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Deuterium enrichments in chondritic macromolecular material—Implications for the origin and evolution of organics, water and asteroids

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Abstract

Here we report the elemental and isotopic compositions of the insoluble organic material (IOM) isolated from several previously unanalyzed meteorites, as well as the reanalyses of H isotopic compositions of some previously measured samples (Alexander et al., 2007). The IOM in ordinary chondrites (OCs) has very large D enrichments that increase with increasing metamorphism and decreasing H/C, the most extreme δD value measured being almost 12,000‰. We propose that such large isotopic fractionations could be produced in the OC parent bodies through the loss of isotopically very light H_2 generated when Fe was oxidized by water at low temperatures (<200 °C). We suggest that similar isotopic fractionations were not generated in the IOM of CV and CO chondrites with similar metamorphic grades and IOM H/C ratios because proportionately less water was consumed during metamorphism, and the remaining water buffered the H isotopic composition of the IOM even a H was being lost from it.

Hydrogen would also have been generated during the alteration of CI, CM and CR carbonaceous chondrites. The IOM in these meteorites exhibit a considerable range in isotopic compositions, but all are enriched in D, as well as ^{15}N, relative to terrestrial values. We explore whether these enrichments could also have been produced by the loss of H_2, but conclude that the most isotopically anomalous IOM compositions in meteorites from these groups are probably closest to their primordial values. The less isotopically anomalous IOM has probably been modified by parent body processes. The response of IOM to these processes was complex and varied, presumably reflecting differences in conditions within and between parent bodies.

The D enrichments associated with H_2 generation, along with exchange between D-rich IOM and water in the parent bodies, means that it is unlikely that any chondrites retain the primordial H isotopic composition of the water ice that they accreted. The H isotopic compositions of the most water-rich chondrites, the CMs and CIs, are probably the least modified and their compositions ($\delta D \leqslant -25$‰) suggest that their water did not form at large radial distances from the Sun where ice is predicted to be very D-rich. Yet models to explain the O isotopic composition of inner Solar System bodies require that large amounts of ice were transported from the outer to the inner Solar System.
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1. INTRODUCTION

Primitive chondritic meteorites contain up to ~2 wt% organic C, and interplanetary dust particles (IDPs) can contain even more (Gilmour, 2003; Pizzarello et al., 2006). This organic C is generally divided into soluble (SOM) and insoluble (IOM) organic matter fractions, the IOM being

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the dominant fraction (75–99%). Both fractions can have large D and ^{15}N enrichments. In the SOM, there are considerable isotopic variations amongst individual compounds within and between meteorites (e.g., Huang et al., 2005; Pizzarello et al., 2008). Similarly, the IOM varies dramatically in isotopic composition on small spatial scales, and in bulk from meteorite to meteorite (Busemann et al., 2006; Alexander et al., 2007; Remusat et al., 2009). The most striking variations within the IOM are to be found in so-called hotspots, some but not all of which appear to be associated with so-called nanoglobules. Nanoglobules are typically submicrometer, roughly spherical objects that are often hollow and are almost always isotopically anomalous (Nakamura-Messenger et al., 2006; Garvie et al., 2008).

It is almost universally accepted that the large D and ^{15}N enrichments in the organics are the products of low temperature chemistry in the interstellar medium (ISM) or the early outer Solar System. If this is the case, all chondrites would have accreted a common organic component and the variations between meteorites, particularly between meteorites from the same chondrite group, must be due to parent body processes (Alexander et al., 2007).

At first glance, it seems plausible that the variations in isotopic composition between meteorites are the products of parent body alteration of a common suite of precursors. For instance, amino acids are most abundant and most isotopically anomalous in the least aqueously altered CM and CR chondrites (Martins et al., 2007; Pizzarello et al., 2008). Also, H, N and O abundances in IOM decrease with increasing metamorphism, as do D and ^{15}N enrichments in CV, CO and E chondrites. On the other hand, there is no strong correlation in the isotopic compositions of IOM with degree of aqueous alteration within and between CI, CM and CR chondrites (Alexander et al., 2007). The most isotopically anomalous CM, Bells, is not the least altered. Even more puzzling is that in the ordinary chondrites (OCs), but not CVs and COs, D enrichments in IOM increase dramatically with increasing metamorphic grade (Alexander et al., 2007). Is this due to preferential preservation of hotspots/globules, or a novel isotopic fractionation process?

There are several observations that suggest that other novel isotopic fractionation processes occurred in meteorite parent bodies. In the CH and CB meteorites there are very large ^{15}N, but not D, enrichments. Some of this isotopically heavy N is in IOM in chondritic clasts and is much more enriched ($\delta^{15}N \approx 900$–$1100‰$ in bulk) than in any typical chondrite (Grady and Pillinger, 1990; Ivanova et al., 2008; Bonal et al., 2009; Briani et al., 2009), but much of the N is in inorganic materials (Prombo and Clayton, 1985; Franchi et al., 1986; Sugiura et al., 2000). The CH/CB group may be the products of an impact (Krot et al., 2005) and, therefore, the N isotopic fractionations may be associated with shock. Isotopically heavy N ($\delta^{15}N$ up to 500–1000‰) is also found in brecciated urelites (Grady and Pillinger, 1988), but not in unbrecciated ones, and in some shocked type 3 OCs (Mostefaoui et al., 2005). For H isotopes, there is the intriguing discovery of very D-rich water in mica and amphibole ($\delta D = 3660‰$) in the R4 La-Paz Ice Field (LAP) 04840 (McCanta et al., 2008). The D enrichment is much higher than in any bulk chondrite or estimates of the water compositions in them, and is comparable to the most enriched IOM. The water could have been produced by oxidation of IOM, but there is no evidence for the CO_2 that would have accompanied the water. Alternatively, it is possible that an unknown fractionation process operating in the R chondrite parent body isotopically fractionated the H.

Given the possibility of unrecognized fractionation processes having operated on chondrite parent bodies, here we further explore the relationship between IOM composition and parent body processes. To this end, we have: (1) prepared IOM-rich residues for several new meteorites that extend the range of parent body processing in CMs covered in the IOM survey of Alexander et al. (2007), (2) prepared larger IOM residues of some meteorites that were included in the survey, and (3) reanalyzed a number of existing IOM residues with low H/C ratios that were prepared for the IOM survey to determine whether adsorbed atmospheric water produced some of the observed scatter in the original H isotope data.

2. SAMPLES

New residues were prepared from several meteorites (summarized in Table 1), and the reasons for their selection are described briefly here.

Rubin et al. (2007) identified Queen Alexandra Range (QUE) 97990 as the least altered CM found to date. Essebi has some petrologic similarities to Bells (CM2) in that they are both heavily brecciated and experienced more oxidizing conditions than most CM2s (Metzler et al., 1992). The IOM of Bells is amongst the most isotopically anomalous of any meteorite studied (Alexander et al., 2007). Essebi is classified as a CM2, but it falls above the typical CM trend in an O three isotope plot and has a larger $\delta^{18}O$ value than most CMs (Clayton and Mayeda, 1999). Kallemeyn (1995) suggested that Bells and Essebi may not be CMs, but Bells, at least, is probably a CM (Rowe et al., 1994; Brearley, 1995; Mittlefehldt, 2002). Two other CMs, Lonewolf Nunataks (LON) 94102 and Alan Hills (ALH) 85013 were also analyzed.

Large residues of Murchison (CM2) and Grosvenor Mountains (GRO) 95577 (CR1) were prepared for new nuclear magnetic resonance (NMR) measurements and other analyses, and their elemental/isotopic compositions were analyzed to check their quality.

GRO 95566 is an ungrouped carbonaceous chondrite (CC) that lies on the bulk CM–CO O isotope mixing line, with a composition that falls between the two groups and that is similar to that of Lewis Cliff (LEW) 85311 (Clayton and Mayeda, 1999). Clayton and Mayeda (1999) concluded that both of these meteorites are probably CMs, and suggested that their low bulk $\delta^{18}O$ values were the result of relatively limited interaction with an altering fluid. The IOM of LEW 85311 was analyzed by Alexander et al. (2007) and was found to be more D-rich than most CMs.

MacAlpine Hills (MAC) 88107 is an ungrouped CC with affinities to the CMs and COs that has undergone an unusual style of hydrothermal alteration under well-con-

Table 1
The new meteorites analyzed, along with their classification, shock and weathering stages, and bulk meteorite insoluble C contents determined in this study. For comparison, in italics are listed previously reported analyses (Alexander et al., 2007) for the same or similar meteorites.

	Fall/Find	Classification	Shock	Weath.	C (wt%)
CM					
QUE 97990	Find	CM2			1.00
Essebi	Fall	CM2	S1		1.30
Murchison	Fall	CM2	S1		1.06
Murchison					*Not deter.*
GRO 95566	Find	C2/CM2		A/Be	0.83
LEW 85311					*0.91*
LON 94102	Find	CM2		Ce	1.05
ALH 85013	Find	CM2		A	0.90
CM heated					
EET 87522	Find	CM		Be	1.27
Y 793321					*1.31*
PCA 91008					*0.74*
CR					
GRO 95577	Find	CR1			1.51
GRO 95577					*0.78*
CO					
Ornans	Fall	CO3.6	S1		0.058
OC					
QUE 97008	Find	L3.05	S2	A	0.31
QUE 97008					*0.25*
MET 00452	Find	H3.5		B/Ce	0.22
MET 00452					*0.27*
WSG 95300	Find	H3.3		A/B	0.23
WSG 95300					*0.25*
Ungrouped					
MAC 88107	Find	C		B	0.62
MAC 87300					*0.72*

strained conditions (Krot et al., 2000)—the secondary fayalite–magnetite–hedenbergite mineral assemblage is similar to that of Kaba (CV3). Its O isotopic composition falls within the CO field and is almost identical to that of the ungrouped MAC 87300 (Clayton and Mayeda, 1999) whose bulk IOM composition was measured by Alexander et al. (2007).

