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Hydrogen isotope evidence for the origin and evolution of the carbonaceous chondrites

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Abstract—We present new hydrogen isotope data for separated matrix, hydrated chondrules, and other hydrated coarse silicate fragments from nine carbonaceous chondrites. These data were generated using a micro-analytical method involving stepped combustion of tens to hundreds of micrograms of hydrous solids. We also re-evaluate hydrogen isotope data from previous conventional stepped combustion experiments on these and other carbonaceous chondrites.

Hydrogen isotope compositions of matrix and whole-rock samples of CM chondrites are correlated with oxygen isotope indices, major and minor-element abundances, and abundance and isotope ratios of other highly volatile elements. These correlations include a monotonic decrease in δD with increasing extent of aqueous alteration and decreasing abundances of highly volatile elements (including C, N and Ar), between extremes of $\sim 0\%$ (least altered, most volatile rich) and $\sim 200\%$ (most altered, least volatile rich). In plots involving only abundances and/or isotope ratios of highly volatile elements, CI chondrites fall on the high- δD , volatile rich end of the trends defined by CM chondrites; i.e., CI chondrites resemble the least altered CM chondrites in these respects. These trends suggest the protoliths of the CM chondrites (i.e., before aqueous alteration) contained an assemblage of volatiles having many things in common with those in the CI chondrites. If so, then the volatile-element inventory of the CI chondrites was a more widespread component of early solar system objects than suggested by the scarcity of recognized CI meteorites. Differences in volatile-element chemistry between the CI and average CM chondrites can be attributed to aqueous alteration of the latter.

Previous models of carbonaceous chondrite aqueous alteration have suggested: (1) the protoliths of the CM chondrites are volatile poor objects like the CO or CV chondrites; and (2) the CI chondrites are more altered products of the same process producing the CM chondrites. Both suggestions appear to be inconsistent with hydrogen isotope data and other aspects of the volatile-element geochemistry of these rocks. We present a model for aqueous alteration of the CM chondrites that reconciles these inconsistencies and suggests revised relationships among the major subtypes of carbonaceous chondrites. Our model requires, among other things, that the water infiltrating CM chondrites had a δD value of $\sim -158\%$, consistent with initial accretion of CM parent bodies at ~ 4 AU. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

The carbonaceous chondrites are among the most primitive solid objects in the solar system (MacPherson et al., 1988; Anders and Grevesse, 1989) and plausibly sample building blocks of the terrestrial planets, moons and asteroids (Anders, 1977; Wetherill and Chapman, 1988). Although they are generally less differentiated and metamorphosed than other meteorite groups, the carbonaceous chondrites are compositionally and texturally diverse (VanSchmus and Wood, 1967), in part reflecting processes acting on them after their accretion (McSween, 1979). One of the more important of these processes was aqueous alteration, either by water formed from melting co-accreted ices or by infiltration of externally derived water produced elsewhere on their meteorite parent bodies (Browning et al., 1996). In this study, we examine the hydrogen isotope compositions of CV, CO, CM and CI carbonaceous chondrites and discuss the significance of these data for the origin of water with which they reacted and the consequences of those reactions for other aspects of their geochemistry. We particularly focus on the CM chondrites, which preserve the most diverse record of aqueous alteration. One of the findings of this study

is a correlation between hydrogen and oxygen isotopes that appears to require revision of previous models of the alteration of and relationships among the various carbonaceous chondrite groups (Clayton and Mayeda, 1999; Young et al., 1999). For this reason, we begin by reviewing the background of these previous models and the observations on which they are based.

The various classes of carbonaceous chondrites differ systematically from one another in their abundances of volatile elements (e.g., carbon, nitrogen and noble gases; Kerridge, 1985). These differences are best described for the CV, CO, CM and CI types, which are the most numerous and well studied. Of these, the CV and CO types are uniformly poor in volatiles, the CI type are uniformly rich in volatiles, and the CM type span a range of intermediate volatile abundances (Fig. 1). Similarly, there are systematic textural differences between these groups (VanSchmus and Wood, 1967; McSween, 1979; Browning et al., 1996): The CO and CV chondrites are rich in anhydrous silicates, including chondrules, CAIs and fine-grained matrix silicates. The CM chondrites also contain these constituents but are rich in hydrous silicates (mostly serpentines), likely produced by reaction between aqueous fluid and preexisting anhydrous minerals. The CI chondrites are dominated by hydrous minerals and lack obvious remains of CAIs and chondrules. A reasonable explanation of these observations is that all the carbonaceous chondrite types accreted as rela-

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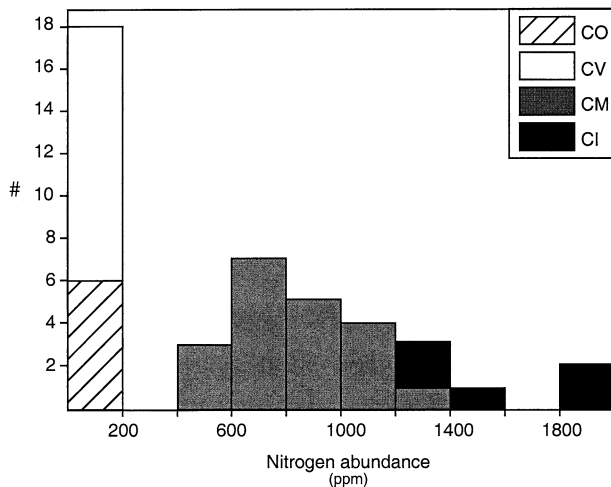


Fig. 1. Nitrogen abundances (in ppm by weight) in whole-rock samples of well-studied groups of carbonaceous chondrites. Data from Kerridge (1985). These groups can be subdivided into volatile-poor (CO and CV types), volatile-rich (CI type) and intermediate volatile abundance (CM type). Similar distributions are observed for carbon, noble gases and, less consistently, hydrogen abundances.

tively volatile-poor collections of anhydrous silicates like the CO and CV chondrites, and those anhydrous components were transformed by aqueous alteration into hydrous silicates and other phases—partially in the case of the CM chondrites and completely in the case of the CI chondrites.

The differences in volatile content and mineralogy between the CV, CO, CM and CI chondrites are mirrored by differences in their oxygen isotope geochemistry (Clayton and Mayeda, 1999). In a plot of $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ (Fig. 2), whole-rock samples of the volatile-poor CV and CO chondrites fall on or near a line of slope 1 also defined by unaltered CAIs and chondrules from CM chondrites. This line has been called the ‘carbonaceous chondrite anhydrous mineral’ line (or CCAM; Clayton and Mayeda, 1999) and has been interpreted to reflect oxygen isotope exchange between ^{16}O -rich solids and ^{16}O -poor vapor when CAIs and chondrules were formed and/or re-heated. In contrast, the CI chondrites fall on or near the terrestrial fractionation line (a line of slope ~ 0.5 passing through the compositions of common terrestrial solids and waters; Robert et al., 1992) and are higher in both $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ than the CV or CO chondrites or anhydrous silicates in the CM chondrites. Finally, whole-rock and matrix samples of the CM chondrites have oxygen isotope compositions defining a line of intermediate slope stretching between the CV and CO chondrites at one extreme and the CI chondrites at the other. Thus, the CM chondrites appear to provide a ‘link’ between the volatile-poor, ^{16}O -rich CO and CV chondrites on one hand and the volatile-rich, ^{16}O -poor CI chondrites on the other, suggesting these groups might collectively define a single, continuous petrogenetic trend.

The petrographic and geochemical constraints summarized above are the basis for several models of the protoliths and aqueous alteration of various carbonaceous chondrite types. These models suggest that the protoliths of the CM and CI chondrites initially accreted as collections of anhydrous solids (and perhaps other minor components) broadly resembling the

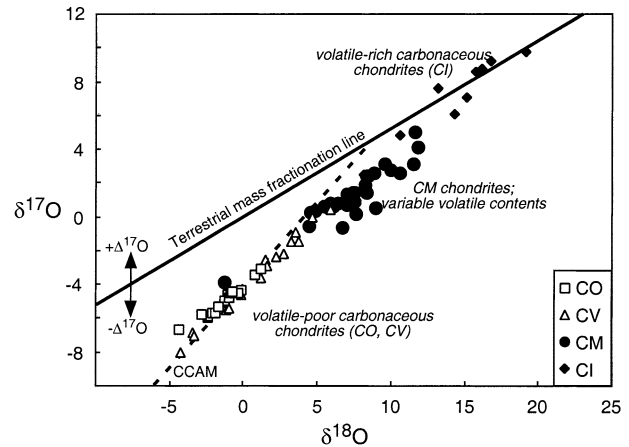


Fig. 2. Oxygen isotope compositions (in per mil vs. SMOW) of whole-rock samples of well-characterized groups of carbonaceous chondrites. Data after Clayton and Mayeda (1999). The terrestrial mass fractionation line (range of compositions of terrestrial rocks and waters) is shown as a solid heavy line. The dashed line of slope 1 is the ‘CCAM’, defined by anhydrous minerals in carbonaceous chondrites. Arrows indicate the vectors implied by variations in the index ‘ $\Delta^{17}\text{O}$ ’ defined in the text. Note that volatile-poor carbonaceous chondrite types fall on or near the CCAM line at low values of $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$; volatile-rich carbonaceous chondrites fall on or near the terrestrial mass fractionation line at high values of $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$; and carbonaceous chondrites having intermediate volatile contents generally have oxygen isotope compositions between these two groups. CM and CI chondrites that are inferred to have undergone significant amounts of oxygen isotope fractionation due to dehydration metamorphism are excluded.

CV and/or CO chondrites and having oxygen isotope compositions falling on or near the CCAM line in Figure 2 (although not necessary at a single point on that line; Clayton and Mayeda, 1999; Young et al., 1999; Airieau et al., 2001; Farquhar et al., 2002; Young, 2002). These protoliths are suggested to have reacted with aqueous fluid having an oxygen isotope composition falling on or above the terrestrial mass fractionation line in Figure 2, producing increasingly hydrated rocks with increasingly higher $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$ (Young et al., 1999; Clayton and Mayeda, 1999; Airieau et al., 2001; Farquhar et al., 2002; Young, 2002). By this interpretation, the CI chondrites are the extreme product of aqueous alteration, the CM chondrites span a range in extent of alteration, and the CO and CV chondrites are relatively unmodified samples of the protoliths of this process. Young et al. (1999) suggest that all types of carbonaceous chondrites could even be the products of reacting a single protolith with a single initial fluid—perhaps on a single parent body. Other studies have suggested that aqueous alteration histories of the various carbonaceous chondrite types are analogous to one another but acted upon two or more protolith types, and in particular that the protoliths of the CI chondrites differed in oxygen isotope composition from the protoliths of the CM chondrites (Clayton and Mayeda, 1999).

