the matrix–water fractionation factor, a value that is consistent with experimental determinations of phyllosilicate–water fractionation factors at low temperatures (Wenner and Taylor, 1971; Savin and Lee, 1988; Zheng, 1993). The modeled water could also be closer to that predicted by Clayton and Mayeda if changes in carbonate–mineral fractionation factors resulting from addition of salts to aqueous solutions (salt effects), such as those documented by Horita et al. (1993a,b, 1995), are considered.

Figure 4a is a plot of $\Delta^{17}O$ vs. $\delta^{18}O$ of the CM carbonate data with the phyllosilicate matrix data of Clayton and Mayeda (1999), showing the wide range of $\delta^{18}O$ values of carbonates in the less altered CMs and the decrease in $\delta^{18}O$ with increasing alteration. Figure 4b is a schematic illustration of the Clayton and Mayeda (1984, 1999) model represented on a plot of $\Delta^{17}O$ vs. $\delta^{18}O$ that also includes a representation of one way that the carbonate data can be reconciled with the Clayton and Mayeda (1984, 1999) model. The Clayton and Mayeda (1984, 1999) model starts with water and rock that have initial compositions at points labeled W_i and R_i. Reaction between water and rock results in the formation of phyllosilicate matrix whose isotopic composition evolves as a consequence of reaction and exchange along trajectory M_i-M_f. The Clayton and Mayeda (1984, 1999) model does not explicitly include carbonate formation or carbonate minerals, but is general enough that our data can be reconciled with the model if several additional conditions are met. In this context, our data imply that carbonate precipitation occurred near point W_4 on the water trajectory, forming carbonates with composition C_i. The offset between points W_4 and C_i is a result of the carbonate–water oxygen isotope fractionation factor. While carbonates are precipitating, phyllosilicates continue to form and evolve toward point M_f, the final $\Delta^{17}O$ of the matrix. Continued reaction between water and rock results in changes in the MAI, and concurrent recrystallization of carbonate mineral grains results in partial exchange of oxygen isotopes which approach composition C_f, the final $\Delta^{17}O$ values of matrix in all samples and carbonates of the most altered samples. In the context of this model, the resorption features of carbonate coupled with more negative carbonate $\Delta^{17}O$ values are most consistent with more altered meteorites reflecting longer interaction with an isotopically evolving
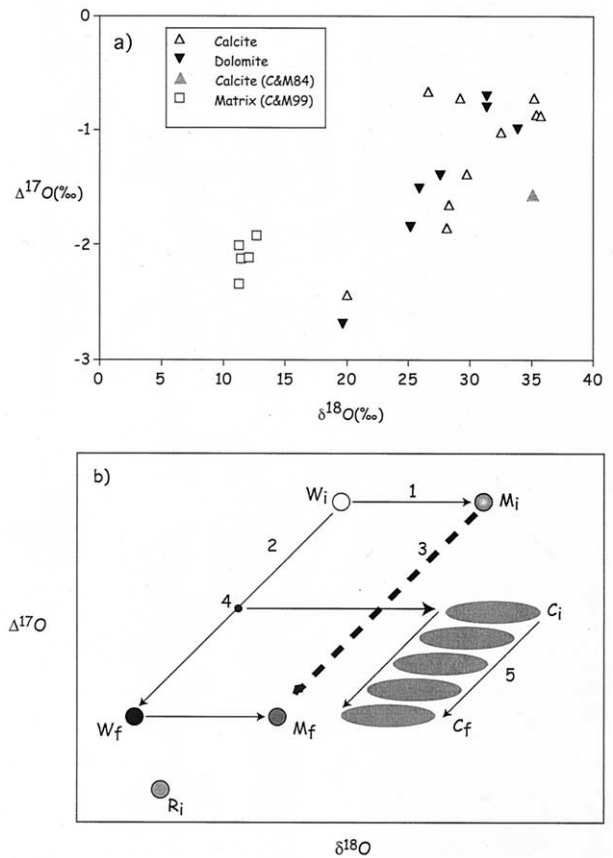