Although nominally classified as a CM2, Elephant Moraine (EET) 87522 has O isotope affinities to both the CMs and COs—it falls between the two groups (Clayton and Mayeda, 1999). Based on its reflectance spectra, EET 87522 was identified as having been mildly heated (Hiroi et al., 1996). However, it does not have the very heavy bulk O isotopic compositions of the most heated CMs (Clayton and Mayeda, 1999).

Ornans is a moderately metamorphosed CO. McSween (1977) noted an apparent "Ornans paradox" in that its C and noble gas contents indicated a higher metamorphic grade than its petrology. Bonal et al. (2007) have questioned whether there is a paradox, but it is clear from its very Ni-rich metal compositions that Ornans experienced more oxidizing conditions during metamorphism than most COs (McSween, 1977). However, Ornans was primarily selected for analysis because Kerridge (1985) reported a bulk H isotopic composition for this meteorite of 2150‰ that is much higher than any other CO. It was suspected that, like the OCs, it contains IOM with a very anomalous H isotopic composition.

Of the OCs analyzed in our earlier survey of IOM compositions (Alexander et al., 2007), QUE 97008 and Meteorite Hills (MET) 00452 contained some of the most primitive IOM, while Mount Wisting (WSG) 95300 had one of the most anomalous H isotopic compositions. New residues of much bigger samples were prepared to try to obtain larger, purer IOM residues for analysis by additional techniques.

3. METHODS

The new IOM residues were prepared and analyzed using the same methods as described in Alexander et al. (2007). The new residues were prepared using the CsF–HF technique in which crushed samples (<106 μm) are first leached with 2 N HCl, followed by rinsing with milliQ water and dioxane, and then shaken in the presence of two immiscible liquids, a CsF–HF solution (1.6–17 g/cc) and dioxane. When liberated from its mineral matrix, the IOM collects at the interface of the CsF–HF solution and

the dioxane, while the denser minerals sink to the bottom. After centrifugation, the IOM is pipetted off and rinsed with 2 N HCl, milliQ water and then dioxane, before being dried down at <30–50 °C. There was no specific attempt to remove soluble organic material. However, the repeated washing with aqueous solutions and dioxane should have effectively removed most soluble organic compounds known to be present in chondrites.

Elemental and isotopic analyses were made with a Finnigan MAT Delta^{plus}XL mass spectrometer. Sample gases were introduced into the mass spectrometer via a molecular sieve gas chromatographic (GC) column (Wooller et al., 2004; Wang et al., 2005) connected to either: a CE Instruments NA 2500 series elemental analyzer (EA) for C and N analyses, or a Thermo Finnigan thermal conversion elemental analyzer (TC/EA) for H and O analyses. For all analyses, internal working gas standards were analyzed with every sample, and external standards were analyzed at regular intervals to monitor the accuracy of the measured isotopic ratios and elemental compositions. A H_3^+ correction applied to the H measurements was determined periodically throughout the day. Typical sample sizes were 0.2–0.4 mg. The only difference with the study of Alexander et al. (2007) was the use for the H and O analyses of a He-flushed autosampler to reduce the amount of water adsorbed from the atmosphere.

In addition to the analysis of the new samples, the H abundances and isotopic compositions of a number of previously analyzed residues with low H/C ratios were remeasured. The aim of this was to use the He-flushed autosampler to determine whether any of the previous analyses were significantly influenced by adsorbed water.

The measurement precision for elemental abundances is typically of the order 1–3% of the reported values. Because C and N are measured in the same samples, the precision of measured N/C ratios is typically about 1% of the reported values. The precision of C and N isotope measurements are generally 0.1–0.3‰, while for O it is typically 0.3–0.5‰. The precision of the H isotope measurements are more difficult to assess because it decreases with increasing D enrichment, and because there is a small memory effect associated with the measurements. Sample heterogeneity is also a potential source of uncertainty in all the measurements. Hence, uncertainties are only given for samples for which two or more measurements were made and they provide the best estimates of the likely uncertainties in the precision of the single measurements.

Finally, we performed secondary ion mass spectrometry (SIMS) imaging of IOM from Krymka to compare the micro-scale distribution of H isotopes in UOCs to that in carbonaceous chondrites (Busemann et al., 2006). Measurement conditions were identical to those used by Busemann et al. (2006). Briefly, 10–20 μm fragments of IOM were pressed flat into clean Au foils and analyzed with the Carnegie ims-6f ion microprobe in scanning imaging mode. A 1.5 μm diameter Cs^+ primary beam (~5–10 pA, 12 keV) was rastered over each fragment and secondary ion images of $^1H^-$, $^2H^-$ and $^{12}C^-$ were collected synchronously with the primary beam raster. Images were analyzed with the L'image software (L.R. Nittler, Carnegie Institution). Instrumental mass fractionation was corrected for based on measurements of terrestrial standards (an anthracite coal and a lipid with the formula $C_{30}H_{50}O$).

4. RESULTS AND COMPARISON WITH PREVIOUS DATA

The yields and compositions of the new IOM residues prepared for this work are given in Tables 1 and 2, respectively. Tables 1 and 2 also compare our results to yields and compositions previously reported by Alexander et al. (2007) for the same or similar meteorites. Table 3 lists the results of the remeasurements of the H elemental abundances and isotopic compositions of previously prepared IOM residues. Only the results for samples that gave significantly lower H abundances are listed.

4.1. New vs. old residues

In general, the yields and IOM compositions for the new, larger IOM residues of meteorites (Murchison, GRO 95577, QUE 97008, MET 00452 and WSG 95300) previously studied by Alexander et al. (2007) compare well with the earlier results. In a review of several studies of IOM, Alexander et al. (2007) found that yields for the same meteorites typically varied by 20–30%. A similar variability in yields for the same meteorites can be seen in Table 1, despite the use of the same extraction techniques in both this study and that of Alexander et al. (2007). Presumably, this variability in yields reflects the heterogeneity of matrix abundances in meteorites at the scales sampled. Organic matter would not survive the high formation temperatures (>1400 °C) of chondrule or CAIs, the other major components of chondrites, so it must be the matrix abundance that controls IOM contents (e.g., Alexander, 2005). For GRO 95577, the yields differ by roughly a factor of two between the two studies, pointing to very large variations in matrix abundance in this meteorite.

Except for the H/C ratios and δD values for the OCs MET 00452 and WSG 95300, the elemental and isotopic compositions found in the two studies are similar. However, even where the values are similar the differences are often larger than the errors reported by Alexander et al. (2007). Those errors were based on the reproducibility of two or more measurements of the residues. The errors, therefore, reflect the precision of the measurements and the homogeneity of the residues at the typical sample size of ~0.2–0.4 mg. The differences between our two studies may include some variability in accuracy between runs but, since the same standards were used in both studies, they must largely reflect small heterogeneities in the meteorites and differences in the purity of the residues. The higher purity of the new WSG 95300 residue may also have contributed to its lower H/C and higher δD value. However, the new QUE 97008 residue is also much purer, but its composition is little different from the previous residue.

The roughly factors of two lower H/C ratios and factors of two higher δD values for the new MET 00452 and WSG 95300 residues, compared to the previous ones, must be due to roughly factors of two less H with a 'normal' isotopic

Table 2
The C contents, elemental ratios (100×) and isotopic compositions of the meteorite residues. Errors are based on the range of compositions obtained for two or more analyses of a residue. Meteorite IOM analyses in italics were reported by Alexander et al. (2007) and are listed for comparison with the results of this study.