2. PRIOR HYDROGEN ISOTOPE STUDIES OF CARBONACEOUS CHONDRITES

The hydrogen isotope geochemistry of carbonaceous chondrites is an attractive target for testing and refining our understanding of their aqueous alteration because hydrogen is abun-

dant in many of these rocks (Kerridge, 1985) and its isotopic composition presumably reflects, at least in part, that of the fluids with which they reacted. Previous studies can be divided into three groups: those determining D/H ratios of water released by combustion or pyrolysis of untreated whole rock samples (Robert and Epstein, 1982; Kerridge, 1985; Robert et al., 1987, and references therein); those analyzing water released from heating extracts and/or residues produced by chemical pretreatments of these rocks (Briggs, 1963; Kolodny et al., 1980; Geiss and Reeves, 1981; Smith and Rigby, 1981; Kerridge, 1983; Halbout et al., 1986; Epstein et al., 1987; Pizzarello et al., 1991; Krishnamurthy et al., 1992; Cronin et al., 1993; Ehrenfreund et al., 2001); and ion microprobe studies designed to search for extreme isotopic variations over short spatial scales (Hinton et al., 1983; McKeegan and Zinner, 1984; Deloule and Robert, 1995; Deloule et al., 1998). The second of these groups of studies (focused on chemical extracts) is arguably the most noteworthy for the remarkable D enrichments they reveal in hydrocarbons and the significance of their findings for the organic chemistry of the early solar nebula. However, the first group of studies might be more important for understanding aqueous alteration processes because they consider the complete hydrogen inventory of these rocks, most of which is hosted by fine-grained hydrous silicates.

The hydrogen isotope compositions of untreated whole-rock samples of CV, CO, CM and CI carbonaceous chondrites are summarized in Figure 3 (data reproduced from Kerridge, 1985). Most analyses of all four chondrite types fall within a range between ~ -250 and $+250$ ‰ that has been referred to as broadly 'terrestrial' (i.e., comparable to the earth's oceans and rocks; Robert et al., 1987). The exceptions range up to 2150‰—comparable to the most D-rich compositions characteristic of hydrocarbons isolated from carbonaceous chondrites. Repeated analyses of the same samples reveal that both broadly 'terrestrial' and extremely D-rich compositions can be obtained from different subsamples of the same rock, suggesting that one or more isotopically distinct components are present as 'nuggets'. Finally, there are no obvious differences in the range of δD exhibited by the well-sampled groups (CV, CO, CM and CI), except that CI chondrites lack any measurements ≤ 0 ‰, which are common in CV, CO and CM chondrites.

Previous interpretations of the data summarized in Figure 3 focus on the isotopic contrast between hydrogen of broadly 'terrestrial' isotopic composition typical of most samples on one hand and D-rich hydrogen observed in a few samples on the other (Kolodny et al., 1980; Robert and Epstein, 1982; Kerridge, 1983, 1985; Robert et al., 1987). To the best of our knowledge, no one has suggested a detailed interpretation of variations *within* the broadly 'terrestrial' range (although see Robert et al., 1987, for discussion of differences in δD between two putative components of Allende and several ordinary chondrites). It would be reasonable to suppose that these variations reflect mixing of abundant D-poor hydrous minerals with unknown proportions of extremely D-rich organics that are known to exist in these rocks.

We have re-evaluated the hydrogen isotope geochemistry of the carbonaceous chondrites in two ways: First, we made new measurements of the hydrogen isotope compositions of several of the best-characterized CV, CM and CI chondrites using a method that permits stepped-heating analyses of small quanti-

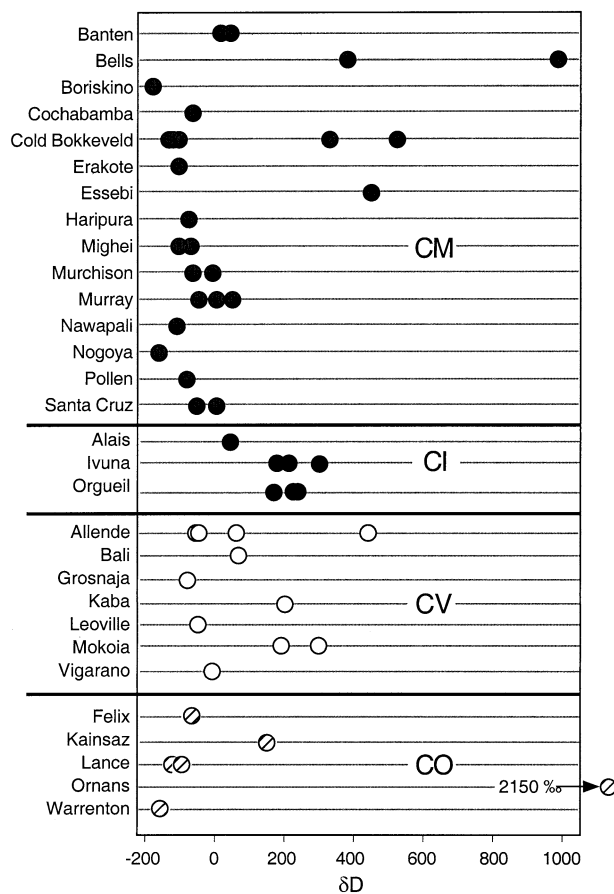


Fig. 3. Hydrogen isotope composition (δD in per mil vs. SMOW) of whole-rock samples of the well-characterized carbonaceous chondrite groups. Repeat measurements of the same sample are shown as separate points on the same gray, horizontal line. Data after Kerridge (1985). Note that ranges for each group are large and generally overlap one another.

ties (tens to hundred of micrograms) of water-rich materials. This method has the advantage of allowing us to analyze texturally resolved components (e.g., matrix vs. chondrules) that might differ from one another in δD , while preserving the relatively high accuracy and precision of conventional vacuum extraction techniques. Second, we compiled and critically examined previous conventional measurements of the hydrogen isotope compositions of whole-rock samples of these and related samples. These data suffer from the analysis of bulk samples of heterogeneous materials, but provide important constraints on relationships between hydrogen isotopes and other volatile elements analyzed on the same sample splits. In the following section (section 3), we detail our method and new results and compare these results to other known geochemical properties of the studied samples, after-which (section 4) we re-examine previous whole-rock data to determine whether they are consistent with and expand upon the systematics revealed by our measurements, and finally (section 5) we discuss the significance of our findings for understanding the origin and evolution of the CO, CV, CM and CI chondrites.

Table 1. Samples and characteristics.

Type	Sample	Sub-sample	$\delta^{18}\text{O}_{\text{whole rock}}$	$\delta^{17}\text{O}_{\text{whole rock}}$	$\delta^{18}\text{O}_{\text{matrix}} - \delta^{18}\text{O}_{\text{whole rock}}$	Alteration index	ppm N
CV	Allende	CIT collections	1.5	-2.7	1.9	nd	21
CV	Mokoia	CIT collections	3.5	-0.9	1.0	nd	66
CM	LEW 85311	Sub-sample 46	-1.2	-3.9	9.5	nd	nd
CM	Murchison	ME 2684 #22	7.3	1.2	5.4	0.43	802
CM	Murray	ME 2612 #5	7.5	0.9	3.7	0.57	1005
CM	Mighei	CIT collections	7.6	1.4	3.9	0.77	750
CM	Cold Bokkeveld	ME 1736 #18	10.0	2.8	2.1	1.03	880
CI	Orgueil	ME 509 #14	16.2	8.8	na	nd	1418
CI	Ivuna	USNM 2478	16.8	9.2	na	nd	1855

Data from Kerridge (1985), Browning et al. (1996), and Clayton and Mayeda (1999). nd: not determined. Sub-samples labeled 'CIT collections' were taken from fractions of these rocks initially allocated to S. Epstein or D. Burnett.

3. MICRO-ANALYSIS OF THE D/H RATIOS OF CV, CM AND CI CHONDRITES

3.1. Samples

We determined the hydrogen isotope compositions of components of five CM chondrites—Murchison, Murray, Mighei, Cold Bokkeveld and LEW 85311—two CV chondrites—Allende and Mokoia—and two CI chondrites—Ivuna and Orgueil. All CM and CV chondrites considered in this study are of the C2 or C3 petrographic grade (i.e., chondrule bearing and weakly or unmetamorphosed). Both CI chondrites examined in this study are of the C1 petrographic grade (i.e., chondrule-free and unmetamorphosed). These samples were acquired from the Field Museum of Natural History in Chicago, Illinois (courtesy of Mini Wadhwa), the Smithsonian Institution in Washington, D.C. (courtesy of Tim McCoy), and the Johnson Space Center in Houston, Texas (courtesy of the Antarctic Meteorite Working Group). Individual subsamples examined in this study are listed in Table 1, along with select aspects of their petrology, mineralogy, and geochemistry. These data are reproduced from Kerridge (1985), Browning et al. (1996), and Clayton and Mayeda (1999). The relative extents of aqueous alteration in the samples considered in this study inferred from petrography, Browning et al.'s (1996) alteration index (based on phyllosilicate chemistry), and oxygen isotope geochemistry is approximately as follows: Ivuna \sim Orgueil $>$ Cold Bokkeveld $>$ Mighei \sim Murray $>$ Murchison $>$ LEW 85311 \sim Allende \sim Mokoia.

Fragments of matrix material, individual aqueously altered chondrules, and altered coarse silicate fragments of uncertain origin (either chondrule fragments or CAIs) were separated from these samples by hand picking under a binocular microscope. Analyzed fragments typically weighed \sim 100 to 300 μg . We estimate that matrix samples lack coarse mineral grains larger than \sim 30 μm and that separated chondrules are \sim 99+% free of adhered matrix (each of these samples is an interior fragment of a manually dis-aggregated chondrule). Altered coarse silicate fragments are less well defined and likely include adhered matrix that we could not visually discriminate from hydrous minerals replacing initially anhydrous silicate.

3.2. Methods

All separated materials were analyzed for their hydrogen isotope compositions using a method of on-line stepped com-

bustion, reduction of evolved water, and continuous flow mass spectrometry described by (Eiler and Kitchen, 2001). Briefly, this method involves the following procedure: (1) samples are loaded in a horizontal 0.125-in O.D. baked alumina tube and heated overnight at \sim 50°C under a He flow of \sim 30 to 50 cm^3/min ; (2) a movable resistance heater positioned over an empty portion of the sample tube is cycled in temperature from 25 to 1200°C one or more times and the blank determined by collecting and analyzing water from the sample tube every several minutes using methods summarized below; (3) the resistance heater is slid over the portion of the alumina tube holding the sample and heated in several steps over a period of \sim 30 to 120 min; water evolved from the sample tube into the He stream is cryogenically collected in a capillary of deactivated fused silica and periodically (every 2–15 min) purged through a reduction furnace (of either graphite and platinum or uranium filings) where it is converted to H_2 , which is swept into the source of a Finnigan Matt Delta-plus gas source mass spectrometer and HH^+ and HD^+ simultaneously detected as brief, time-varying signals.