Fig. 4. (a) $\Delta^{17}O$ vs. $\delta^{18}O$ for CM calcite and dolomite (triangles), Clayton and Mayeda's (1999; C&M99) matrix data (squares) for the same meteorites, and Clayton and Mayeda's (1984; C&M99) single Murchison carbonate analysis (large triangle). Our Murchison and Murray analyses make up the cluster of data points in the upper right that span a range of ~10‰ in $\delta^{18}O$ and ~0.5‰ in $\Delta^{17}O$. In general, carbonates from the least altered samples plot in the upper right with the trend being that $\delta^{18}O$ composition decreases with alteration. (b) Conceptual model of the evolution of isotopic compositions of water (W), carbonate (C), and matrix (M) during alteration on the CM parent body. Horizontal lines on this diagram represent slope-1/2 lines on a traditional three-isotope plot. Initial water (W_i) and rock (R_i) interact to form matrix (M_i) with an isotopic composition offset from the water composition by a fractionation factor that is represented by the length of line 1. The water evolves in isotopic composition as alteration proceeds along the line labeled 2. The matrix composition evolves along the dashed line 3. The line is dashed to represent that the matrix isotopic composition is constantly changing during alteration and ends at the final matrix composition (M_f). The earliest formed carbonates, which are in equilibrium with the water at point 4, are represented by C_i. The ellipse represents the variability of $\delta^{18}O$ and $\Delta^{17}O$. The fluid continues to evolve to its final composition (W_f), further changing the composition of the carbonates through various episodes of dissolution/reprecipitation (possibly freeze–thaw) following the path denoted by the solid line 5 and ending at C_f.

fluid. The point of this exercise has been to illustrate one way that our data can be reconciled with the Clayton and Mayeda (1984, 1999) model. Our data suggest that the principal conditions to be met are carbonate precipitation during the alteration sequence, partial exchange of oxygen isotopes between carbonate and water in samples that underwent more alteration, and either a slightly larger fractionation factor between serpen-
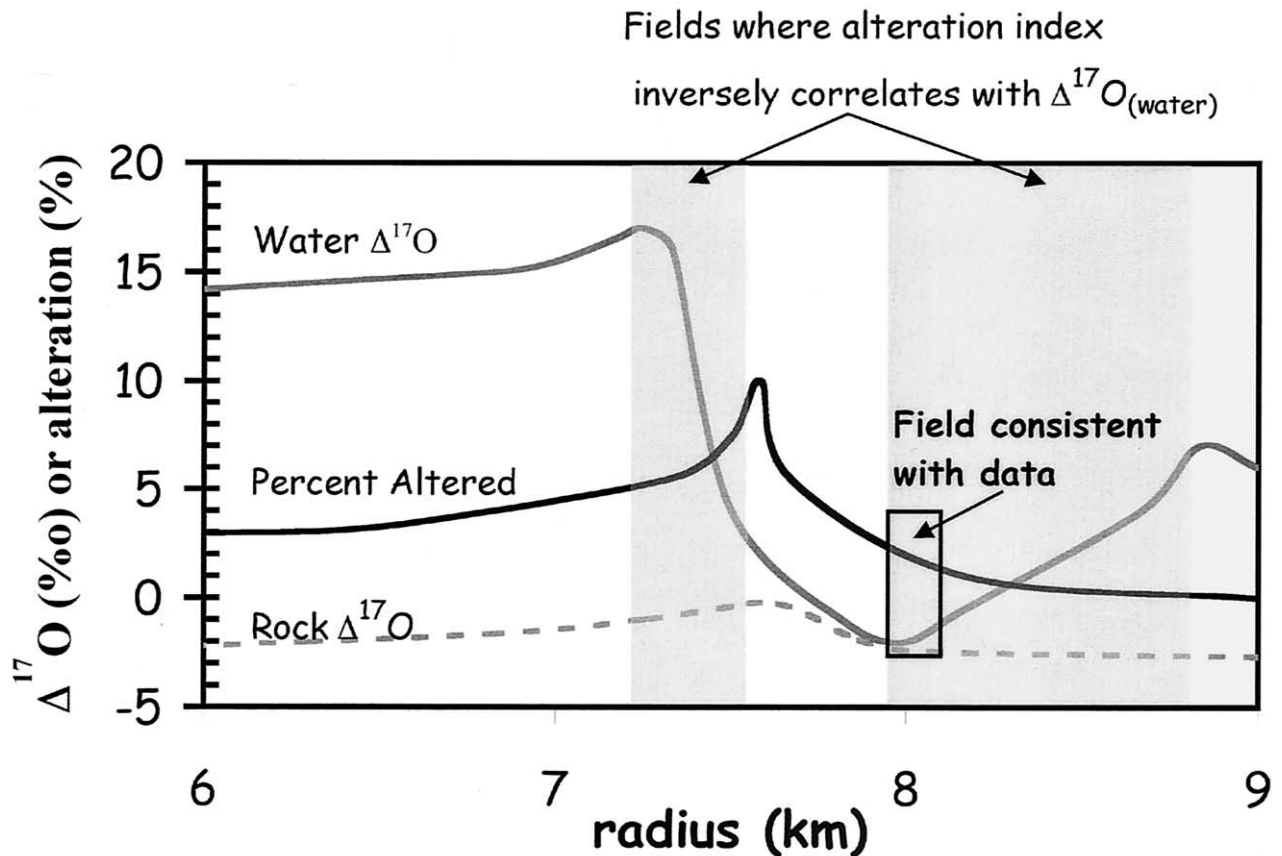
Fig. 5. Results from Young's (2001) thermal model for a 9-km-radius planetesimal. Data were extracted from figure 4 in Young (2001) for t = 0.5 my. Arrays are defined on the plot. The gray areas represent fields where alteration and $\Delta^{17}O$ of the water are inversely correlated. The small rectangular area is the region of the 9-km-radius body where the $\Delta^{17}O$ of the fluid is in agreement with the carbonate and matrix data (i.e., the data are anticorrelated with $\Delta^{17}O$ decreasing as alteration increases).