	C (wt%)	H/C (at.)	N/C (at.)	O/C (at.)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	δD (‰)	$\delta^{18}O$ (‰)
CM								
QUE 97990	60.8 ± 0.4	70.1 ± 0.7	3.75 ± 0.05	13.2	−16.20 ± 0.12	17.3 ± 0.4	1218 ± 5	4.6
Essebi	70.5 ± 0.9	68.5 ± 1.6	3.42 ± 0.01	17.7 ± 0.2	−17.97 ± 0.03	28.8 ± 0.6	1518 ± 20	−3.7 ± 0.3
Murchison	71.2	61.8	3.15	13.4	−17.75	7.3	811	14.4
Murchison	*66.5 ± 0.6*	*58.8 ± 1.6*	*3.27 ± 0.03*	*18.3 ± 0.3*	*−18.91 ± 0.01*	*−1.0 ± 0.4*	*777 ± 27*	*13.2 ± 0.6*
GRO 95566	68.9 ± 0.5	66.5 ± 0.5	3.57 ± 0.08	13.3	−15.86 ± 0.10	18.0 ± 1.6	1138	10.7
LEW 85311	*58.1 ± 0.5*	*69.6 ± 0.7*	*4.64 ± 0.01*	*17.4 ± 1.5*	*−15.62 ± 0.17*	*−0.5 ± 0.1*	*1008 ± 2*	*10.4 ± 0.5*
LON 94102	65.3 ± 0.1	63.3 ± 2.8	3.96 ± 0.02		−15.47 ± 0.12	15.1 ± 0.4	1093 ± 12	
ALH 85013	67.6 ± 2.3	67.2 ± 4.2	3.80 ± 0.04		−15.79 ± 0.27	8.2 ± 0.1	1028 ± 1	
CM heated								
EET 87522	70.2 ± 0.2	33.8	3.06 ± 0.01	18.5	−11.11 ± 0.02	26.4 ± 0.8	81	4.3
Y 793321	*67.2 ± 0.3*	*42.2 ± 0.7*	*3.00 ± 0.06*	*15.9 ± 0.3*	*−8.39 ± 0.07*	*35.1 ± 0.7*	*95 ± 7*	*9.2 ± 0.1*
PCA 91008	*62.5 ± 0.4*	*24.2*[a]	*2.85 ± 0.02*	*20.0 ± 0.3*	*−11.38 ± 0.09*	*26.0 ± 0.2*	*347*[a]	*7.8 ± 0.1*
CR								
GRO 95577	72.5	72.4	2.94		−26.09	228.4	3303	
GRO 95577	*75.5*	*78.6*	*3.16*	*11.4*	*−26.58*	*233.2*	*2973*	*15.0*
CO								
Ornans	55.5	19.4	1.19		−8.83	−6.9	139	
OC								
QUE 97008	64.4	34.6	1.19		−20.62	−0.4	3428	
QUE 97008	*50.6 ± 1.4*	*37.9 ± 1.0*	*1.68 ± 0.01*	*24.4 ± 0.7*	*−20.35 ± 0.09*	*−0.7 ± 0.1*	*3199*	*8.4*
MET 00452	72.8	23.7	1.22		−15.24	−6.7	4892	
MET 00452	*71.5*	*42.3*	*1.43*	*15.5*	*−16.05*	*−7.2*	*2678*	*7.9*
WSG 95300	81.3	10.3	0.63		−12.65	−24.7	11,850	
WSG 95300	*64.0*	*20.9*	*0.56*	*14.1*	*−12.00*	*−38.5*	*6181*	*6.1*
Ungrouped								
MAC 88107	67.5 ± 1.0	19.6 ± 0.3	0.89 ± 0.03	13.8	−9.09 ± 0.07	−4.2 ± 1.2	677	0.2
MAC 87300	*76.1*	*39.5*	*1.12*	*10.6*	*−7.95*	*0.8*	*437*	*8.5*

[a] Remeasured for this study (see also Table 3).

Table 3
Residues that were reanalyzed for the H contents using the He-flushed autosamples and that produced significantly lower H/C ratios than reported by Alexander et al. (2007).

	H/C (at.)	δD (‰)		H/C (at.)	δD (‰)
CM heated			*OC*		
PCA 91008	24.2	347	Krymka	30.9	2592
CV			GRO 95504	15.0	5886
MET 00430	24.2	178	GRO 95505	14.9	5875
Bali	27.4	193	MET 96515	17.4	5108
CO			LEW 86018	17.1	4663
Colony	30.4	729	MET 00506	19.4	5029
Y 81020	31.0 ± 1.3	562 ± 28	*EH*		
Y 791717	18.7	477	EET 87746	15.1 ± 0.6	619 ± 35
ALH 77003	11.6	566			

Reanalyzed residues that did not give significantly lower H/C were CO—ALH 77307, Kainsaz, ALH 83108; CV—ALH 84028; OC—Semarkona, MET 00526, MET 96503, Tieschitz.

composition in both new samples. This isotopically normal H is presumably mostly adsorbed atmospheric water that was released from the new residues while they resided in the He-flushed autosampler. This autosampler was not available for the Alexander et al. (2007) study.

We also reanalyzed many of the residues from the Alexander et al. (2007) study that had low H/C ratios using the new autosampler (Table 3). A reanalysis of our earlier Murchison residue, as well as the analysis of our new residue, showed little difference in either H abundance or isotopic

composition. Consequently, the CIs, CMs and CRs with their high H/C ratios were not remeasured. Most, but not all, remeasured samples gave significantly lower H/C ratios and proportionately higher δD values. For the OCs, the new data result in much better defined trends in plots of δD or $\delta^{13}C$ vs. H/C (Figs. 1 and 2).

4.2. New meteorites

Just as the bulk O isotopic compositions of GRO 95566 and LEW 85311 suggest that they are related, the IOM abundances and compositions in these two meteorites are very similar. Clayton and Mayeda (1999) concluded that

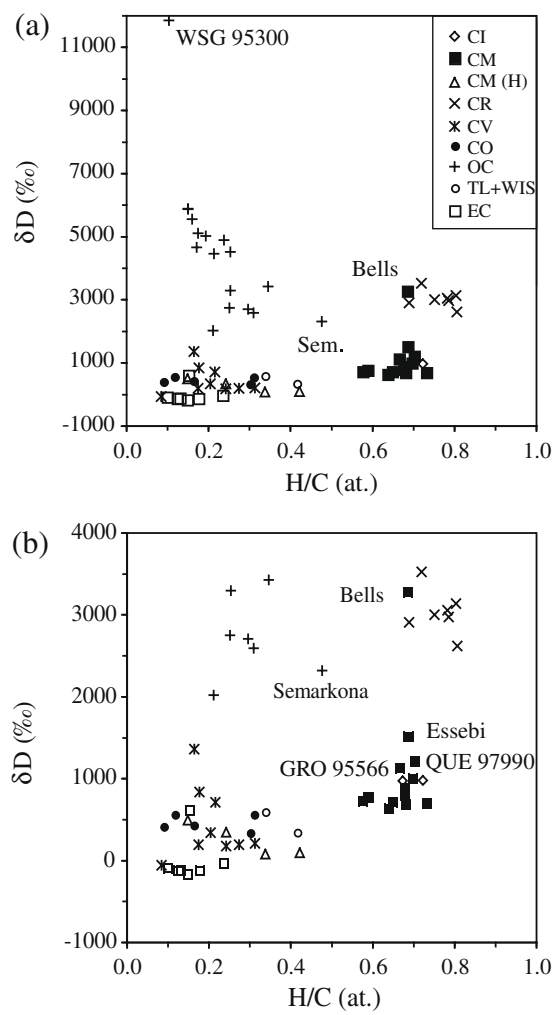

Fig. 1. The range of H isotopic compositions and H/C ratios in chondritic IOM. (a) The full range of IOM compositions and (b) an expanded view to show the range of compositions in CIs, CMs and CRs. The OCs show a dramatic increase in δD with decreasing H/C. The COs, CVs, ECs and heated CMs have similar ranges of H/C ratios to the OCs but much more subdued D enrichments. The CRs exhibit some scatter in H/C, but relatively constant δD values. The principle trend in CMs is of fairly constant H/C ratios, but with the δD values that vary considerably, the most extreme being that of Bells. The CIs plot with the CMs. Data are from this work and Alexander et al. (2007).

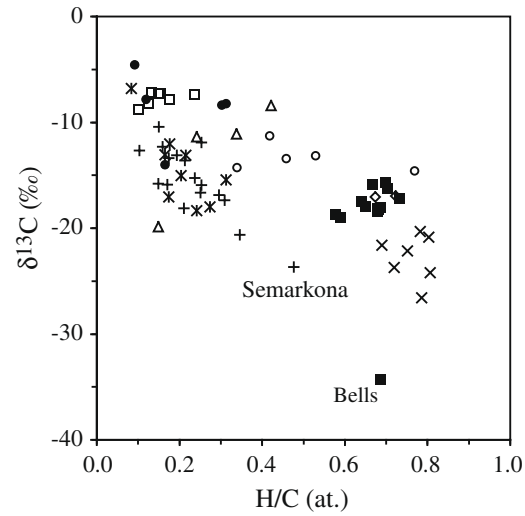

Fig. 2. The variation in C isotopic compositions with H/C ratios. The OCs form a linear trend, with Semarkona at one extreme and WSG 95300 at the other. While more scattered, the COs, CVs and enstatite chondrites lie on or near this trend. Bells (CM2) lies on an extension of this trend. The remainder of the CMs, as well as the CRs and CIs, fall above the OC trend. The symbols are the same as those in Fig. 1.

both meteorites are CMs. This is consistent with the abundances and compositions of their IOM that generally fall within the range observed for CMs, although their δD values (GRO 95566 1138‰ and LEW 85311 1008 ± 2‰) are higher than almost all CMs (typically 700–900‰). For the remainder of the paper, they will be considered to be CMs. The yield and composition of IOM from QUE 97990 are also like most CMs, except for its relatively high D/H ratio (δD = 1220 ± 5‰). Essebi has an even more D-rich bulk IOM composition (1540‰). Amongst the CMs, only Bells (3285‰) has a higher H isotopic composition than these four meteorites. The N isotopic compositions of QUE 97990 and Essebi IOM are also heavier than is typical for CMs ($\delta^{15}N = -10‰$ to 10‰), but again are much less enriched than Bells ($\delta^{15}N = 415‰$). In terms of their IOM abundances and compositions, LON 94102 and ALH 85013 appear to be fairly typical CMs, although their IOM H isotopic compositions suggest that they are more primitive than most.

The abundance of IOM in the heated CC EET 87522 is very similar to that of the heated CM Yamato (Y) 793321. Except for Essebi, the IOM abundances in these two meteorites (C wt% 1.27 and 1.31) are higher than in unheated CMs (C wt% 0.76–1.06), perhaps because some solvent soluble organic material has been thermally converted to insoluble material. On the other hand, another previously studied heated CM, Pecora Escarpment (PCA) 91008, contains less IOM (C wt% 0.74) than either EET 87552 or Y 793321. In metamorphosed meteorites, the H/C ratio of IOM is an indicator of the degree of heating (Naraoka et al., 2004; Alexander et al., 2007). The H/C ratio of EET 87522 is intermediate between those of Y 793321 and PCA 91008, suggesting that EET 87522 was more heated than Y 793321 and less heated than PCA 91008.