This analytical method has accuracy and precision for water molarity of \sim 5% relative, and accuracy and precision for D/H of \sim 2 to 3‰ (Eiler and Kitchen, 2001). All measurements must be corrected for blank contributions, which vary from negligible ($<$ 1% of recovered water) to almost complete dominance of the collected water, depending on the water content of the sample, the sample temperature, and the duration of prior heating at that temperature. Blanks are generally reproducible in both size (\pm \sim 5% relative) and isotopic composition (\pm \sim 2–5‰) during a given analytical session and therefore can be subtracted from sample measurements with relative confidence. Blanks influencing measurements reported in this study are substantially less than those previously reported in studies using similar apparatus (Eiler and Kitchen, 2001; Eiler et al., 2002) because components that most strongly contribute to the blank (glass, metal and graphite) were replaced with lower-blank materials (baked ceramic alumina and poly-ether-etherketone, or PEEK).

The accuracy of our stepped-heating analyses was checked by analysis of \sim 20- to 30- μg aliquots of a serpentine standard acquired from Bruce Taylor (Geological Survey of Canada) and having a nominal $\delta\text{D}_{\text{SMOW}}$ value of $-81.4 \pm 0.5\text{‰}$ (1σ) (B. Taylor, personal communication). The average $\delta\text{D}_{\text{SMOW}}$ value for eight analyses of this material using our methods was

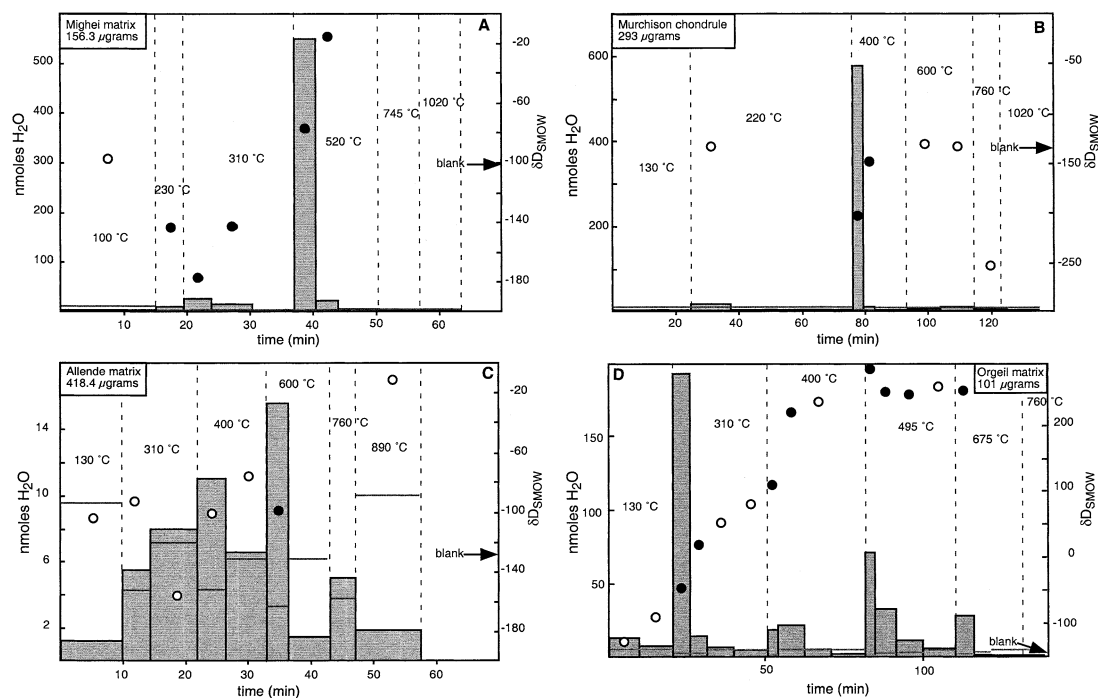


Fig. 4. Representative stepped-heating experiments conducted on CM chondrite matrix (A), a chondrule separated from a CM chondrite (B), matrix of a water-poor CV chondrite (C) and matrix of a CI chondrite (D). The heights of gray boxes indicate the yields of water released over each time interval and refer to the left vertical axis. All yields of sample water have been corrected for blank contributions; horizontal gray lines (generally near the bottom axis) indicate the size of the blank for each time step. Circles indicate the δD (vs. SMOW) of water released at each time step and refer to the right vertical axis. All have been blank corrected. Filled circles indicate time steps in which recovered water was $< 25\%$ blank, unfilled circles are time steps with $> 25\%$ blank contributions; these latter data are relatively uncertain. The δD of the blank is indicated with an arrow on the right axis. See text for discussion of these data and similar data on other samples. Full stepped-heating release data for other samples are provided in the Electronic Annex (Elsevier Website, Science Direct).

$-81.1 \pm 3.6\%$ (1σ) after subtracting the blank contribution ($\sim 2\text{--}5\%$ of the total H_2O recovered) but not considering any other method- or instrument-specific corrections. We applied a daily correction to all sample measurements equal to the difference between the nominal and measured values for this serpentine standard on that day ($\sim 0\text{--}5\%$). These corrections are small in comparison to the intersample differences examined in this study and do not significantly impact any of our interpretations.

3.3. Results

Figures 4a through 4d present representative results of stepped-heating experiments conducted on a subset of samples examined in this study. The release spectra for the samples most important to our interpretations—matrix and hydrous chondrules from CM chondrites—are relatively simple (Figs. 4a and 4b): Most of the water released from these materials is evolved over a narrow temperature interval near 500°C , and blank contributions are a small fraction of that water. All such samples also typically evolve a variable but generally small amount of water at temperatures near 250°C having an isotopic composition similar to our laboratory blank. We infer that this component is terrestrial contamination either introduced during our sample preparation and analysis, or perhaps added to these samples before entering our laboratory. This interpretation is

consistent with recent measurements of $\Delta^{17}\text{O}$ on water released by stepped pyrolysis of CM chondrites (Baker et al., 2002). We disregard this minor component of nominally terrestrial water when calculating the integrated δD values of the matrix and chondrules of CM chondrites. While this is only one of several possible interpretations, the integrated δD values of these samples are dominated by one or two large, high-temperature steps in each experiment and are minimally influenced by inclusion or exclusion of minor components extracted during other steps.

Analyses of the water-poor CV chondrites and the CM chondrite, LEW 85311, yielded amounts of water barely resolved from our analytical blanks (Fig. 4c). Similar results were previously obtained by conventional stepped-heating experiments on these and similar samples (Kerridge, 1985). Values of δD for these samples are correspondingly less certain, and are particularly suspect when similar to our blank ($\sim -100\%$; e.g., Allende matrix). We have little confidence that the measured δD values of these materials (either our measurements or previous conventional stepped heating extractions) accurately reflect the δD values of their preterrestrial components. However, the importance of these samples for our interpretations stems from the fact that they are hydrogen poor, regardless of their δD , and of this we are confident.

Analyses of CI chondrites yield abundant water that is well-resolved from our analytical blank both in amount and isotopic

Table 2. Bulk δD values and water-contents, this study.

Type	Matrix	wt.% H ₂ O	δD	Altered coarse silicate	wt.% H ₂ O	δD
CV	Allende	0.24	-101			
CV	Mokoia	0.97	-1.3			
CM	LEW 85311	0.17	BDL	Murchison chondrule 1	3.88	-200
CM	Murchison 1	7.11	-31	Murchison chondrule 2	2.49	-185
CM	Murchison 2	9.25	-34	Murchison silicate frag.	4.36	-123
CM	Mighei	7.33	-82	Murray silicate frag. 1	2.84	-183
CM	Murray	6.7	-119	Murray silicate frag. 2	1.98	-147
CM	Cold Bokkeveld	9.13	-197	Cold Bokkeveld chondrule	8.64	-191
CI	Orgueil 1	9.19	93			
CI	Orgueil 2	7.75	97			
CI	Orgueil 3	7.3	112			
CI	Ivuna 1	6.65	77			
CI	Ivuna 2	9.09	133			

BDL: Below detection limit. All values in per mil vs. SMOW.

composition (Fig. 4d), and we find repeat measurements of the same sample to be relatively reproducible (Table 2; Fig. 5). All stepped-heating spectra for these samples show a gradual rise in δD with increasing temperature that could be interpreted to reflect mixing between terrestrial and preterrestrial components. However, relatively low- δD water evolved from these samples at low temperatures is far more abundant than the terrestrial contamination observed in CM or CV chondrites (Figs. 4a–4c), and differs significantly in δD from our laboratory blank. It seems unlikely to us that terrestrial contamination would manifest itself as such an abundant and reproducible component, particularly given the care with which veins or

other non-representative portions of these samples were avoided by our micro-analyses. Nevertheless, it is difficult to know whether this variation in δD with increased heating reflects differences in δD between ‘high temperature’ and ‘low temperature’ water intrinsic to these samples, or decreasing contributions from relatively abundant terrestrial contamination with increasing heating. Measurements of the $\Delta^{17}O$ values of water evolved from CI chondrites (Baker et al., 2002) are unlikely to resolve this question because bulk oxygen in the CI chondrites resembles terrestrial materials in this index. We conclude that there is uncertainty about the causes of isotopic variations observed over the course of stepped heating experiments of CI chondrites, but no clear basis for disregarding lower- δD components. We therefore include all temperature steps when calculating integrated δD values of CI chondrites (Table 2).

Full stepped heating release spectra for all samples considered in this study, including data for blanks, are provided in the Electronic Annex (Elsevier Website, Science Direct). Table 2 and Figure 5 present integrated δD values of water released from all samples analyzed in this study (i.e., summing water released in each step, with exceptions as described above). We make no specific interpretations of the details of the stepped release spectra in the remainder of this paper, and instead focus only on weighted average δD values for each sample.

3.3.1. CV Chondrites

We find that the matrix of one CV chondrite (Allende) is very water-poor and has a δD value that is indistinguishable from our laboratory background. We consider it likely that this result is dominated by laboratory or other terrestrial contamination (as also seems likely of similar results from previous conventional stepped heating experiments; Kerridge, 1985). Matrix of the other CV chondrite analyzed in this study (Mokoia) is more water-rich and has a δD value that appears to be resolved from background at -2‰ . This compares with a range of -77 to $+440\text{‰}$ for previous analyses of whole-rock samples of CV chondrites (Fig. 3).