tine and water ($\alpha_{serpentine–water}$) or a smaller fractionation factor between carbonate and water ($\alpha_{carbonate–water}$).

Recently, Young and colleagues (Young et al., 1999; Young, 2001) presented a model to describe the isotopic evolution of the fluid phase in a system where fluids were mobile, and to explore the possibility that a system with mobile fluids can account for oxygen isotope observations in the meteorites. This open system model is attractive because many studies (e.g., Grimm and McSween, 1989; Wilson et al., 1999; Young et al., 1999) argue that heterogeneous fluid flow is a necessary consequence of chemical reaction in and heating of small primitive, ice-bearing planetesimals.

Young and colleagues (Young et al., 1999; Young, 2001) conclude generally that $\Delta^{17}O$, $\delta^{18}O$ and $\delta^{17}O$ values of the alteration products should increase as alteration increases. The CM carbonate data do not follow this relationship. However, the new observations can be explained by tracking the isotopic evolution of water in a restricted region of the Young (2001) model asteroid just downstream of the alteration front. Figure 5 shows results extracted from Young's (2001) model calculations for a 9-km-radius planetesimal. On the graph, data for amount of meteorite alteration, $\Delta^{17}O$ of the rock (anhydrous plus altered minerals), and $\Delta^{17}O$ of the water at the end of the simulation (i.e., at 0.5 my) are presented. The CM carbonate

data can be reconciled with this simulation of the $\Delta^{17}O$ of the water in a 100-m-thick zone ~1 km from the surface of the planetesimal, in a region where $\Delta^{17}O$ of the water decreases as alteration increases. This is consistent with assertions by Young and colleagues (Young et al., 1999; Young, 2001) that the different carbonaceous meteorite types derive from different radial shells in the parent planetesimals. One way that the flow model could more broadly fit the meteorite data would be if the initial water had a lower $\Delta^{17}O$ value, but also retained its high $\delta^{18}O$ value. This would cause the amplitude of the water $\Delta^{17}O$ line in Figure 5 to decrease, but would keep the same shape and might create a larger region of alteration in the planetesimal that samples lower $\Delta^{17}O$ values. This composition lies on the extrapolation of the evolutionary array for our model water and would be closer to the Clayton and Mayeda (1984, 1999) initial water than the Young (2001) initial water.

In summary, consideration of the carbonate isotopic data in the context of previously proposed models for aqueous alteration of carbonaceous chondrites has provided important insights into the evolving alteration conditions and allows refinements on models parameters to be made. For the Clayton and Mayeda (1999) model, the data are generally consistent with previous conclusions about the isotopic composition of the evolving fluid, with more altered samples largely reflecting

greater reaction progress and thus probably indicating more extended times of fluid exposure. For the data to be consistent with the flow models of Young (2001) and Young et al. (1999), the CM chondrites would have to sample a restricted region of the parent body near, but not at the surface. If this is the case, then the variation in $\Delta^{17}O$ value of the carbonate (and fluid) with MAI is caused by factors that are related to the fluid flow path and reaction history. The fit to the fluid flow models could be improved if model parameters are adjusted on the basis of the compositions recorded by the meteorites. Further data on secondary phases such as carbonate and sulfate (see Airieau et al., 2001) should provide additional constraints on these models.