In most other respects, the IOM from the three meteorites have similar elemental and isotopic compositions, although PCA 91008 is somewhat more D-rich. Thus, EET 87522 is probably a heated CM.

While the bulk O isotopic composition and IOM contents of MAC 88107 resemble those of MAC 87300, the H/C ratio of MAC 88107 IOM is much lower suggesting that it has been more heated.

The low abundance of IOM in Ornans resembles those of the more metamorphosed COs, like Isna (Alexander et al., 2007). Despite the very high δD value for bulk Ornans reported by Kerridge (1985), the bulk δD of Ornans IOM is only 139‰. The H/C ratio obtained for Ornans IOM is higher than in other COs with higher IOM C contents, such as Allan Hills (ALH) 77003. Since the IOM C content is an indicator of the degree of metamorphism within a chondrite group and the H/C ratio tends to decrease with increasing metamorphism (Naraoka et al., 2004; Alexander et al., 2007), the comparatively high H/C ratio obtained for Ornans (0.194) suggests that the residue contains significant terrestrial H. However, it is unlikely that this contamination is so high that it has completely obscured a small amount of isotopically very heavy H associated with the IOM. The lowest H/C ratio measured by Alexander et al. (2007) for any IOM was ~0.08. Thus, it is unlikely that the ratio of terrestrial to indigenous H in Ornans is greater than three and, therefore, the actual δD value for Ornans IOM is probably ⩽550‰. A δD of ~500‰ would be in line with IOM compositions for other COs (Alexander et al., 2007). The cause of the high D enrichment in bulk Ornans is unclear. Spallation produced H is one possibility, but the exposure age for Ornans is not particularly long (Scherer and Schultz, 2000).

Several of the remeasured residues gave lower H contents and higher δD values than previously reported (Alexander et al., 2007), resulting in clearer correlations between δD or $\delta^{13}C$ and H/C in the OCs (Figs. 1 and 2). However, none of these meteorites have as D-rich IOM as WSG 95300 (11,850‰). This is the most D-rich composition reported to date for any bulk IOM. In other respects, the IOM of WSG 95300 is unremarkable—its low H/C and N/C ratios, relatively heavy C and light N isotopic compositions resemble those of the other more metamorphosed OCs previously analyzed.

4.3. D/H imaging

A total of six fragments (with total area ~2700 μm^2) of Krymka IOM were imaged. Unlike for IOM from CCs analyzed under identical conditions, no evidence of micrometer-scale D/H heterogeneity was found in the Krymka samples. For example, Fig. 3 shows δD images of similarly sized fragments of IOM from Krymka (bulk δD ≈ 2600‰, Table 3) and the CR2 EET 92042 (Alexander et al., 2007). Whereas small sub-regions with greatly enhanced D/H ratios (hotspots) are clearly visible in the EET 92042 image, the Krymka image is homogeneous within statistics. We estimate an upper limit on the abundance of D hotspots in Krymka IOM of <0.1 area%, compared to 2.4 area% for EET 92042 (Busemann et al., 2006).

5. DISCUSSION

5.1. The ordinary chondrites

With increasing thermal metamorphism, the H/C ratio of the IOM decreases (Naraoka et al., 2004; Alexander et al., 2007). Thus, the correlations seen in the OC data in Figs. 1 and 2 clearly point to a metamorphic control of the H and C isotopic compositions. The COs and CVs have seen similar ranges of metamorphic temperatures (Bonal et al., 2006, 2007; Busemann et al., 2007; Cody et al., 2008a) and have similar IOM elemental compositions (Alexander et al., 2007) to the OCs. The COs and CVs scatter about the OC trend in Fig. 2, but they do not exhibit the large increases in δD values with decreasing H/C seen in the OCs (Fig. 1).

Alexander et al. (2007) attributed the contrasting behaviors of the IOM during metamorphism in OCs and CO–CVs to differential preservation of a D-rich component in the IOM under the range of chemical conditions that existed in the various parent bodies. However, the H isotopic homogeneity of Krymka IOM (Fig. 3), compared to the striking degree of heterogeneity in Type 1 and 2 CCs (Busemann et al., 2006), argues against this. This spatial heterogeneity in CCs is preserved across a range of parent body processing histories, with less extreme D hotspots found in IOM with lower bulk D/H ratios (e.g., Murchison) compared to more primitive meteorites (e.g., EET 92042). In addition, it has been shown that heating destroys D/H hotspots (Remusat et al., 2009). Thus, it is unlikely that the spatially homogeneous H composition of the OCs could be the result of the preservation during metamorphism of a primitive component with a specific high D/H ratio.

Alexander et al. (2007) rejected isotopic fractionation associated with the loss of H from the IOM because the OC data would require a Rayleigh fractionation factor that was much larger than predicted even for loss as atomic H. However, H isotopic fractionations between H_2O and H_2 can be very large ($1000 \ln \alpha = \sim 700$–$1400‰$, where α is the fractionation factor and H_2 is depleted in D relative to H_2O) when produced either by radiolysis of H_2O (Lin et al., 2005) or equilibrium exchange (Suess, 1949; Bottinga, 1969) at low temperatures (<200 °C). In a system where H_2 is lost continuously, resulting in a Rayleigh-type isotopic fractionation process, the fractionation factors of both mechanisms would produce large D enrichments in the residual water that could then exchange with the IOM. It is therefore intriguing that the OCs, but not the COs and CVs, appear to have behaved as partially open systems for volatile elements like Cd during metamorphism (Wombacher et al., 2008).

5.1.1. Radiolysis

The decay of the short-lived radionuclide ^{26}Al ($t_{1/2}$ = 717,000 years) is generally assumed to have been the energy source that drove the metamorphism in the chondrite parent bodies (e.g., Ghosh et al., 2006). As the dominant radiation source, ^{26}Al would also have driven any radiolysis. The total energy released by the decay of ^{26}Al is ~4 MeV/atom—mostly as a 1.8086 MeV γ-ray and an up

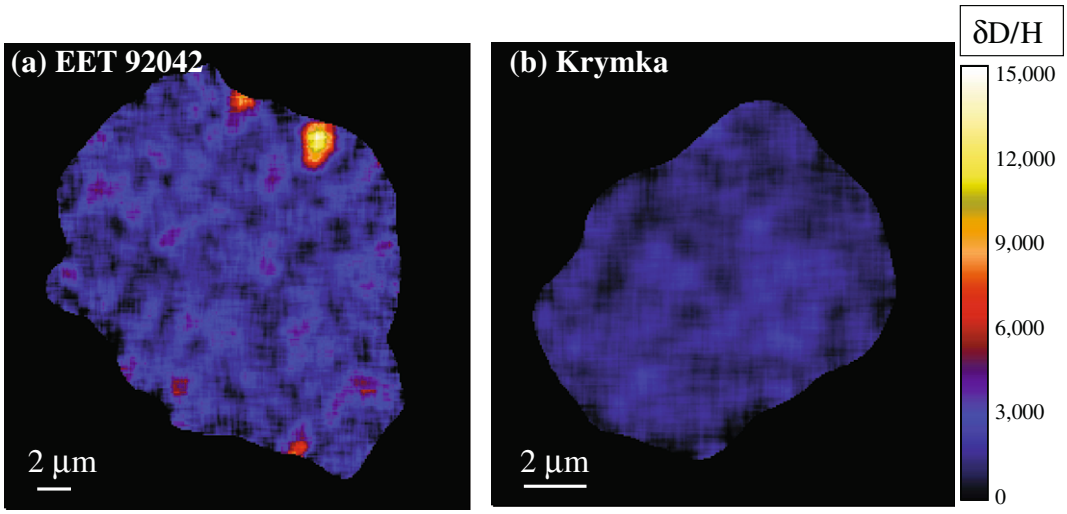

Fig. 3. SIMS H isotope images of similarly sized fragments of IOM from the LL3.2 Krymka (bulk δD ≈ 2600‰, Table 3) and the CR2 EET 92042 (Alexander et al., 2007). Despite the similar bulk H isotopic compositions, the two images are quite different—hotspots with greatly enhanced D/H ratios are clearly visible in the EET 92042 image, but the Krymka image is homogeneous within the statistics of the measurements.

to 1.17 MeV β^+ particle (depending on the energy of the associated neutrino) that, after losing most of its kinetic energy, annihilates in an encounter with an electron to produce two 511 eV γ-rays.

The fraction of water that would be dissociated by the decay of ^{26}Al in meteorites can be estimated using the approach of Hoffmann (1992) and Lin et al. (2005). The H_2 yields, GH_2, for γ and β irradiation of water are 0.4 and 0.6 molecules/100 eV, respectively. In rocks/meteorites, the emitted particles lose much of their energy through their interactions with the minerals present. The net energy not lost to the minerals, E_{net}, and available to dissociate water can be estimated from the expression:

$$E_{net,i} = E_i * W * S_i/(1 + W * S_i), \quad (1)$$

where i is a γ or β particle, E is the energy of the particle, W is the water/rock weight ratio, and S is the stopping power in rock ($S_\gamma = 1.25$, $S_\beta = 1.14$). The yield in molecules of H_2 per decay is then given by:

$$Y = \Sigma E_{net,i} G_i. \quad (2)$$

The fraction of water that would be dissociated is then given by:

$$F = (C_{Al}/27) * R_{26} * (Y/N_A)/(C_{H2O}/18), \quad (3)$$

where C is the concentration of Al or water (wt%), R_{26} is the ^{26}Al/^{27}Al ratio, and N_A is Avogadro's number. Assuming an Al content of 1.2 wt%, an initial water content of 1 wt% and an initial ^{26}Al/^{27}Al ratio of 5×10^{-5}, only about 1% of the water would be dissociated. Such a low level of dissociation would not isotopically fractionate the remaining water sufficiently to explain the IOM compositions in the OCs.