3.3.2. CM Chondrites

The matrix of one CM chondrite (LEW 85311) is also very water poor and did not yield a reliable δD value (i.e., one

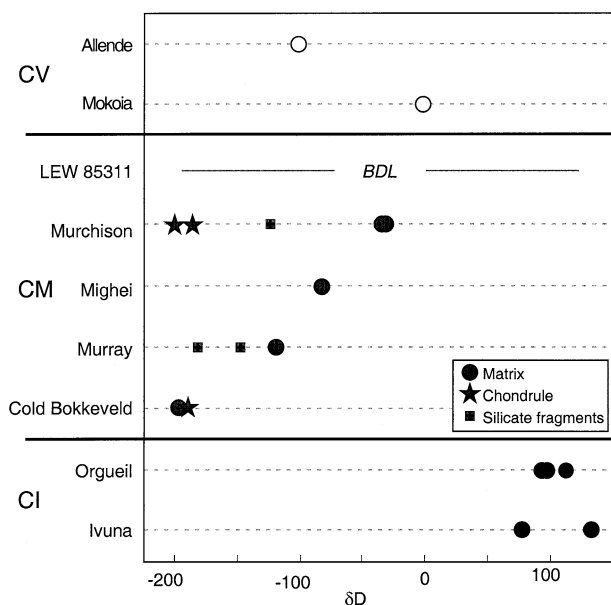


Fig. 5. δD values (vs. SMOW) of matrix, altered chondrules, and altered silicate fragments (circles, stars, and squares, respectively) of CV, CM and CI chondrites analyzed in this study. All values are weighted averages of water released over the course of stepped heating experiments; see text and Figure 4 for details. Note replicate measurements of Orgueil, Ivuna and Murchison matrix samples and Murchison altered chondrules suggest these materials are approximately homogeneous on the scale sampled. ‘BDL’ stands for ‘below detection limit’ and indicates the sample’s yield of water was comparable to our blank.

well-resolved from background); however, all others (Murchison, Mighei, Murray, and Cold Bokkeveld) are water-rich and yield δD values between $-31 \pm 1\%$ (two indistinguishable measurements of Murchison matrix) and -197% (Cold Bokkeveld). This compares with a range of -160 to $+990\%$ for previous analyses of whole-rock samples of CM chondrites (Fig. 3). Within the group of five analyses of four water-rich samples reported in this study, δD of matrix decreases from the least to most aqueously altered samples (Fig. 5). We find that altered chondrules from Murchison and Cold Bokkeveld (both CM chondrites) have δD values between -185 and -200% —closely similar to each other and to the matrix of Cold Bokkeveld, but lower in δD than any other sample of matrix material analyzed in this study. It is particularly noteworthy that altered chondrules from Murchison are $\sim 150\%$ lower in δD than co-existing matrix. Finally, altered coarse silicate fragments from Murchison and Murray range in δD from -123 to -183% —also always lower in δD than co-existing matrix and having a minimum similar to the values near -190% for altered chondrules. This result is consistent with the interpretation that all altered, coarse silicates in the CM chondrites have δD values of ~ -185 to -200% but that we only succeeded in separating such materials from adhered matrix when we dissected large, altered chondrules.

3.3.3. CI Chondrites

The matrices of both CI chondrites analyzed in this study (three analyses of Orgueil and two of Ivuna) are similar to one another in δD and span a range between $+77$ and $+133\%$ for all five measurements; this compares with a range of $+44$ to $+300\%$ for previous analyses of whole-rock samples of CI chondrites (Fig. 3).

3.4. Comparison of Hydrogen Isotope Micro-Analyses With Other Geochemical Properties

Figure 6 compares the δD values reported here with other, previously reported properties of those same samples. We chose for this purpose the oxygen isotope index: $\delta^{18}O_{\text{matrix}} - \delta^{18}O_{\text{whole rock}}$ (suggested by Clayton and Mayeda, 1999, to be inversely correlated with extent of fluid-rock reaction), the whole-rock abundance of a refractory element (Mg), the whole-rock abundance of a highly volatile element (^{36}Ar) and the whole-rock abundance of a moderately volatile element (Na). These elemental abundance data are taken from (Kallemeyn and Wasson, 1981; Schultz and Kruse, 1989; Wolf and Palme, 2001). Note that elemental concentrations in these variably altered rocks partly reflect dilution of constituents of the protoliths by water structurally bound in the rock during aqueous alteration. For example, the Mg content of an equi-molar mixture of forsterite and enstatite is ~ 24 atom %, but complete hydration of those minerals to form stoichiometric serpentine reduces this concentration to ~ 17 atom % even if no Mg is leached from the rock. ^{36}Ar abundances of the samples we have studied vary too greatly for dilution to be the primary control, but Mg and Na concentrations vary by only tens of percent relative and might be largely or entirely controlled by variable addition of water. We discuss in section 5 (below) the relative

importance of leaching/metasomatic additions vs. dilution in producing trends in Figure 6.

In all plotted dimensions, the matrices of CM chondrites form continuous trends; the sense of these trends is that δD decreases with increasing extent of fluid-rock reaction (i.e., decreasing $\delta^{18}O_{\text{matrix}} - \delta^{18}O_{\text{whole rock}}$), and decreasing concentration of both refractory and volatile elements. We examine the generality of these trends in the following section using the larger data set of previous conventional analyses of whole-rock samples.

The trends defined by CM chondrite matrix have different relationships to data for CI and CV chondrite matrix for the volatile vs. non-volatile elements: In the case of volatile elements (Figs. 6c and 6d), CI chondrites fall on the extension of CM trend in a position suggesting the CM chondrites become progressively less like the CI chondrites (i.e., lower in δD , lower concentrations of some volatile elements) as a result of increasing degrees of aqueous alteration. In the case of the non-volatile elements (Figs. 6a and 6b), the trends defined by CM chondrite matrix do not intersect the compositions of the CI chondrites. Mokoia and Allende (CV chondrites) do not lie near the trends collectively defined by the CM and CI samples in Figures 6c and 6d.

4. HYDROGEN-ISOTOPE SYSTEMATICS OF CARBONACEOUS CHONDRITE WHOLE ROCKS

Before further exploring the possible meanings of our results, we examine previous hydrogen isotope analyses of whole rock samples of the same and related samples and ask two questions: (1) Do these data re-enforce or contradict the trends described above? And, (2) if they re-enforce those trends, can we call on other known properties of whole-rock splits of these samples to further detail correlations between δD and other properties of the carbonaceous chondrites? We first note that there could be systematic differences between prior hydrogen isotope data and new measurements presented in the preceding section (e.g., due to differences in treatment of blank corrections; analytical isotopic fractionations; judgements regarding the fraction of sample water interpreted as laboratory contamination). These differences cannot be assessed easily because of the lack of interlaboratory standards similar to the samples in question. Therefore, we treat the data from prior conventional stepped combustion experiments as a parallel but separate set of constraints.

4.1. Identification of Representative Whole Rock Samples

The principle difficulty with assessing relationships between δD values and other properties for whole-rock samples of the carbonaceous chondrites is that their δD values vary tremendously, even with repeat measurements of the same samples; this is particularly true of the CM chondrites (Fig. 3). As mentioned above, a possible explanation of this scatter is heterogeneously distributed ‘nuggets’ of D-rich organic matter that might control the δD of any sample in which they are present in anomalously high concentrations. We attempted to remove this effect (and thereby examine the systematics of more representative samples) by culling whole-rock analyses

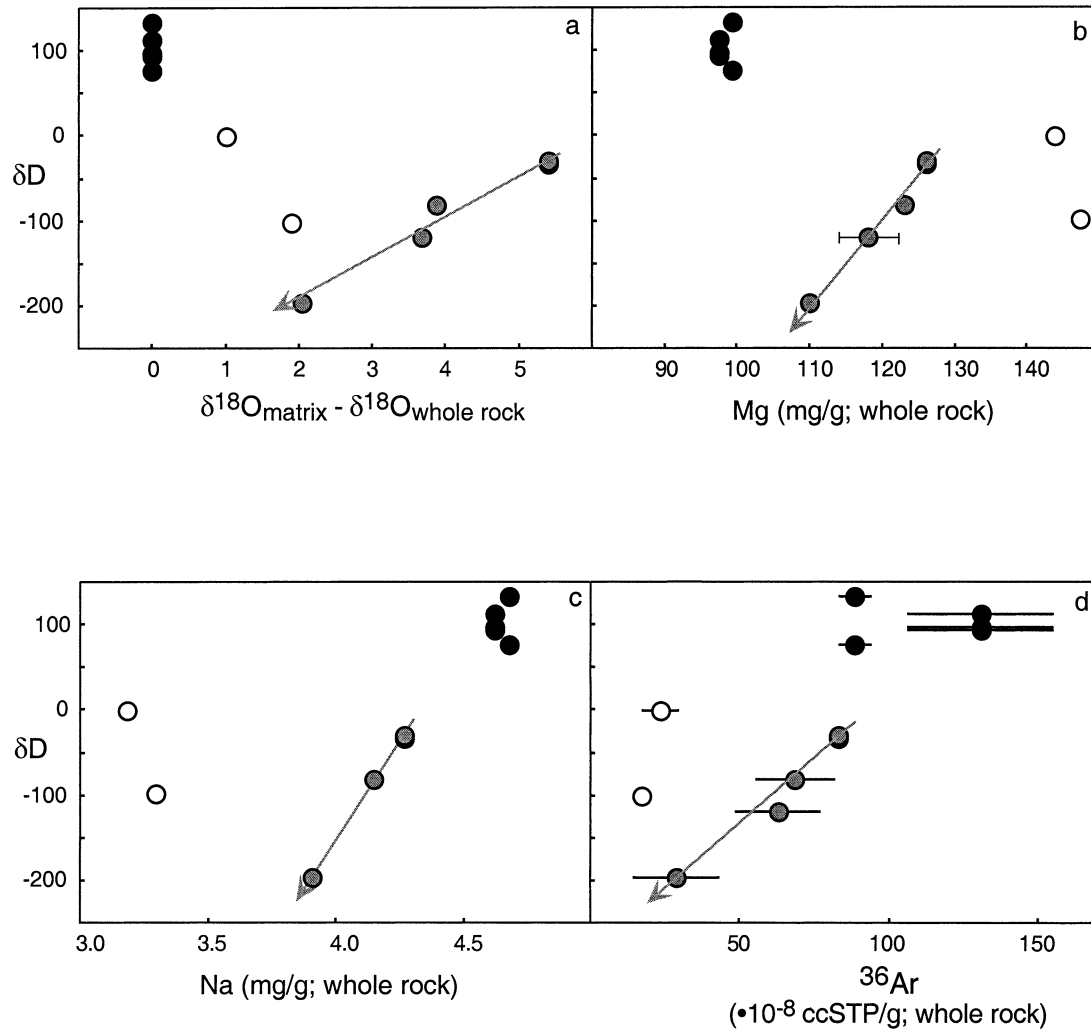


Fig. 6. Hydrogen isotope compositions of matrix from carbonaceous chondrites compared to other geochemical variables. Symbols are as in Figure 5. The gray arrow overlaid onto data for CM chondrites (gray circles) indicates the order of increasing degree of aqueous alteration, as inferred from petrography, mineral chemistry and oxygen isotopes (Browning et al., 1996; Clayton and Mayeda, 1999). Oxygen isotope data are from Clayton and Mayeda (1999); CI chondrites are plotted assuming the matrix is indistinguishable from the whole rock in oxygen isotope composition. Mg and Na abundances are taken from Wilk (1956), Kallemeyn and Wasson (1981), and Wolf and Palme (2001). Note Murray has anomalously low alkali abundances (e.g., 0.7 mg/g Na) and relatively variable Mg contents; it is not plotted in panel c and its range in Mg content is shown as a horizontal line in panel b (see Kallemeyn and Wasson, 1981). ^{36}Ar abundances are averages of data compiled in Schultz and Kruse (1989); outliers are omitted from these averages, following the procedure of Browning et al. (1996). We adopt the Browning et al. (1996) value for the ^{36}Ar abundance in Murchison.

based on other properties that plausibly reflect ‘nuggets’ of organic matter.