4.2. Implications of Petrographic Observations

The petrographic observations of the carbonates are consistent with the hypothesis that the fluid evolved during alteration. The idea that different extents of interaction of carbonates with fluid in meteorites of different alteration index is consistent with the morphologies of the carbonates (Fig. 1) as described in the results section. Petrographic observations suggest that carbonates precipitated relatively early in the parent body alteration, consistent with their generally higher $\Delta^{17}O$ values than the matrix (Bunch and Chang, 1980; Johnson and Prinz, 1993; Benedix et al., 2000b,c). In the more altered samples (Nogoya and Cold Bokkeveld) carbonates continue to equilibrate (or dissolve and reprecipitate) as the fluid evolved isotopically, whereas carbonates in the less altered samples (such as Murchison and Murray) "freeze in" the earlier fluid composition. This is in agreement with petrographic studies of carbonates in Antarctic meteorites ALH 84034 (Brearley and Hutcheon, 2000) and Y-791198 (Brearley et al., 2001).

5. CONCLUSIONS

The results reported here add to the array of oxygen isotopic compositions of individual mineral phases in CM2 chondrites in several important ways. They provide further information about the aqueous alteration process that took place on the parent body and critical data that can be evaluated in the context of conceptual models of the alteration process. Although our data do not yet provide a means of discriminating between the closed system model (e.g., Clayton and Mayeda, 1984, 1999) and the open system model (e.g., Young et al., 1999; Young, 2001), they place constraints on the composition of the initial fluid, the isotopic evolution of the fluid phase, and the conditions of alteration.

The correlation of carbonate $\Delta^{17}O$ values with MAI (Fig. 3) tracks the evolution of fluid composition with alteration on the CM parent body. Similar $\Delta^{17}O$ values for calcite and dolomite fractions from the same splits of the same meteorites indicate that calcite and dolomite in each split precipitated from a single fluid reservoir. However, reversed calcite–dolomite fractionations ($\delta^{18}O_{dol} - \delta^{18}O_{cc}$), indicate that the fluid was itself subject to processes, such as freeze–thaw or evaporation, that fractionated isotopes in a mass-dependent way. The data as a whole indicate that the isotopic evolution of the fluid was similar to that predicted by the Clayton and Mayeda (1984, 1999) model, but that a slightly larger matrix–water fraction-

ation factor may apply (16 to 20‰ instead of 12‰). The data as a whole also indicate that the isotopic composition of the initial fluid was more like the Clayton and Mayeda (1984, 1999) initial water than the initial waters of Young and co-workers (Young et al., 1999; Young, 2001).

This work presents a new tool for evaluating fluid evolution in the primitive planetesimals that incubated the CM chondrite meteorites. The same approach can be applied to other secondary oxygen-bearing phases and primitive meteorite types. At present, our data do not rule out any of the proposed models for meteorite alteration; however, they provide important new constraints, and it is anticipated that further study will extend the impact of this methodology.

REFERENCES

Airieau S. A., Farquhar J., Jackson T. L., Leshin L. A., Thiemens M. H., and BaoH. (2001) Oxygen isotope systematics of CI and CM chondrite sulfate: Implications for evolution and mobility of water in planetesimals (abstract 1744). In *Lunar and Planetary Science,* Vol. 32. Lunar and Planetary Institute.

Al-Aasm I. S., Taylor B. E., and South B. (1990) Stable isotope analysis of multiple carbonate samples using selective acid extraction. *Chem. Geol.* **80,** 119–125.

Ash R. D., Young E. D., Alexander C. M. O'D., Rumble D. III and MacPherson G. J. (1999) Oxygen isotope systematics in Allende chondrules (abstract 1836). In *Lunar and Planetary Science,* Vol. 30. Lunar and Planetary Institute.