5.1.2. Isotopic fractionation via oxidation of Fe by H_2O

The equilibrium isotopic fractionation between H_2 and H_2O below ~200 °C is of a similar order to that for radiolysis. There is abundant petrologic evidence that metal and sulfide in the most unequilibrated OCs (UOCs) have undergone oxidation (Taylor et al., 1981; Hutchison et al., 1987; Alexander et al., 1989a; Krot et al., 1997; Choi et al., 1998). The oxidant was presumably water and it would have reacted with the metal via reactions such as,

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2. \quad (R1)$$

Oxidation of FeO (in altering silicates) and FeS can also generate H_2. Magnetite and maghemite, as well as clays, are abundant in Semarkona (Taylor et al., 1981; Hutchison et al., 1987; Alexander et al., 1989a; Krot et al., 1997; Choi et al., 1998), but the abundance of Fe-oxides decreases rapidly in more metamorphosed meteorites, probably because they reacted with amorphous silicates to make fayalitic olivine (Alexander et al., 1989b; Brearley et al., 1989). Nevertheless, there is other petrologic evidence that all OCs experienced aqueous alteration prior to metamorphism (Grossman et al., 2000).

Thus, an alternative mechanism to radiolysis for producing H_2 is oxidation of Fe in metal, sulfides and silicates. However, the large range of isotopic fractionations found in the OCs cannot be the result of isotopic fractionation in a closed system. They must be the product of some Rayleigh-type process in which there was little or no back reaction between the H_2 and the H_2O it was generated from. For this to be the case, presumably the isotopic fractionation between H_2 and H_2O would have to have been established at the Fe–H_2O reaction interface. We are not aware of any experimental studies that have measured the H isotopic fractionation during oxidation of Fe by H_2O. It is possible that kinetic rather than equilibrium processes determine the isotopic fractionation, but it seems likely that kinetic processes will also favor the preferential fractionation of H over D into the H_2. Measurement of the H isotopic fractionation associated with oxidation of Fe would be an important test of this model. For the present and in

the absence of any experimental constraints, we use the equilibrium fractionation factor (α) in the standard Rayleigh fractionation equation to estimate the variation in the H isotopic composition of residual water as a function of the fraction of water remaining (f):

$$\delta D \approx 1000\left(\left(\frac{\delta D_0}{1000}+1\right)f^{1/\alpha-1}-1\right), \quad (4)$$

where δD_0 is the initial H isotopic composition and from Suess (1949) the α for water–H_2 isotopic exchange is given by:

$$1000 \ln \alpha = 467,600/T - 303.9. \quad (5)$$

The equilibrium isotopic fractionation factor decreases with increasing temperature. To avoid unreasonably large initial water contents to achieve the fractionations seen in the OCs, temperatures during the oxidation must have been relatively low, probably less than 200 °C. Water and H_2 isotopically re-equilibrate on timescales of roughly 10^3–10^2 years between 20 °C and 100 °C (Lin et al., 2005). These equilibration timescales set the upper limits for the timescales over which H_2 must be lost after its generation for isotopic Rayleigh fractionation to occur. These timescales for the removal of H_2 from the system after its generation are probably not unreasonable for diffusive loss of H_2. Helium pycnometer measurements of chondrite porosity show that He rapidly diffuses into them, at least on scales of up to tens of cm (e.g., Consolmagno and Britt, 1998), and Cd seems to have been quite mobile in the OC parent bodies (Wombacher et al., 2008). Being significantly less massive, H_2 would have diffused even more rapidly than He and Cd.

It should be emphasized that the timescales over which the oxidation of Fe took place could have been much longer than these H_2 removal timescales. Detailed modeling of the length of time over which the oxidation of metal and sulfide could have taken place is beyond the scope of this paper. Nevertheless, to explain the IOM H isotopic compositions the timescales for oxidation of the metal/sulfide and IOM–H_2O H isotopic exchange must be consistent with metamorphic/alteration timescales for type 3 OCs ($\leqslant$10 Ma: Krot et al., 2006), and if the oxidation ultimately consumed all the water it must have taken at least as long as the time required for IOM–H_2O H isotopic exchange. The initial water abundances required to produce the H isotopic fractionations must also be reasonable (i.e., similar to Semarkona bulk). Below we briefly explore what the timescales for oxidation and isotopic exchange are likely to have been, and estimate the initial water abundances that are necessary.

5.1.2.1. Timescales of oxidation. Oxidation rates of Fe-metal by water are a complex function of conditions—T, pH, fO_2, minerals present, etc. Possible analogs for the oxidation that occurred in the OCs are corrosion studies, conducted for the nuclear waste industry, of iron/steel by artificial ground water under anaerobic conditions in the presence of clay minerals and/or basalt (e.g., Anantatmula et al., 1987; Smart et al., 2001; de Combarieu et al., 2007). Hydrogen generation is one of the techniques used for monitoring oxidation rates, although we are not aware of any isotopic measurements being made. Long term corrosion rates under the above conditions and measured over days to months range from ~1 μm/year to <0.1 μm/year. The range of corrosion rates seems to be controlled by whether or not a stable protective layer composed of magnetite, or perhaps $Fe(OH)_2$ at low temperatures, develops. The formation of a protective layer in turn depends less on temperature than on the composition of the ground water and the minerals present.

If we take this range of measured corrosion rates and assume that the largest metal grains in OCs are 1000 μm across, oxidation of metal could have taken from hundreds to tens of thousands of years. Oxidation times would have been even longer if the metal was protected in some way, such as being enclosed within chondrules. Oxidation rates for sulfides and silicates are largely unconstrained.

5.1.2.2. Timescales of IOM isotopic exchange. Hydrogen isotope exchange between water and organic material depends on, amongst other things, the nature of the organic material, temperature, pH and the minerals present (Sessions et al., 2004). The IOM in primitive chondrites is a macromolecular material with a complex and irregular structure that is predominantly composed of small aromatic/olefinic moieties that are cross-linked by short, highly branched and oxygenated aliphatic material.

Alexander et al. (1982) determined the kinetics of H isotope exchange between naphthalene (composed of two aromatic rings) and water in the presence of bentonite (a clay). Clays are present in CI–CM–CRs and Semarkona (Hutchison et al., 1987; Alexander et al., 1989a; Brearley, 2006). Clay minerals catalyze exchange reactions, and their efficacy depends on their compositions. In the experiments, Na-bentonite was found to be orders of magnitude less catalytic than Al- and H-forms of the clay (Alexander et al.,

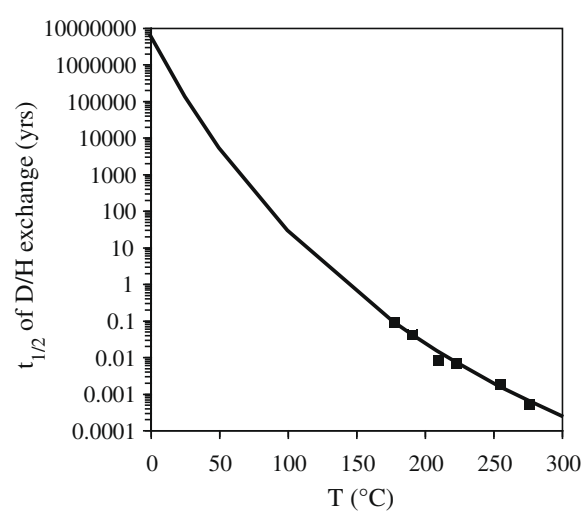

Fig. 4. The half-time ($t_{1/2}$) for H isotope exchange between naphthalene and water as a function of temperature. The measured data (squares) are for exchange in the presence of a Na-bentonite catalyst (Alexander et al., 1982). The curve is a fit to the data assuming Arrhenius-like rate behavior.

1982). The results for Na-bentonite are illustrated in Fig. 4, where the half-life for isotopic exchange is plotted against temperature. At temperatures above 200 °C, the exchange rates are quite fast with $t_{1/2} \approx 14$ h at 250 °C and 2 h at 300 °C. Oba and Naraoka (2003) found little H isotopic exchange between water and either fluoranthene or pyrene at between 170 °C and 220 °C under neutral pH conditions and without clay minerals present. However, under acidic conditions (pH 2), complete exchange was observed within 24 h at 220 °C and within ~100 h at 170 °C.

Rapid isotopic exchange is also observed during hydrous pyrolysis of IOM—at 270–330 °C there is extensive to almost complete H isotope exchange between water and IOM in 3–6 days (Yabuta et al., 2007; Oba and Naraoka, 2009). There is also some degradation of the IOM. In the experiments of Oba and Naraoka (2009), after three days of reaction there is a systematic decrease in the δD of the residual IOM with increasing temperature of the experiment—δD = 307‰ at 270 °C, 64‰ at 300 °C and 25‰ at 330 °C from a starting IOM composition of 986‰ (the water composition was −75‰). These compositions reflect ~64% exchange at 270 °C, ~87% exchange at 300 °C and ~91% at 330 °C, and, provided that there is no unexchangeable H, suggest $t_{1/2}$ for the exchange of roughly 2, 1 and 0.87 days at the three temperatures, respectively.