Figure 7 compares the δD value of whole rock samples of CM chondrites to C/H ratios determined as part of the same combustion or pyrolysis measurements of the same whole-rock subsample. These are a subset of the analyses presented in Figure 3. The highest δD values are only found in samples having anomalously high C/H ratios, consistent with an anomalously high abundance of the D-rich hydrocarbons known to be present in these rocks. We exclude these exceptional D- and C-rich whole-rock analyses from further discussion in this section, focussing instead on the majority having low C/H ratios and broadly terrestrial δD values. We do not infer that the low-C/H majority of the CM chondrite samples lack D-rich

organic materials, simply that those materials are not present in anomalously and non-representatively high abundance.

Similar culling of data for the CI chondrites is not justified (or likely required) because this latter group displays relatively little range in δD (Fig. 3) and does not include any measurements that are obviously non-representative of the mean. Finally, there is no obvious relationship between δD and any other volatile element abundance or isotope ratio among the volatile-poor CV and CO chondrites, with the exception that their range in δD rises dramatically with decreasing H abundance (not shown but reproducibly using data from Kerridge, 1985). We suspect that the hydrogen-isotope variability of the CO and CV chondrites reflects the sensitivity of such H-poor rocks to ‘nugget’ effects and terrestrial contamination, but we

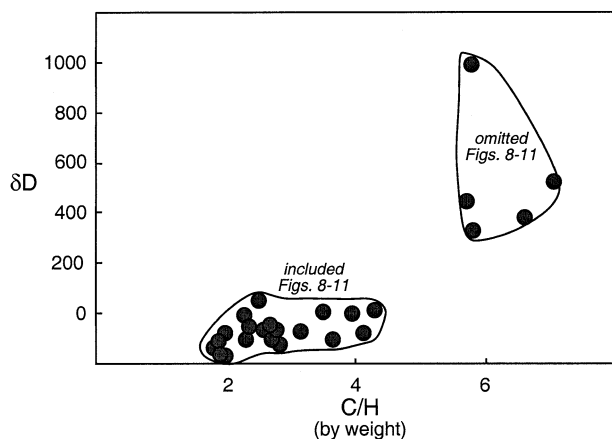


Fig. 7. Comparison of δD values (per mil, vs. SMOW) to C/H ratios (by weight) of whole-rock samples of CM chondrites. Repeat measurements of different splits of the same sample are shown as separate points. These data are a subset of measurements plotted in Figure 3. Data from Kerridge (1985). Note that whole-rock samples of CM chondrites fall into two groups: those with relatively low C/H ratios and δD values comparable to terrestrial materials, and those with high C/H ratios and strongly elevated δD values. Different splits of the same sample can be in either group. We infer that high-C/H and $-\delta D$ analyses reflect sampling of non-representative ‘nuggets’ of deuterated hydrocarbons known to be present in these rocks. Only low-C/H and $-\delta D$ samples are plotted in Figures 8 through 11.

can think of no robust basis for systematically choosing measurements that lack such effects. Therefore, we show all data for CV and CO whole rocks in subsequent figures but place little weight on them. We simply note that all carbonaceous chondrites of this type are very poor in hydrogen compared to the CM and CI chondrites. This fact, though simple, has a significant impact on our interpretations in section 5.

4.2. Combined Hydrogen- and Oxygen-Isotope Systematics of CM Whole Rocks

Figure 8 compares δD values for the low-C/H majority of the CM chondrites to their whole-rock $\Delta^{17}O$ values; where multiple measurements are available, the total range in δD is shown by the height of a rectangular field. As stated above, the difference, $\delta^{18}O_{\text{matrix}} - \delta^{18}O_{\text{whole rock}}$, is preferable as a measure of extent of aqueous alteration (Clayton and Mayeda, 1999) and is used here when possible (Fig. 6a). However, $\delta^{18}O_{\text{matrix}}$ is not known for several of the CM chondrites for which hydrogen isotope data are available and thus these samples cannot be plotted in such a diagram. The index, $\Delta^{17}O_{\text{whole rock}}$, is predicted and generally observed to increase with increasing extent of aqueous alteration among carbonaceous chondrites (Clayton and Mayeda, 1999); thus it provides an approximately equivalent and more widely applicable basis for judging correlations between H and O isotopes of whole rocks.

There is a negative correlation between δD and $\Delta^{17}O$ among CM chondrite whole rocks (Fig. 8). In the context of models for aqueous alteration of these rocks (Clayton and Mayeda, 1999; Young et al., 1999; Airieau et al., 2001; Farquhar et al., 2002; Young, 2002; see also Fig. 2), this is consistent with water-rock reaction leading to a decrease in the δD values of altered rocks. Therefore, the previously existing whole rock data base, filtered

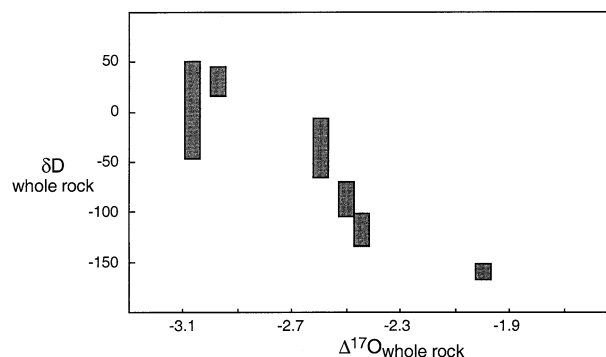


Fig. 8. Hydrogen isotope compositions of CM chondrite whole-rocks, omitting analyses of anomalously high C/H splits (Fig. 7), compared to whole-rock $\Delta^{17}O$ values (calculated as $\delta^{17}O - 0.52 \times \delta^{18}O$) measured on separate splits. The height of the box indicates the range for repeat measurements of separate splits if more than one was made. Note that $\Delta^{17}O_{\text{whole rock}}$ generally increases with increasing extent of aqueous alteration in carbonaceous chondrites (Clayton and Mayeda, 1999), and thus the trend to these data has the same significance as that for CM chondrites in Figure 6a (i.e., δD decreases with increasing extent of alteration). Data from Kerridge (1985) and Clayton and Mayeda (1999).

to remove inferred signatures of D-rich ‘nuggets’, confirms the existence and sense of the correlation we observe between H and O isotope compositions of CM chondrite matrix (Fig. 6a). We conclude that hydrogen isotope compositions of both representative whole rocks and matrix materials are correlated with oxygen isotope compositions of those rocks, record similar processes (although perhaps with greater fidelity in samples of pure matrix material) and both constrain models of carbonaceous chondrite aqueous alteration. Finally, we note that the trends defined by CM chondrites in Figures 6a and 8 are approximately straight lines, and we re-iterate that altered chondrules from CM chondrites span a narrow range in δD over a large range in extent of host-rock alteration (Fig. 5).

4.3. Comparison of Hydrogen Isotope Compositions Carbonaceous Chondrite Whole Rocks With Other Geochemical Properties

We compare $\delta D_{\text{whole rock}}$ values for CI, CV and CO chondrites, and our filtered set of CM chondrite analyses (i.e., excluding high C/H samples) to a variety of other elemental abundances, abundance ratios, and isotope ratios in Figure 9. We also show plots of $\delta^{15}N$ vs. $1/N$ and N/H vs. C/H for these samples to illustrate relationships among volatile element indices other than δD for this suite. All data plotted as filled or unfilled circles are measurements of both variables on the same sample split; data are shown as filled or unfilled boxes when each variable was measured on different sample splits. This latter type of data is compromised by comparing measurements on two different portions of heterogeneous materials; nevertheless, they preserve first-order trends consistent with those defined in other panels in Figure 9 and in Figure 6, and thus they appear to provide useful constraints. For reference, we include an arrow in all plots showing the order of increasing extent of aqueous alteration among CM chondrites, based on common interpretations of oxygen isotope geochemistry and mineralogy

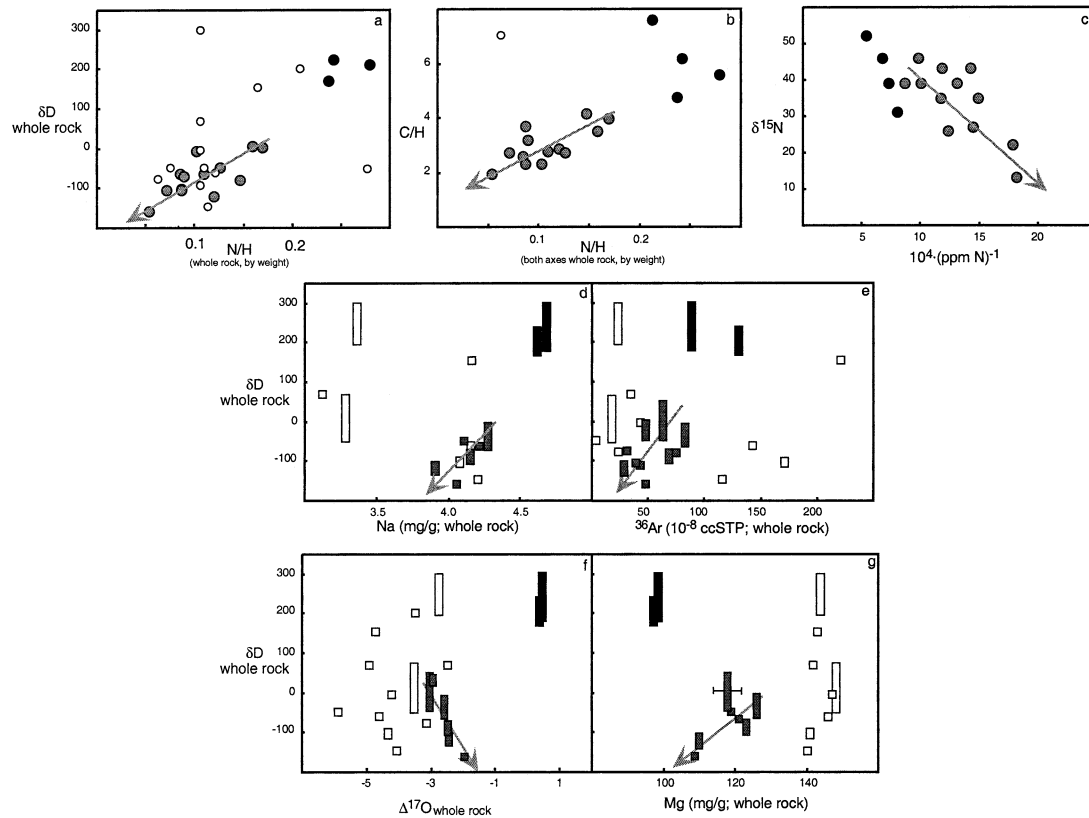


Fig. 9. δD values (vs. SMOW) of whole rock samples of CO, CV, CM and CI chondrites plotted vs. other geochemical parameters. Circles indicate measurements of both plotted variables on the same sample split. Boxes indicate measurements of the two plotted variables on different splits; in this case, the height of the box indicates the range in δD values for repeat measurements of separate splits of a given sample. Sample heterogeneity likely contributes to scatter in panels 'd' through 'g'. In both cases, symbol filling is as in Figure 5. The gray arrow overlaid onto data for CM chondrites (gray circles) indicates the order of increasing degree of aqueous alteration, as inferred from petrography, mineral chemistry and oxygen isotopes (Browning et al., 1996; Clayton and Mayeda, 1999). Oxygen isotope data are from Clayton and Mayeda (1999); Mg and Na abundances are taken from Wilk (1956), Kallemeyn and Wasson (1981), and Wolf and Palme (2001). ^{36}Ar abundances are averages of data compiled in Schultz and Kruse (1989); outliers are omitted from these averages, following the procedure of Browning et al. (1996). We adopt the Browning et al. (1996) value for the ^{36}Ar abundance in Murchison. Ranges in repeat measurements of Na and Mg abundance and $\Delta^{17}\text{O}$ on separate whole rock splits are small compared to the plotted range, excepting Mg in Murray, the range of which is shown with a horizontal bar. Ranges in ^{36}Ar (panel 'e') are large for some samples even at the plotted scale, but are omitted for clarity; see Figure 6d for standard deviations of some of these samples. Note Murray has anomalously alkali abundances and is not plotted in panel d (see Kallemeyn and Wasson, 1981). CO and CV chondrites plot outside the plotted range in panels b and c and are omitted so that detail of the CM and CI chondrites can be seen.