Baker L., Franchi I. A., Maynard J. M., Wright I. P., and Pillinger C. T. (1998) Measurement of oxygen isotopes in water from CI and CM chondrites (abstract 1740). In *Lunar and Planetary Science,* Vol. 29. Lunar and Planetary Institute.

Barber D. J. (1981) Matrix phyllosilicates and associated minerals in CM2 carbonaceous chondrites. *Geochim. Cosmochim. Acta* **45,** 945–970.

Benedix G. K., Leshin L. A., Farquhar J., Jackson T. L., and Thiemens M. H. (2000a) Carbonates in CM chondrites. Oxygen isotope geochemistry and implications for alteration on the CM parent body (abstract 1840). In *Lunar and Planetary Science,* Vol. 31. Lunar and Planetary Institute.

Benedix G. K., Cosarinsky M., and Leshin L. A. (2000b) Carbonate petrography along the CM chondrite alteration sequence. *Meteor. Planet. Sci.* **35,** A24.

Benedix G. K., Farquhar J., Leshin L. A., Jackson T. L., and Thiemens M. H. (2000c) The nature of the alteration on the CM parent body. *Meteor. Planet. Sci.* **35,** A24–A25.

Bhattacharya S. K. and Thiemens M. H. (1989) Effect of isotopic exchange upon symmetry dependent fractionation in the O+CO-CO_2 reaction. *Z. Naturforsch A.* **44,** 811–813.

Boggs S. A. Jr. (1987) *Principles of Sedimentology and Stratigraphy.* Merrill.

Brearley A. J. (1998) Carbonates in CM carbonaceous chondrites: Complex zoning revealed by high resolution cathodoluminescence studies (abstract 1216). In *Lunar and Planetary Science,* Vol. 29. Lunar and Planetary Institute.

Brearley A. J. and Jones R. H. (1998) Chondritic meteorites. In *Planetary Materials* (ed. J. J. Papike), chap. 3. Reviews in Mineralogy 36.

Brearley A. J., Saxton J. M., Lyon I. C., and Turner G. (1999) Carbonates in the Murchison CM chondrite: CL characteristics and oxygen isotopic compositions (abstract 1301). In *Lunar and Planetary Science,* Vol. 30. Lunar and Planetary Institute.

Brearley A. J. and Hutcheon I. D. (2000) Carbonates in the CM1 chondrite ALH 84034: Mineral chemistry zoning and Mn-Cr systematics (abstract 1407). In *Lunar and Planetary Science,* Vol. 31. Lunar and Planetary Institute.

Brearley A. J., Hutcheon I. D., and Browning L. B. (2001) Compositional zoning and Mn-Cr systematics in carbonates from the Y791198 CM2 carbonaceous chondrite (abstract 1458). In *Lunar and Planetary Science,* Vol. 32. Lunar and Planetary Institute.

Browning L. B., McSween H. Y. Jr., and Zolensky M. E. (1996) Correlated alteration effects in CM carbonaceous chondrites. *Geochim. Cosmochim. Acta* **60,** 2621–2633.

Browning L. and Bourcier W. (1998a) Constraints on the anhydrous precursor mineralogy of fine-grained materials in CM carbonaceous chondrites. *Meteor. Planet. Sci.* **33,** 1213–1220.

Browning L. B. and Bourcier W. L. (1998b) On the origin of rim textures surrounding carbonate grains in CM matrices (abstract 1533). In *Lunar and Planetary Science,* Vol. 29. Lunar and Planetary Institute.

Bunch T. E. and Chang S. (1980) Carbonaceous chondrites—II: Carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta* **44,** 1543–1577.

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

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

Clayton R. N. and Mayeda T. K. (1963) The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analyses. *Geochim. Cosmochim. Acta* **27,** 43–52.

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

Clayton R. N. and Mayeda T. K. (1999) Oxygen isotope studies of carbonaceous chondrites. *Geochim. Cosmochim. Acta* **63,** 2089–2104.

Dufresne E. R. and Anders E. (1962) On the chemical evolution of the carbonaceous chondrites. *Geochim. Cosmochim. Acta* **26,** 1085–1114.

Endress M. and Bischoff A. (1996) Carbonates in CI chondrites: Clues to parent body evolution. *Geochim. Cosmochim. Acta* **60,** 489–507.