The IOM in the hydrous pyrolysis experiments exchanged more slowly than naphthalene in the experiments illustrated in Fig. 4, but the hydrous pyrolysis experiments did not include potential mineral catalysts, such as clays, and the pHs of the solutions are likely to have been close to neutral. In the meteorites, H isotopic exchange may have been much faster than in the experiments if any minerals acted as catalysts for the exchange or, as seems likely, the solutions did not have neutral pH. Also, the nature of the purified IOM residues might inhibit exchange compared to what would have taken place in the meteorites. In the meteorites, the IOM is present as micron to submicron particles in the matrix. In contrast, on being dried down the purified IOM residue tends to form very much larger particles that even after crushing are likely to be orders of magnitude larger than the *in situ* grains. This much larger grain size may reduce the rate of exchange, for instance by decreasing the surface area available and forcing the water to diffuse into the grains. Assuming that the naphthalene exchange data provide lower limits for the time required for IOM–water exchange, the $t_{1/2}$ is roughly 30 years at 100 °C, 5000 years at 50 °C and 130,000 years at 25 °C. Hence, above 50 °C it seems likely that extensive isotopic exchange between IOM and water would occur on geologically short timescales that are comparable to the estimated timescales for Fe oxidation.

5.1.2.3. Initial water contents. In reality, the evolution of the isotopic composition of water (and IOM) in any region of an asteroid would have been more complex that the simple picture outlined above. In an internally heated asteroid, meteorites will not have behaved as isolated systems. As the asteroid warmed up, reaction between H_2O and Fe would have begun in the deep interior and the reaction front would have then migrated outwards. At higher temperatures, pyrolysis and oxidation of the organics would also have occurred. Both processes will have produced H_2, as well as other gases, that will have flowed through the asteroid towards its surface. Potentially, these gases could have at least partially isotopically exchanged with the water that was present in the outer parts of the asteroid. Modeling how this flow of H_2 and other gases (e.g., CH_4 and H_2O) from the interior to the exterior of an asteroid would have modified the Rayleigh fractionation behavior assumed here is beyond the scope of this paper. Under some circumstances it could actually have enhanced the isotopic fractionation that develops in the water/IOM in the cooler outer portions of an asteroid. However, here we will treat each meteorite as a simple, isolated system.

Fig. 5 shows the range of H isotopic fractionations that would be possible assuming: (i) a loss of H_2, generated via oxidation of Fe by H_2O, under Rayleigh conditions, (ii) H_2–H_2O equilibrium isotopic fractionation factors (Suess, 1949; Bottinga, 1969) and (iii) ambient temperatures of between 0 °C and 200 °C. To achieve H isotopic fractionations like that in WSG 95300 IOM requires losses of ~80% to >99% of the H from the system, depending on the temperature (0–200 °C) and starting isotopic composition (0–3000‰). The upper limit on the initial H isotopic composition is from the isotopic compositions of the most anomalous primitive (CM/CR) IOM (Alexander et al., 2007), as well as the water in Semarkona matrix (Deloule

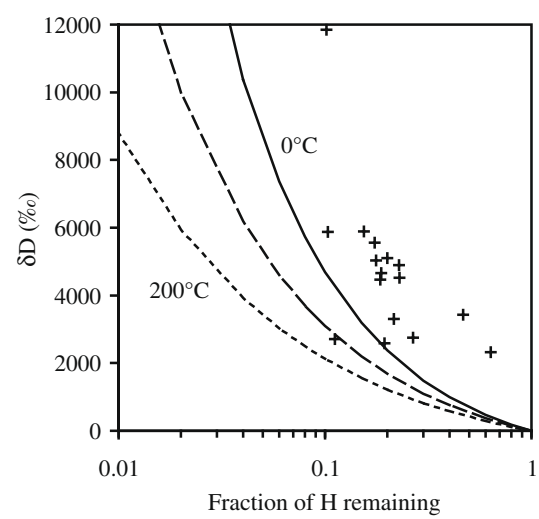

Fig. 5. The predicted variation of the H isotopic composition of residual water as a function of the fraction of H remaining in the system (water + IOM) as the water is consumed by oxidation of metal and the resulting H_2 is lost from the system. It is assumed that equilibrium exists between H_2 and H_2O at the reaction interface only, and the fractionations are calculated (Suess, 1949) for three different reaction temperatures (0 °C, 100 °C and 200 °C). The initial H isotopic composition of the water was assumed to be like that of standard mean ocean water (SMOW). Also shown are points for the OC IOM. In this case, the fraction of H remaining is that in the IOM only and was estimated assuming initially CR-like IOM H/C ratios and Semarkona-like matrix-normalized IOM abundances. The OC points are minimum estimates of the fraction of the total H that must have been lost from the system because they do not take into account the H_2O that was lost. Hence, it is not surprising that the curves do not go through all the points.

and Robert, 1995) and hydrated chondrule glasses (up to 2300‰; Grossman et al., 2000, 2002).

Since it is assumed that the water and IOM isotopically exchanged H, the H in both water and IOM must be included in the fractionating reservoir. The H in IOM is only 0.002 wt% of bulk WSG 95300. Assuming an upper limit on the amount of H loss of 99%, the IOM H content of WSG 95300 implies an initial H content of ⩽0.2 wt%. The bulk H content of the IOM in even the most primitive OC, Semarkona (LL3.0), is only 0.014 wt%. Thus, the bulk of the initial H would have been in water and requires an initial water content of ⩽1.8 wt%. The H content of Semarkona measured by Yang and Epstein (1983) is between 0.04 and 0.09 wt%, depending on whether the H released at low temperature is included. Semarkona contains considerable secondary magnetite and maghemite (Taylor et al., 1981; Hutchison et al., 1987; Alexander et al., 1989a; Krot et al., 1997; Choi et al., 1998), suggesting that its original water content was significantly higher. The high D content of water in Semarkona could be at least partially the result of this loss. If we assume initial and current δD values of 0‰ and 2000‰ for the water in Semarkona, this would imply a H loss of 75–90%, depending on the temperature (0–200 °C), and initial H contents of 0.16–0.9 wt%. Thus, an initial H content of ⩽0.2 wt% (⩽1.8 wt% water) for the OCs is not unreasonable.

5.1.2.4. Implications. If this water produced equivalent moles of H_2 via oxidation and was unable to escape, then, assuming a porosity of 10% and a temperature of 300 K, the H_2 pore pressure would have reached ~75 MPa or 750 bars. The oxidation of IOM C that occurred in the OCs from initially Semarkona-like levels (C = 0.36 wt%) would add a further 6 MPa of CO_2. Such a high pore pressure would be more than enough to potentially completely disrupt even a 100 km radius body, although gas is likely to start escaping when pore pressures exceed ~2 MPa (Wilson et al., 1999). Thus, it is not surprising that the OCs behaved as partially open systems to volatile elements like Cd during metamorphism (Wombacher et al., 2008).

Given the apparently reasonable scenario outlined above for the OCs, it is puzzling that CV and CO chondrites do not show evidence for open system behavior or a similar fractionation of H isotopes in IOM with increasing metamorphism. There was a similar destruction of the IOM during metamorphism as in the OCs, and their initial IOM abundances were at least 1.5–2 times higher than in Semarkona (Alexander et al., 2007). Thus, even if there was no oxidation of metal by water to generate H_2 in the COs and CVs, the CO, CO_2, CH_4 and H_2O generated by the destruction of the IOM should have produced sufficient internal pore pressure to drive crack propagation, gas loss and, therefore, open system behavior. There is also ample evidence for the presence of water during metamorphism of the CVs at least (Brearley, 2006). The fact that D enrichments in the CV and CO IOM do not increase with increasing metamorphism, even modestly as would be expected from H elimination, suggests that exchange with water buffered the H isotopic composition of the IOM and that the fraction of water that was consumed by oxidative reactions prior to and during metamorphism in the CVs and COs was much less than in the OCs.

Finally, on the assumption that the isotopic composition of the water has remained unchanged since accretion of the OC parent bodies, a number of papers have used the D enrichments in OC water to constrain models of solar nebula evolution, as well as the formation of comets and the giant planets (Drouart et al., 1999; Mousis et al., 2000; Hersant et al., 2001; Robert, 2002). In the light of the results presented here, these models will have to be reassessed.

5.2. The CI, CM and CR chondrites and Tagish Lake

In studies of chondritic organic matter, the general assumption has been that the more isotopically anomalous it is, the more primitive it is. The OC data demonstrate that this is not necessarily the case. In the light of this result, we explore whether the D and ^{15}N bulk enrichments in CIs, CMs, CRs and Tagish Lake (hereafter collectively referred to as the C1–2s) could also be secondary products.