(Table 1, Figs. 2, 6a, 6b, and 8). Note that Figure 9f reproduces data for CM chondrites from Figure 8, but shows them at an expanded scale so that the trend they define can be compared with the CI, CO and CV chondrites.

There are several systematic relationships in Figure 9 (whole rocks) resembling those discussed above and illustrated in Figure 6 (micro-analyses of matrix). In particular, in plots of $\delta D_{\text{whole rock}}$ vs. an abundance or abundance ratio of a highly or moderately volatile element (^{36}Ar , Na, N/H), CM and CI chondrites together define a single trend. In all of these trends, the CI chondrites lie at one extreme (the volatile rich, high δD , high N/H, C/H, high $\delta^{15}\text{N}$ end) and the CM chondrites diverge away from that extreme toward lower δD and $\delta^{15}\text{N}$ values, volatile abundances and N/H and C/H ratios with increasing extent of aqueous alteration. These relationships are the same as those defined by CM and CI chondrite matrix in Figures 6c

and 6d. Note that, as discussed above in reference to Figure 6, correlations involving small ranges in elemental concentration (e.g., Na) could simply result from dilution of those elements by structurally bound water added during aqueous alteration.

It is particularly significant that in Figures 9a through 9e (as in Figs. 6c and d) the *least* aqueously altered CM chondrites are closest in composition to the CI chondrites and increasing degrees of aqueous alteration are consistently associated with greater differences from the CI chondrites. This contrasts with the relationship among these samples in a plot of $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ (Fig. 2), in which the least altered CM chondrites are least like the CI chondrites and increasing degrees of alteration are associated with a shift toward CI-like compositions.

In plots of $\delta D_{\text{whole rock}}$ vs. $\Delta^{17}\text{O}$ or abundances of refractory lithophile elements (Figs. 9f and 9g), the CM chondrites also define trends in which increasing degree of aqueous alteration

is associated with both decreasing δD and changes in the oxygen isotope or lithophile element index. However, unlike Figures 9a through 9e, the CI chondrites do not fall on extensions of these trends. Instead, the CI chondrites have oxygen isotope and lithophile-element compositions closely approaching the *most* altered CM chondrites (Nogoya and Cold Bokkeveld) but differing greatly from them in δD . These relationships resemble those for data for CM and CI chondrite matrix in Figures 6a and 6b.

Collectively, these trends indicate that increasing degrees of aqueous alteration of the CM chondrites makes their volatile-element geochemistry *less* like and their lithophile-element chemistry *more* like the CI chondrites. Finally, the trends defined by CM and CI chondrites in Figures 9a through 9e appear to bear little relationship to the compositions of the CV and CO chondrites, which are volatile-poor overall, vary greatly in δD , N/H and C/H, and are exceptionally low in $\delta^{15}N$ (Kerridge, 1985).

5. DISCUSSION

There are two respects in which the observations summarized in the preceding sections are inconsistent with previous models for the aqueous alteration of carbonaceous chondrites, particularly those implying that the protoliths of the CM chondrites were volatile-poor rocks resembling the CO or CV chondrites, and/or that the CI chondrites are even more altered versions of the CM chondrites:

1. Hydrogen isotope and highly-volatile-element systematics of CM chondrites indicate that increasing degrees of aqueous alteration make them progressively less like the CI chondrites (Figs. 6c, 6d, and 9a–9f), rather than more like them as suggested by oxygen isotope systematics alone (Fig. 2) or by considering only abundances of refractory elements (e.g., Fig. 6b). Thus, while $\delta^{18}O$, $\delta^{17}O$ and $\Delta^{17}O$ increases continuously from the CM to CI groups (Fig. 2), there is a sharp jump of $\sim 300\%$ in δD between the highest $\delta^{18}O$ CM chondrite and the CI chondrites (Figs. 6a and 9f).
2. The linear slope of correlations between H and O isotope compositions of CM chondrites (Figs. 6a and 8) is inconsistent with models in which relatively H-poor rocks like the CV and CO chondrites react with water. In such cases, reacting water quickly overwhelms the hydrogen isotope compositions of altered rocks and causes them to have approximately constant δD values over large ranges in extent of aqueous alteration. In contrast, oxygen isotope compositions change more gradually with increasing extent of alteration because silicate rocks are rich in oxygen. As a result, trends of δD vs. oxygen isotope indices should form sharply curved hyperbolae rather than gradual, approximately linear trends (Criss and Taylor, 1986). The inconsistency between data and these predictions is illustrated in Figure 10, which compares data for CM chondrites with the predictions of a model similar to that of Clayton and Mayeda (1999), in which a δD of -158% was assumed for infiltrating water, and assuming that the protolith has a H content typical of CO or CV chondrites. Similar results are obtained for calculations based on more recent models of the same processes, including those considering chromatographic flow and variations in temperature (Young et al.,

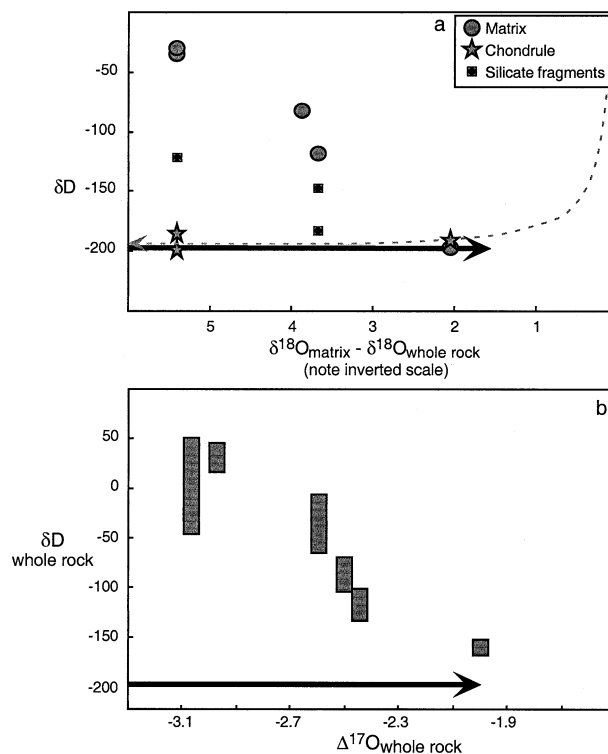


Fig. 10. Comparison of correlations between hydrogen-isotope and oxygen-isotope compositions of CM chondrites (reproduced from Figs. 5, 6a, and 9f; gray filled symbols) on one hand and predictions of a zero-dimensional water-rock model (black heavy arrow) on the other. The model shown is like that in Clayton and Mayeda (1999), in all respects except a δD value of -158% has been assumed for reactant water, $\Delta D_{\text{fluid-serpentine}}$ is taken to be 50% , and the protolith is assumed to have hydrogen abundance comparable to CO and CV chondrites (500 ppm H; Kerridge, 1985) and δD of $+300\%$ (similar to the highest values seen in CO and CV chondrites; Fig. 3). The dashed gray line in panel 'a' shows the path taken during the first stages of water-rock reaction, when little of matrix is serpentinized and whole-rock $\Delta^{17}O$ values are $< -4\%$ (off scale to the left in panel 'b'). This model of water-rock reaction predicts that δD values of altered rocks are buffered by that of infiltrating fluid when the extent of alteration is large enough to explain observed oxygen isotope compositions. More sophisticated models (e.g., 1-D chromatographic model of Young et al., 1999) differ in detail, but also predict nearly constant, low δD values for moderately- to highly-altered rocks. In both cases, this is a simple consequence of the low H content of the assumed protolith.

1999). It is significant that chondrules from both weakly and strongly altered CM chondrites (Murchison and Cold Bokkeveld) agree with these models, in contrast with data for matrix (and whole rocks, which are matrix-dominated). A simple explanation for these observations is that the H/O ratio of the matrix in the protoliths of the CM chondrites was much higher than those of the CV and CO chondrites, such that both the hydrogen and oxygen isotope compositions of matrix could change gradually with increasing degrees of aqueous alteration. In this case, only anhydrous coarse silicates in the CM chondrites (e.g., chondrules) that exhibit the coupled H-O isotope systematics predicted for H-poor protoliths.

We conclude that no model requiring the CV or CO chondrites (or materials like them) to be the protoliths of the CM

chondrites can be correct because the CV and CO chondrites are too poor in H and other highly volatile elements, and also differ in proportions and isotopic compositions of some highly-volatile elements. Similarly, no model that describes the CI chondrites as products of higher degrees of aqueous alteration of the same type and involving the same protoliths that made the CM chondrites can be correct because such a model would, barring some special mechanism that did not occur to us, predict the CI chondrites to be lower in δD than the most altered CM chondrites rather than higher in δD than the least altered CM chondrites (i.e., they should fall on the opposite side of the trends defined by CM chondrites in Figs. 6c and 6d and Figs. 9a through 9e). In the remainder of this section, we suggest an alternative model that attempts to reconcile the long-standing oxygen isotope and petrographic constraints on this problem with the constraints provided from hydrogen isotope and other highly-volatile-element compositions.

5.1. A Model for the Origin and Evolution of CM Chondrites

Our approach is to define a model protolith, a metasomatizing fluid, and a single metasomatic reaction that describes the geochemical and petrographic variability of the CM chondrites. Although this model does not explicitly attempt to model the properties of the CI, CV, and CO chondrites, it provides a basis for re-evaluating the relationships between these meteorite types and our putative protolith of the CM chondrites. Before detailing our model, we note one characteristic that, once recognized, makes it easier to have an intuition for its expected results: We treat the hydrogen isotope budget of the reacting CM chondrites as a simple mixing problem. They begin their alteration with an inventory of high- δD hydrogen (in an unspecified phase, but plausibly in kerogens), and that initial hydrogen is both leached or burned out of the rock and diluted by new-grown, low- δD hydrous silicates during aqueous alteration. Thus, increasing reaction progress is associated with gradual reduction of the mixing ratio of initial to newly-added hydrogen.