Farquhar J., Thiemens M. H., and Jackson T. (1998) Atmosphere–surface interactions on Mars: $\Delta^{17}O$ measurements of carbonate from ALH 84001. *Science* **280,** 1580–1582.

Farquhar J. and Thiemens M. H. (2000, 1997) Oxygen cycle of the Martian atmosphere–regolith system: $\Delta^{17}O$ of secondary phases in Nakhla and Lafayette. *J. Geophys. Res.* **105,** 11991–1.

Farquhar J., Benedix G., Airieau S., Leshin L. A., Thiemens M. H., and Jackson T. L. (2002) Initial water compositions: Aqueous alteration of planetesimals (abstract 1850). In *Lunar and Planetary Science,* Vol. 33. Lunar and Planetary Institute.

Farver J. R. (1994) Oxygen self-diffusion in calcite: Dependence on temperature and water fugacity. *Earth Planet. Sci. Lett.* **121,** 575–587.

Fredriksson K. and Kerridge J. F. (1988) Carbonates and sulfates in CI chondrites: Formation by aqueous activity on the parent body. *Meteoritics* **23,** 35–44.

Friedman I., O'Neil J. R. (1977) Compilation of stable isotope fractionation factors of geochemical interest. Prof. Pap. 440-KK. U.S. Geological Survey.

Fuchs L. H., Olsen E., and Jensen K. J. (1973) Mineralogy mineral chemistry composition of Murchison (C2) meteorite. *Smithsonian Contrib. Earth Sci.* **10,** 1–39.

Grady M. M., Wright I. P., Swart P. K., and Pillinger C. T. (1988) The carbon and oxygen isotopic composition of meteoritic carbonates. *Geochim. Cosmochim. Acta* **52,** 2855–2866.

Gregory R. T. and Criss R. E. (1986) Isotopic exchange in open and closed systems. In *Stable Isotopes in High Temperature Geological Processes* (eds. J. W. Valley, H. P. Taylor Jr., and J. R. O'Neil), chap. 3. Reviews in Mineralogy 16.

Grimm R. E. and McSween H. Y. Jr (1989) Water and the thermal evolution of carbonaceous chondrite parent bodies. *Icarus* **82,** 244–280.

Horita J., Wesolowski D. J., and Cole D. R. (1993a) The activity–composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions: I. Vapor–liquid water equilibration of single salt solutions from 50 to 100°C. *Geochim. Cosmochim. Acta* **57,** 2797–2817.

Horita J., Cole D. R., and Wesolowski D. J. (1993b) The activity–composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions: II Vapor–liquid water equilibration of mixed salt solutions from 50 to 100°C and geochemical implications. *Geochim. Cosmochim. Acta* **57,** 4703–4711.

Horita J., Cole D. R., and Wesolowski D. J. (1995) The activity–composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions: III Vapor–liquid water equilibration of NaCl solutions to 350°C. *Geochim. Cosmochim. Acta* **59,** 1139–1151.

Johnson C. A. and Prinz M. (1993) Carbonate compositions in CM and CI chondrites and implications for aqueous alteration. *Geochim. Cosmochim. Acta* **57,** 2843–2852.

Kerridge J. F. and Bunch T. E. (1979) Aqueous activity on asteroids: Evidence from carbonaceous meteorites. In *Asteroids* (ed. T. Gehrels), pp. 745–765.

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

Matsuhisa Y., Goldsmith J. R., and Clayton R. N. (1978) Mechanisms of hydrothermal crystallization of quartz at 250°C and 15 kbar. *Geochim. Cosmochim. Acta* **42,** 173–182.

McCrea J. M. (1950) On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.* **18,** 849–857.

McSween H. Y. Jr. (1977a) The composition of carbonaceous chondrite matrix. *Geochim. Cosmochim. Acta* **41,** 1145–1161.

McSween H. Y. Jr. (1977b) On the nature and origin of isolated olivine grains in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **41,** 411–418.

McSween H. Y. Jr. (1979) Alteration in CM carbonaceous chondrites inferred from modal and chemical variations in matrix. *Geochim. Cosmochim. Acta* **43,** 1761–1770.

McSween H. Y. Jr. (1987) Aqueous alteration in carbonaceous chondrites: Mass balance constraints on matrix mineralogy. *Geochim. Cosmochim. Acta* **51,** 2469–2477.