The mechanism proposed above to explain the H isotopic compositions of IOM in OCs (i.e., isotopic fractionation associated with loss of H_2 generated through the oxidation of Fe by water) suggests a possible mechanism for modifying the δD values of IOM in C1–2s. Barnes et al. (2004) invoked a similar explanation for D enrichments, albeit comparatively small ones, in an alpine serpentinite. The C1–2s have undergone a process akin to serpentinization that took place over several million years (Krot et al., 2006) and that would also have generated H_2 (Rosenberg et al., 2001). Guo and Eiler (2007) proposed that Fischer–Tropsch-type synthesis of CH_4 from CO_2 and H_2 during alteration could explain the heavy C isotopic compositions of carbonates in carbonaceous chondrites. The loss of the H_2 and CH_4, which is necessary to generate the large D enrichments in the IOM of these meteorites, would also have produced more oxidizing conditions. Thus, if this is the mechanism for generating the D enrichments in the IOM of these chondrites, there should be a clear correlation between D enrichments in the IOM and the oxidation state of the bulk meteorites. Other associations between IOM composition and bulk meteorite mineralogy may also shed light on the mechanism(s) responsible for the range of IOM compositions in C1–2s.

5.2.1. Patterns of isotopic variations in IOM

There is a gross correlation between the IOM H isotopic compositions and the oxidation states of the meteorites—the fO_2 during alteration seems to have increased from CMs to CIs to CRs (Brearley, 2006), and this is also the general order of increasing D enrichment in bulk IOM. The most obvious exceptions to this gross correlation are Tagish Lake and the possibly related meteorite WIS 91600. They experienced very oxidizing conditions during alteration (Zolensky et al., 2002), but have relatively modest D enrichments of 596‰ and 349‰, respectively, in their IOM (Alexander et al., 2007).

Even within the CMs, the isotopic variations do not simply correlate with oxidation state. The two CMs with the highest D enrichments in their IOM are Bells and Essebi

(Table 2 and Alexander et al., 2007). They are also the most oxidized and the most brecciated of the known CMs (Metzler et al., 1992; Brearley, 1995). When the brecciation occurred is not certain, but if it occurred before or during alteration it is likely that it would have aided gas loss and the development of more oxidizing conditions. It is even possible that explosive degassing due to a local build-up of gas pore pressure was responsible for the brecciation (Wilson et al., 1999).

On the other hand, the relatively unaltered CM QUE 97990, which is not brecciated and like most CMs contains the mineral tochilinite (an indicator of relatively reducing conditions) (Rubin et al., 2007), has IOM that is more D-rich than all CMs except Bells and Essebi (Table 2 and Alexander et al., 2007). In the same vein, the IOM in LEW 85311 and GRO 95566 are more D-rich than most CMs (Table 2 and Alexander et al., 2007). Their low bulk $\delta^{18}O$ values have been interpreted to indicate limited exchange with an altering fluid (Clayton and Mayeda, 1999). However, there is no clear correlation between bulk meteorite $\delta^{18}O$ and δD of the IOM in the CMs or any other chondrite group (Fig. 6). Type CM1s, by contrast, tend to be the most D-poor of the CMs.

Thus, there seems to be two distinct associations with relatively D-rich IOM in CMs: (1) meteorites that experienced more oxidizing conditions during alteration (e.g., Bells and Essebi), and (2) CMs that experienced the least alteration. The former association could be due to H_2 loss, but it seems more likely that the latter association reflects more limited IOM–H_2O exchange of an already fairly D-rich precursor.

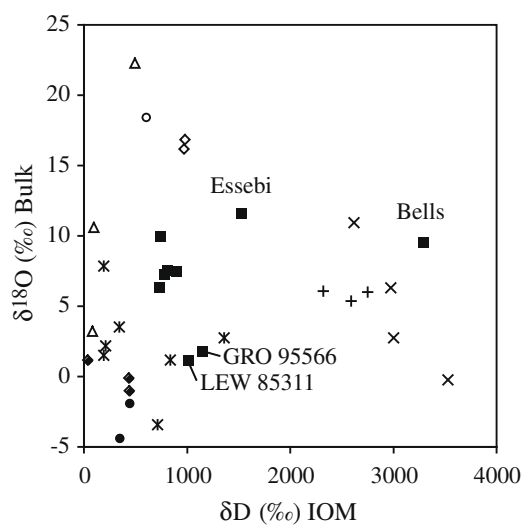

Fig. 6. The H isotopic composition of the IOM vs. the $\delta^{18}O$ of the bulk meteorites. For individual chondrite groups, Clayton and Mayeda (1999) proposed that the bulk rock $\delta^{18}O$ is a measure of the degree of interaction between initially anhydrous minerals and an aqueous fluids—the larger the $\delta^{18}O$, the greater the degree of isotopic exchange. The degree of fluid–rock interaction was presumably largely a function of water/rock ratio, temperature and time. If IOM H isotopic compositions were also determined by exchange with the fluid, one might expect there to be a correlation between bulk $\delta^{18}O$ and the H isotopic composition of the IOM, but there is no such correlation. The symbols are the same as for Fig. 1.

Unlike in the CMs, in the CRs there is no apparent correlation between degree of alteration of the bulk meteorites and IOM isotopic compositions—the least (MET 00426 and QUE 99177) and most (GRO 95577) altered CRs have very similar IOM compositions (Alexander et al., 2007).

Recent results for three new Tagish Lake lithologies with varying degrees of aqueous alteration, on the other hand, show that parent body alteration can dramatically alter IOM compositions. Herd and Alexander (2009) found that the elemental and isotopic compositions of IOM from these three lithologies vary considerably, and that there is an almost linear correlation between H/C ratio and δD value—as the atomic H/C ratios increased from 0.46 to 0.77, so the δD values increased from 789‰ to 1834‰. The upper H/C ratio is similar to that in CI, CM and CR IOM, and presumably reflects an IOM that is quite aliphatic. The lower H/C ratio is slightly higher than previous reports for Tagish Lake IOM that was found to be very aromatic (Pizzarello et al., 2001; Cody and Alexander, 2005). Despite the range of H/C ratios, the total amount of C in the IOM in these three lithologies is very similar, suggesting that the change in H/C was not accompanied by a significant loss of C and, therefore, that H isotopic exchange and/or D loss occurred during conversion of aliphatic material to aromatic material in Tagish Lake. In the CMs, there is no significant variation in aliphatic/aromatic ratio despite a range of isotopic compositions that is larger than observed in Tagish Lake (Cody et al., 2008b).

Although the focus of this paper has been the H isotopes, N isotopes may also help to constrain the cause(s) of the isotopic variations amongst C1–2s. There is a suggestion of a correlation between the D and ^{15}N enrichments in their IOM (Fig. 7a). In the less anomalous CMs, there is a steep increase in both δD and $\delta^{15}N$ values. Semarkona falls approximately on an extension of the CM trend, even though the N isotopic composition used here (Alexander et al., 2007) is less anomalous than that measured by Alexander et al. (1998) ($\delta^{15}N$ of 27‰ vs. 56‰, respectively). The CIs lie close to this trend, but the heated CMs, Tagish Lake and WIS 91600 are displaced to heavier N and lighter H isotopic compositions. If the CRs and Bells are part of the same trend as the CMs, the slope of the trend must flatten as the δD approaches ~3000‰. There is also the suggestion of a relationship between N and C isotopes (Fig. 7b).

The causes of the correlations between H, N and, possibly, C are unclear. In the OCs, the correlation between H and C isotopes is the reverse of what is seen in the CIs, CMs and CRs (Figs. 1 and 2), and there is no correlation between H and N isotopes. Stepped combustion studies have shown that the IOM in the most primitive OCs contain an isotopically heavy N component (up to ~250‰), but this component is lost during metamorphism (Alexander et al., 1998), while the H isotopic compositions become increasingly heavy.

5.2.2. H_2–H_2O–IOM exchange?

The complex and sometimes contradictory inter- and intra-group variations in the isotopic compositions of IOM

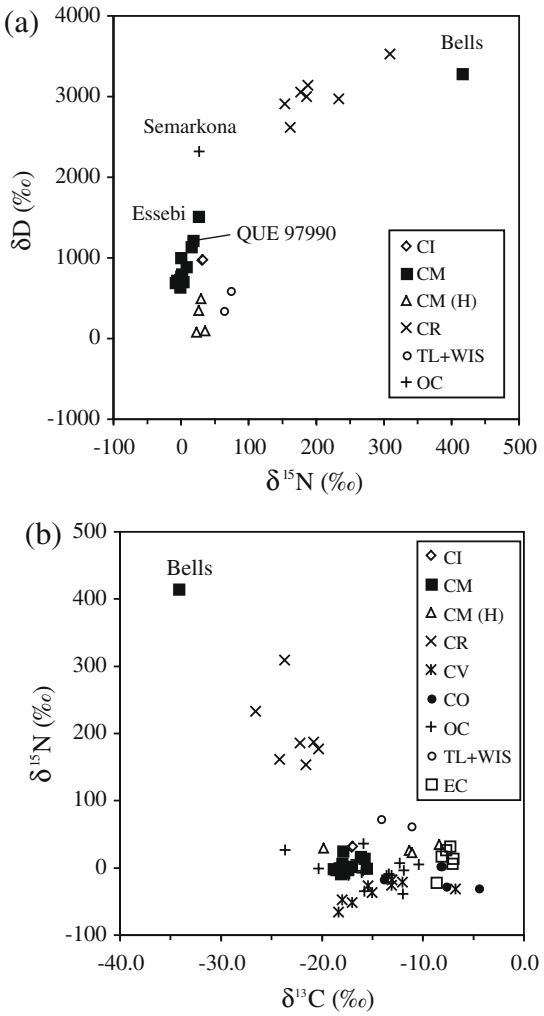

Fig. 7. Possible relationships between H, N and C isotopes in chondritic IOM. Most CMs exhibit a steep linear trend between H and N isotopes (a). If Bells is part of this trend, it must turn over and would roughly pass through the CR IOM. Semarkona also lies close to this trend. The CIs lie close to the main CM trend, but the heated CMs, Tagish Lake and WIS 91600 fall below and to the right of it. In (b), if there is a genetic relationship between Bells and the other CMs, the line connecting them would also pass through the CRs. Again, the CIs fall close to the bulk of the CMs, and the heated CMs, Tagish Lake and WIS 91600 are displaced from them.

from C1–2s suggest that there was more than one mechanism responsible for modifying the IOM. Nevertheless, the fact that the most D-rich (and ^{15}N-rich) meteorites (Bells and the CRs) are also amongst the most oxidized means that it is worth pursuing the Fe oxidation with H_2 loss mechanism further. If the IOM in Bells and Essebi became as D-rich as they are through exchange with water that itself was isotopically enriched by formation and loss of H_2 and CH_4, there should be some evidence for this D-rich water.