We describe the protolith of the CM chondrites as a mixture of subequal amounts of coarse, anhydrous silicates (Chondrules and CAIs) on one hand and a fine-grained, volatile rich component on the other; we refer to this initial complement of fine grained material as ‘fines’ to distinguish it from ‘matrix’, which is a petrographic term that can include phyllosilicates replacing original coarse anhydrous minerals. Table 3 summarizes the properties of this model protolith. We assume that the oxygen isotope composition of initial anhydrous silicates equals those in average carbonaceous chondrite anhydrous minerals, which also approximately equals those in average CV chondrite whole rocks. We assume that whole-rock abundances and isotopic compositions of all highly volatile elements in the CM chondrite protolith are similar to those in the CI chondrite, Orgueil. This is a reasonable premise for our model because Figures 2, 6 and 9 make it obvious that the protoliths of the CM chondrites had many volatile-element properties in common with the CI chondrites and an oxygen isotope composition resembling the CV chondrites. Furthermore, we show below that this assumption leads to a model that is successful at describing a wide range of observations that are otherwise hard to explain. How-

Table 3. Model constants.

<i>Reactant rock</i>	
Initial mol/g O ^a	0.027
Enstatite:forsterite	1:1
Modal fraction fines	0.4
Modal fraction coarse	0.6
$k_{\text{fines}}/k_{\text{coarse}}$ fraction	2.4
mg/g Na in whole rock	4.8
wt.% C in whole rock	4.94
ppm N in whole rock	2036
ppm H in whole rock	7820
⁸ ccSTP/g ³⁶ Ar in whole rock	130
$\delta^{18}\text{O}$	-4.2
$\delta^{17}\text{O}$	-7.4
δD of H	240
$\delta^{15}\text{N}$ of N	55
<i>Reaction water</i>	
$\delta^{18}\text{O}$	15.9
$\delta^{17}\text{O}$	9.2
δD	-158
<i>Fractionations</i>	
$\Delta^{18}\text{O}_{\text{serpentine-H}_2\text{O}}$	12
$\Delta^{17}\text{O}_{\text{serpentine-H}_2\text{O}}$	6.2
$\Delta D_{\text{serpentine-H}_2\text{O}}$	-50
$\Delta^{15}\text{N}_{\text{ammonia-residual N}}$	35

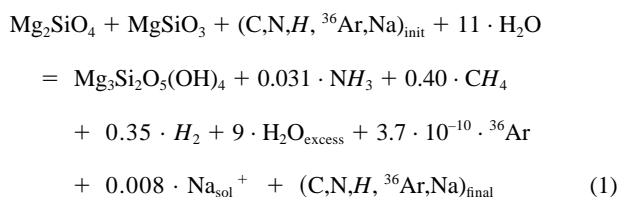
^a Used to convert between the stoichiometry of reactions 1 and 2 and weight fraction units.

ever, no objects like our putative CM chondrite protolith are recognized in meteorite collections. This could be because such objects are rare and have not yet been found, or that they exist in our collections but are not yet recognized (only four CI chondrites are recognized). The Tagish lake meteorite, a recent carbonaceous chondrite fall, has many properties in common with CI chondrites and contains chondrules (Brown et al., 2000); thus, while it differs in some respects from our model protolith, it at least provides evidence for the existence of rocks combining these volatile-element and petrographic properties. Finally, note that we propose the protoliths of the CM chondrites had things in common with the CI chondrites (in particular, a shared component of highly volatile elements), but we do not suggest that CI chondrites actually are samples of those protoliths. The CI chondrites appear to be aqueously altered rocks that underwent parent-body processing after their accretion (Brearley and Jones, 1998), they contain remnant anhydrous silicates that differ in oxygen isotope composition from those in CM chondrites (Clayton and Mayeda, 1999, and references therein), and they are characterized by ratios of refractory and moderately volatile elements that make them inappropriate choices as CM chondrite protoliths. Thus, the protoliths of the CI and CM chondrites must have differed in their lithophile element chemistry (and perhaps other respects), and they may have had divergent histories of aqueous alteration.

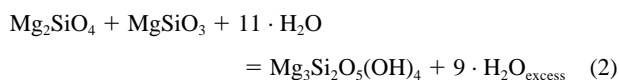
We assume that aqueous alteration was driven by reaction between model protolith and liquid water having the oxygen isotope composition suggested by Clayton and Mayeda (1999) and a δD of -158‰ (which will produce serpentine having a δD of -200‰ at relevant water/rock ratios; Wenner and Taylor, 1973). We describe fluid-rock interaction using a zero-dimensional, or ‘box’, model; this has the effect that all protolith rocks react with metasomatizing fluid of identical initial composition and metasomatized products differ only in the amount

of fluid to which they were exposed and in the progress of reactions involving components of the fluid (which are strictly coupled in our model). Our handling of the oxygen isotope geochemistry of aqueous alteration follows that of Clayton and Mayeda (1999), and therefore implicitly assumes that water-rock reaction took place at 0°C. Other elements of our model do not explicitly specify reaction temperature, but should at least be consistent with this assumption.

The stoichiometry of the reaction between fluid and protolith rock is key to our model because it defines the relationships among a large number of elemental abundances, isotopic compositions and petrographic characteristics of variably altered rocks. The reaction we propose for the volatile-rich ‘fines’ is



Whereas the reaction we propose for chondrules and CAIs is



The subscript ‘init’ denotes the volatile-element inventory of the fines before reaction; the subscript ‘final’ denotes the fraction of that initial inventory left after reaction. Progress of reaction 2 is prescribed to be 0.4 times progress of reaction 1 per molar unit of reactant; i.e., matrix is more reactive than coarse anhydrous silicates. This assumption was made based on petrographic data presented by Browning et al. (1996), but it also contributes significantly to the goodness of fit between the model and the hydrogen and oxygen isotope data. Reactant olivine and pyroxene in the fines are exhausted when the progress of reaction 1 is ~ 0.06 per mole initial O in the rock; for reaction progress values greater than this, no more serpentine is grown at the expense of fine anhydrous silicates, but highly-volatile elements and a small amount of Na continue to be removed from the rock. The ratios of input H_2O to evolved H_2 and CH_4 are fit to our data as free parameters, but they are similar to those estimated for low-temperature (25°C) aqueous alteration of CM chondrites by (Rosenberg et al., 2001) based on thermodynamic modeling, and to ratios of these gases in natural gas seeps from terrestrial serpentinites (Abrajano et al., 1988).

Our model distinguishes between two pools of hydrogen that do not undergo isotopic exchange with one another: (1) hydrogen that is introduced to the system as water and may be either bound as OH groups in serpentine or remain in the excess fluid phase (for instance, as a pore fluid or fluid expelled from the rock after reaction); this pool of hydrogen is designated with an ‘H’ in normal font in the reactions listed above. And, (2) hydrogen that is initially present in the rock as part of its CI-like, primitive volatile inventory and is either driven out of the rock as reduced gases (CH_4 , H_2 and NH_3) or retained in residual matrix material; this pool of hydrogen is designated with an ‘H’ in italics. This separation into two pools of hydrogen that do not exchange with one another is required by the

observation that aqueous alteration was accompanied by hydrogen isotope dis-equilibrium between matrix and newly formed hydrous minerals in chondrules (Figs. 5 and 10), and is also consistent with the slow approach of co-existing water, kerogens and reduced gases to hydrogen isotope exchange equilibrium at low temperatures (Abrajano et al., 1988). We assume that formation of serpentine involves hydrogen isotope fractionation relative to metasomatizing water ($\alpha_{\text{serp-H}_2\text{O}} = 0.95$), consistent with data for terrestrial serpentinites (Wenner and Taylor, 1973). Finally, we assume there is nitrogen isotope fractionation between residual nitrogen and evolved ammonia, consistent with the observation that N in metasediments is isotopically fractionated by devolatilization reactions (Haendel et al., 1986). However, we assume the evolved species is reduced (NH_3) rather than N_2 as in most terrestrial rocks and therefore we adopt a value of $\alpha_{\text{res.N-NH}_3} = 0.965$, similar to ammonia/ammonium fractionations at ~ 0 to 25°C (Kierschenbaum et al., 1947).

Calculations with the preceding model are made by specifying the progress of reaction 1 (and therefore the proportional progress of reaction 2), calculating the change in volatile-element composition and $\delta^{18}\text{O}$ of protolith chondrules and ‘fines’ required by our assumed reaction stoichiometry and calculating the new whole rock composition based on the weighted average of chondrules and ‘fines’. None of the parameters defined above (protolith or fluid composition; stoichiometric coefficients in reactions 1 and 2; relative rates of reactions 1 and 2; isotopic fractionations) are allowed to vary.

Table 4 presents results of these calculations for representative values of the progress of reaction 1, including: the oxygen and hydrogen isotope compositions of fines and whole rock, the N/H and C/H ratios, Na and ${}^{36}\text{Ar}$ abundances and $\delta^{15}\text{N}$ values of the whole rock, and the fraction of chondrules and initial fines that have been replaced by serpentine (these are comparable to those values reported in Browning et al., 1996, although we did not attempt to fit those data exactly because of the simplified mineralogical model of our model altering assemblage). Figure 11 graphically compares calculated variables with data. The model we propose simultaneously describes first-order variations of all of the geochemical and petrographic properties of the CM chondrites considered in this study and their relationships to the compositions of CI chondrites, including both the micro-analytical data presented here and previous conventional measurements of whole-rock samples.

6. SUMMARY AND CONCLUSIONS

The model we present in the preceding section is relatively simple and succeeds at describing many properties of the CM chondrites. Furthermore, its assumptions, if correct, have implications for our understanding of the origin and evolution of carbonaceous chondrites and for sources of volatiles in the early solar system and planets. In this section we discuss these issues.

The hydrogen-isotope and highly-volatile-element geochemistry of CM chondrites are not consistent with them being the products of aqueous alteration of CV or CO chondrites or of volatile-poor rocks closely resembling those meteorite groups. Instead, the protoliths of the CM chondrites were volatile-rich objects resembling the CI chondrites in certain respects but

Table 4. Representative model output.