Metzler K., Bischoff A., and Stöffler D. (1992) Accretionary dust mantles in CM chondrites: Evidence for solar nebula processes. *Geochim. Cosmochim. Acta* **56,** 2873–2897.

Miller M. F. (2002) Isotopic fractionation and the quantification of ^{17}O in the oxygen three-isotope system: An appraisal and geochemical significance. *Geochim. Cosmochim. Acta* **66,** 1881–1889.

Morse J. W. and Mackenzie F. T. (1990) *Geochemistry of Sedimentary Carbonates.* Elsevier.

O'Neil J. R., Clayton R. N., and Mayeda T. K. (1969) Oxygen isotope fractionation in divalent metal carbonates. *J Chem. Phys.* **51,** 5547–5558.

Richardson S. M. (1978) Vein formation in the C1 carbonaceous chondrites. *Meteoritics* **13,** 141–159.

Riciputi L. R., McSween H. Y. Jr., Johnson C. A., and Prinz M. (1994) Minor and trace element concentrations in carbonates of carbonaceous chondrites, and implications for the compositions of co-existing fluids. *Geochim. Cosmochim. Acta* **58,** 1343–1351.

Rosenbaum J. and Sheppard S. M. F. (1986) An isotopic study of siderites, dolomites, and ankerites at high temperature. *Geochim. Cosmochim. Acta* **50,** 1147–1150.

Rowe M. W., Clayton R. N., and Mayeda T. K. (1994) Oxygen isotopes in separated components of CI and CM meteorites. *Geochim. Cosmochim. Acta* **58,** 5341–5347.

Savin S. M. and Lee M. (1988) Isotopic studies of phyllosilicates. In *Hydrous Phyllosilicates* (ed. S. W. Bailey), chap. 8. Reviews in Mineralogy 19.

Tomeoka K. and Buseck P. R. (1985) Indicators of aqueous alteration in CM carbonaceous chondrites: Microtextures of a layered mineral containing Fe, S, O, and Ni. *Geochim. Cosmochim. Acta* **49,** 2149–2163.

Urey H. C. (1947) The thermodynamic properties of isotopic substances. *J. Chem. Soc.* **592,** 562–581.

Wenner D. B. and Taylor H. P. Jr. (1971) Temperatures of serpentinization of ultramafic rocks based on $^{18}O/^{16}O$ fractionation between coexisting serpentine and magnetite. *Contrib. Mineral. Petrol.* **32,** 165–185.

Wilson L., Keil K., Browning L. B., Krot A. N., and Bourcier W. (1999) Early aqueous alteration explosive disruption and reprocessing of asteroids. *Meteor. Planet. Sci.* **34,** 541–557.

Young E. D. (2001) The hydrology of carbonaceous chondrite parent bodies and the evolution of planet progenitors. *Phil. Trans. R. Soc. Lond. A* **359,** 2095–2110.

Young E. D. and Russell S. S. (1998) Oxygen reservoirs in the early solar nebula inferred from an Allende CAI. *Science* **282,** 452.

Young E. D., Ash R. D., England P., and Rumble D. (1999) Fluid flow in chondritic parent bodies: Deciphering the compositions of planetesimals. *Science* **286,** 1331–1335.

Young E. D. and Ash R. D. (2000) The hydrology of icy planetesimals inferred from carbonaceous chondrite oxygen isotope ratios (abstract 1658). In *Lunar and Planetary Science,* Vol. 31. Lunar and Planetary Institute.

Zheng Y.-F. (1993) Calculation of oxygen isotope fractionation in hydroxyl-bearing silicates. *Earth Planet. Sci. Lett.* **120,** pp. 247–263.

Zolensky M. E., Bourcier W. L., and Gooding J. L. (1989) Aqueous alteration on the hydrous asteroids: Results of EQ3/6 computer simulations. *Icarus* **78,** 411–425.

Zolensky M., Barrett R., and Browning L. (1993) Mineralogy and composition of matrix and chondrule rims in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **57,** 3123–3148.

Zolensky M. E., Mittlefehldt D. W., Lipschutz M. E., Wang M.-S., Clayton R. N., Mayeda T. K., Grady M. M., Pillinger C., and Barber D. (1997) CM chondrites exhibit the complete petrologic range from type 2 to 1. *Geochim. Cosmochim. Acta* **61,** 5099–5115.