Reaction 1 progress per mole initial O	Whole-rock N/H by weight	Whole-rock C/H by weight	Whole-rock Na (mg/g)	^{36}Ar 10^{-8} ccSTP/g	Fraction of O in serpentine	
					Matrix	Chondrules
0.01	0.22	5.4	4.7	122	0.21	0.09
0.02	0.18	4.7	4.6	113	0.41	0.17
0.03	0.15	4.1	4.5	105	0.59	0.25
0.04	0.13	3.6	4.5	96	0.75	0.33
0.05	0.11	3.2	4.4	88	0.90	0.40
0.06	0.09	3.0	4.3	79	1.00	0.47
0.07	0.09	2.9	4.3	71	1.00	0.54
0.08	0.08	2.8	4.2	62	1.00	0.61
0.09	0.07	2.7	4.1	53	1.00	0.67
0.10	0.06	2.6	4.1	45	1.00	0.73
0.11	0.05	2.5	4.0	36	1.00	0.79
0.12	0.04	2.4	3.9	28	1.00	0.85

Reaction 1 progress per mole initial O	$\delta^{18}\text{O}_{\text{matrix}}$	$\delta^{18}\text{O}_{\text{whole rock}}$	$\delta^{17}\text{O}_{\text{whole rock}}$	$\Delta^{17}\text{O}_{\text{whole rock}}$	$\delta\text{D}_{\text{whole rock}}$	$\delta\text{D}_{\text{matrix}}$	$\delta^{15}\text{N}_{\text{whole rock}}$
	(‰, SMOW)	(‰, SMOW)	(‰, SMOW)		(‰, SMOW)	(‰, SMOW)	(‰, air)
0.01	-0.3	-1.7	-5.6	-4.7	154	182	53
0.02	3.3	0.7	-3.8	-4.2	87	129	50
0.03	6.5	2.9	-2.2	-3.8	32	81	48
0.04	9.5	5.1	-0.7	-3.3	-12	38	45
0.05	12.3	7.1	0.8	-2.9	-49	-1	42
0.06	14.3	8.8	2.0	-2.6	-78	-32	39
0.07	15.2	10.1	2.9	-2.3	-99	-51	36
0.08	15.8	11.3	3.7	-2.1	-120	-73	32
0.09	16.3	12.4	4.6	-1.9	-140	-98	28
0.10	16.8	13.5	5.3	-1.7	-161	-128	23
0.11	17.2	14.6	6.1	-1.5	-182	-163	18
0.12	17.5	15.6	6.8	-1.3	-200	-200	12

with a large abundance of ^{16}O -rich chondrules and CAIs and other differences in lithophile-element geochemistry not considered here.

We also conclude the CI chondrites are not the products of more extensive aqueous alteration of the same type and involving the same protoliths as that producing the CM chondrites. That is, if the CI chondrites underwent aqueous alteration (as seems likely) it involved protoliths and/or infiltrating water different in composition from those producing the CM chondrite series.

Our conclusion that the protoliths of the CM chondrites contained a high concentration of the same “package” of volatile elements found in the CI chondrites raises several issues. One explanation of this shared volatile component is that both groups of meteorites originally accreted with large concentrations of that component, and that it was modified by aqueous alteration in the CM chondrites but preserved (at least in its elemental and isotopic abundances if not in the phase identity of its original hosts) in the CI chondrites. This conclusion raises two difficult questions: (1) The CI chondrites also appear to have undergone aqueous alteration after their accretion (Brearely and Jones, 1998). If so, then why did they retain this putative primary volatile component through aqueous alteration when the CM chondrites did not? And, (2) by what mechanisms did volatile-rich protoliths initially accrete to form the protoliths of the CM chondrites? We have no clear answer to the first question and suggest more work will be needed to understand the impact aqueous alteration had on volatiles in CI chondrites. We speculate that this alteration might have taken place under

a combination of temperatures, oxidation-states and fluid/rock ratios that prevented or minimized decomposition and loss of primary volatile-rich constituents. The second question touches on a long-standing conundrum: it seems reasonable to imagine that volatile-rich solids could have formed early in solar system history due to reaction between vapor and dust, but experiments suggest those reactions are too sluggish at inferred early-solar-system temperatures and pressures (Fegley, 2000). However, it has recently been suggested that shock waves passing through the early solar nebula would produce brief (~hours to days) periods of warm temperatures and high gas pressures when gas-dust reactions could produce volatile-rich solids (Ciesla et al., 2003). If this was a common process, we hypothesize it could have generated fine-grained, volatile-rich material that was a component of the CM chondrite protolith. The preservation of that primitive volatile component in the CI chondrites might be attributed to accretion of similar materials, perhaps followed by parent body processing in an approximately closed system. This suggestion is consistent with evidence that the CI chondrites are the oldest of the chondritic meteorites (Birck et al., 1999) and contain complex hydrocarbons that could be a starting point, or organic ‘protolith’, of those found in other meteorite groups (Cody et al., 2002). Alternatively, the CI chondrites and volatile-rich components of the CM chondrite protoliths might have formed in a different, earlier, generation of aqueous alteration than that recorded by the CM chondrites. Break-up of such aqueously altered planetesimals and re-accretion with anhydrous chondrules and CAIs would form a second generation of bodies resembling our putative CM chondrite

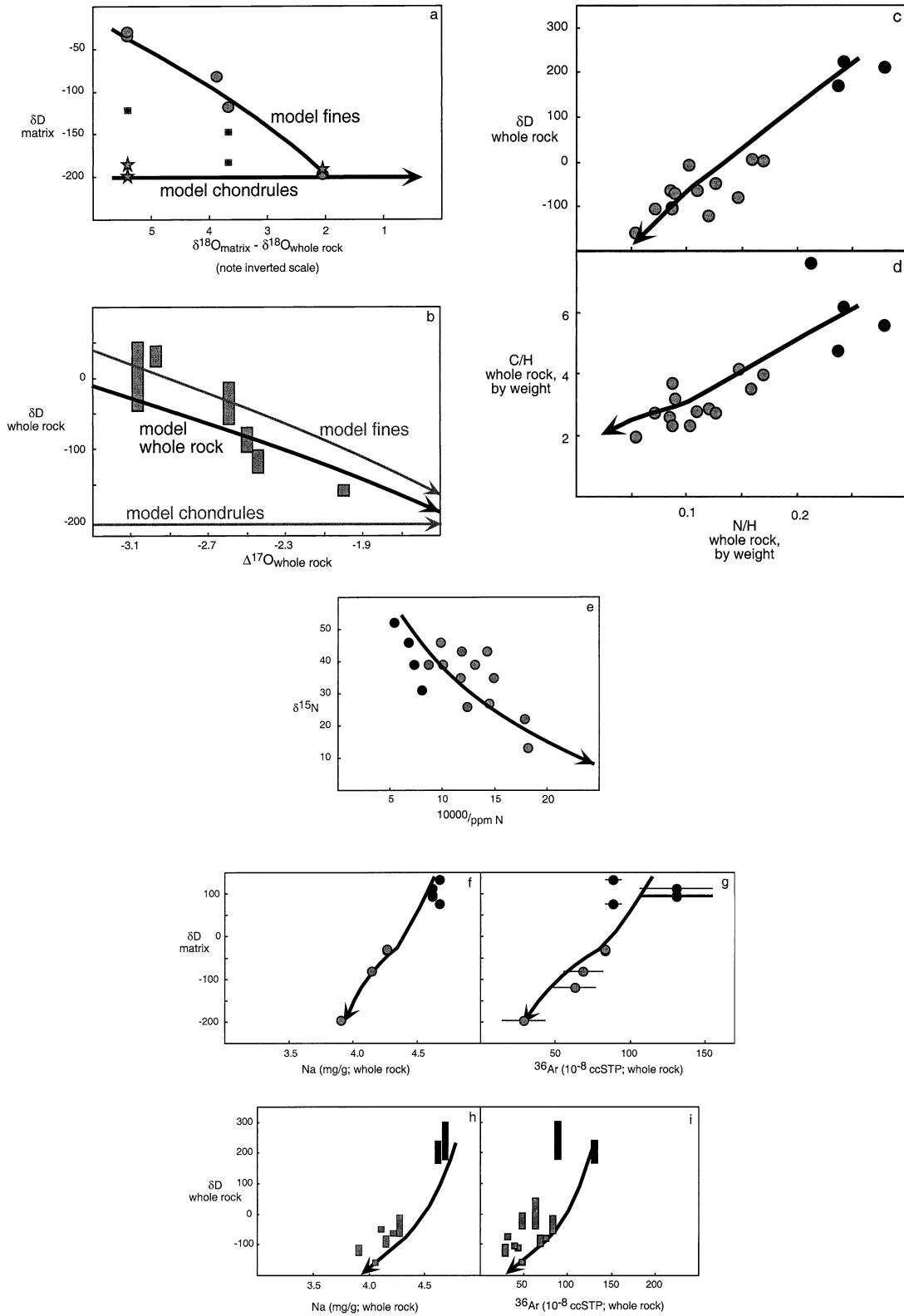


Fig. 11. Comparison of correlations involving hydrogen isotopes and select other geochemical properties in CI and/or CM chondrites (data reproduced from Figs. 6, 9 and 10; symbols as in Fig. 5) on one hand and predictions of the zero-dimensional water-rock reaction model described in the text on the other (heavy black curves; arrow indicates direction of increasing extent of aqueous alteration). Data for CO and CV chondrites are omitted for clarity. The model shown is principally fit to data in panels 'a' and 'c' through 'g'; comparisons in panels b, h and i are shown for completeness, but involve data that are relatively susceptible to scatter due to analysis of different splits of heterogeneous materials. This model is similar in many respects to that of Clayton and Mayeda (1999), but assumes the protolith of the CM chondrites was similar in volatile element chemistry to the CI chondrites, that matrix and chondrules undergo aqueous alteration at different rates (as required by petrographic data of Browning et al., 1996), that reactant water has a δD of -158% , and that H, C and N in the protolith break to evolve reduced gases during aqueous alteration. See text for other details.

protolith. If this more elaborate sequence of events is correct, it seems likely to us that the initial stage of aqueous alteration must have involved more D-rich water than that infiltrating the CM chondrites (i.e., because the CI chondrites and CM chondrite protoliths are D-rich). These issues are attractive targets for future studies focusing more closely on the hydrogen isotope geochemistry of CI chondrites and related meteorites (e.g., Tagish lake, and others with 'CI'-like affinities or clasts).

It is less obvious what our results mean for the relationship between the volatile-poor and volatile rich carbonaceous chondrites (i.e., CV and CO vs. CM and CI), other than that the latter are not produced by aqueous alteration of the former. Many CV and CO chondrites contain evidence of relatively intense thermal metamorphism (VanSchmus and Wood, 1967) and are systematically younger than the CI and CM groups (Birck et al., 1999). We suggest they might be objects that either accreted with little or none of our putative 'CI-like' highly volatile component, or that initially contained such a component but lost it due to thermal metamorphism.

Finally, our data suggest the water that metasomatized the protoliths of the CM chondrites had a δD value of -158% , corresponding to a D/H ratio of 131×10^{-6} . This value can be compared with the predictions of models of the distribution of HDO in the early solar system to estimate where and when the parent bodies of the CM chondrites first accreted. There is nothing in our results that can clearly test or disprove those models. Nevertheless, if we accept a recent and relatively detailed of one as valid (Mousis et al., 2000), we conclude that the water which infiltrated the CM chondrite parent bodies first condensed at a distance 4 AU from the sun at a time $> 10^5$ years after the collapse of the presolar nebula.

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