The bulk H isotopic compositions of water in chondrites have not been measured directly because of the difficulty of separating the water, mostly in hydrated minerals, from the organic matter. Listed in Table 4 and plotted in Fig. 8 are estimates of the water compositions in several meteorites calculated by subtracting IOM from their bulk H contents. Similar estimates were made by Robert (2002). Where possible, we chose to use the bulk H data of Pearson et al. (2001), rather than Kerridge (1985) for instance. Unlike most earlier studies, Pearson et al. (2001) did not preheat their samples. The preheating drives off not only adsorbed atmospheric water, but also the loosely bound structural water in minerals, resulting in significantly lower H contents that do not correlate with the degree of alteration. However, the loosely bound water is also susceptible to exchange with atmospheric water, which will modify the bulk H isotopic compositions and means that the estimated water compositions should be treated as lower limits if they are heavier than terrestrial and upper limits if they are lighter than terrestrial.

No bulk H data has been reported for Essebi, but the Essebi matrix separate analyzed by Kerridge (1985) is D-rich (450‰). If we assume that the matrix makes up 50 wt% of the meteorite and that the remaining material is anhydrous, subtraction of the IOM produces a water H isotopic composition of ~120‰.

It can be seen from Fig. 8 that in general the chondrites with the most D-rich IOM also have the most D-rich estimated water compositions. It is also clear from the CIs and most CMs that the water itself, at least in these meteorites, is not D-rich—except for Bells and Essebi, they all have δD values that are <0‰. For Bells, Essebi and the CRs, there is a suggestion of a linear correlation between IOM and estimated water compositions. However, this apparent correlation should be treated with caution. The estimates of the Bells and Essebi water compositions relied on the water contents measured by Kerridge (1985) rather than Pearson et al. (2001). Hence their estimated water compositions are likely to be systematically enriched compared to the other meteorites. Also, the contributions from the SOM in the meteorites have not been taken into account, and the SOM tends to be enriched in D. Finally, there are uncertainties (20–30%) in the measured IOM abundances in these meteorites, but these uncertainties introduce relatively small variations in the estimates of isotopic compositions of the water. That the D abundances in the water might be somewhat overestimated due to the inclusion of the SOM is supported by the few measurements of H isotopic compositions of CM materials that should contain little organic matter (Table 4). Nevertheless, at least in the case of the OC Semarkona, the estimated water compositions are consistent with *in situ* measurements of hydrated chondrule glasses (Table 4).

While in chondrites with the most D-rich IOM the water also seems to be enriched, the degrees of D enrichment in the bulk water are always much smaller than in the IOM. This would seem to rule out exchange of IOM with D-rich water producing the IOM H isotopic compositions. Equally problematic is the apparent correlation between H and N isotopic compositions in the IOM. By analogy with the model for H isotopic fractionation, one candidate reaction for producing the ^{15}N enrichments would be equilibrium isotopic exchange between NH_3 in solution and N_2 gas. However, at least for gaseous reactants, the N isotopic

Table 4
The abundances and H isotopic compositions of water in bulk chondrites estimated after subtracting the IOM H from the bulk meteorite H. The CM and CR chondrites are listed in order of increasing degree of alteration.

	Bulk H[a] (wt%)	Bulk δD[a] (‰)	IOM H[b] (wt%)	IOM δD[b] (‰)	H_2O[c] (wt%)	H_2O δD[c] (‰)	H_2O δD[d] (‰)
CI							
Ivuna	1.75	53	0.136	978	14.5	−25	
Orgueil	1.62	−30	0.112	972	13.6	−105	
CM							
Bells	0.418	990	0.055	3285	3.3	642	
Murchison	1.01	−53	0.060	810	8.6	−108	−123 to −200
Murray	0.96	−79	0.054	892	8.2	−137	−147 to −183
Mighei	1.21	−92	0.053	803	10.4	−133	
Cold Bokkeveld	1.59	−91	0.041	734	13.9	−113	−191
ALH 83100	1.60	−156	0.041	723	14.0	−179	
C2							
Tagish Lake	1.37	374	0.056	596	11.8	365	
CR							
EET 87770	0.47	366	0.029	3002	4.0	193	
Renazzo	0.43	429	0.047	2318	3.4	198	
Al Rais	1.43	644	0.090	2620	12.1	512	
CV							
Kaba	0.24	−66	0.018	209	2.0	−89	
LL							
Semarkona	0.038	2595	0.014	2322	0.2	2756	1185–2340
Semarkona	0.093	1347	0.014	2322	0.7	1173	1185–2340

[a] All bulk data are from Pearson et al. (2001), except for Bells which is from Kerridge (1985) and Semarkona which is from Yang and Epstein (1983). Kerridge (1985) heated the samples at 200 °C in vacuum prior to analysis, so the bulk H contents are likely to be underestimated. Two Semarkona bulk compositions are included to illustrate the sensitivity of the estimates to the exclusion and inclusion of H released at low temperatures (<350 °C).

[b] All IOM data are from Alexander et al. (2007), except for Renazzo which is from Robert and Epstein (1982).

[c] Water abundances and isotopic compositions estimated by subtracting the H in the IOM from the bulk H. This ignores H in soluble organics, etc. and consequently the results are likely to be overestimates.

[d] Measurements of water compositions in altered chondrules and coarse silicate fragments where the contribution from D-rich organic matter is likely to be minimal (Grossman et al., 2000, 2002; Eiler and Kitchen, 2004). Multiple ion probe measurements of individual Semarkona chondrules are very variable, and only the highest values in each are used on the assumption that these areas were the least contaminated by the making of the thin sections.

fractionations at temperatures above 0 °C are small (⩽11‰) and it is the N_2 that becomes enriched in ^{15}N (Richet et al., 1977), which is the reverse of what is needed. An alternative is Rayleigh loss of NH_3, and exchange between the remaining ammonia in solution and the IOM. Assuming a purely kinetic fractionation factor, this would require loss of >99.999% of the NH_3 to produce the N isotopic composition of Bells IOM from an initial composition near 0‰. This is an impossibly large amount given that the amount of N in IOM in the bulk meteorite is 0.038 wt%. The most straightforward interpretation of the N isotopic behavior is that the heavy N is a primordial component, supporting the conventional interpretation that IOM evolved from initially Bells- or CR-like IOM in response to varied parent body conditions.

Perhaps the strongest argument against any model seeking to produce the H and N isotopic fractionations in chondritic IOM during aqueous alteration is presented by IDPs. Both aqueously altered and unaltered IDPs contain organic material (Flynn et al., 2003; Keller et al., 2004) that, at least isotopically, is very similar to IOM in Bells and the CRs. As their name suggests, anhydrous IDPs are largely free of hydrous phases, with submicron crystalline and amorphous silicates, and much of the Fe in nanophase Fe–Ni metal. Primary Fe-oxide minerals are absent in anhydrous IDPs. The anhydrous IDPs tend to have the most isotopically anomalous compositions (Messenger, 2000; Aléon et al., 2001; Busemann et al., 2009). Since these IDPs contain little or no hydrated material, except for implanted solar wind, their H and N is presumably all in organic material, and their isotopic compositions resemble those of the most anomalous IOM found in chondrites. Simple hydrothermal experiments have shown that alteration of silicates in IDPs occurs rapidly—within 12 h at 150 °C (Nakamura et al., 2005). Given the absence of evidence for extensive aqueous activity in anhydrous IDPs, at present it is hard to envisage how the D (and ^{15}N) enrichments in their IOM can be the result of oxidation of metal by water in an open system. If anhydrous IDPs are as primitive as they appear to be, it seems inescapable that the isotopic compositions of their IOM predate formation of their parent body. It would also be a remarkable coincidence if the isotopic compositions of

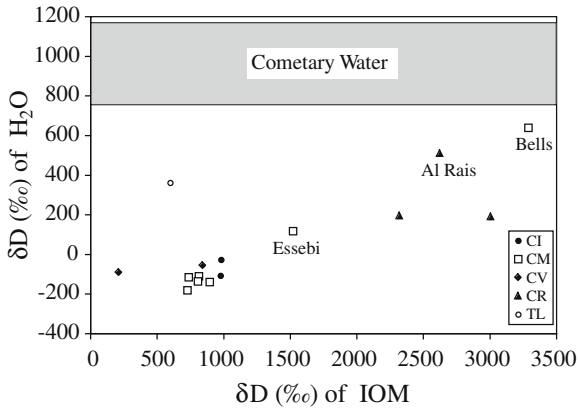

Fig. 8. The H isotopic compositions in carbonaceous chondrites of IOM and water estimated by subtracting the IOM from the bulk H (see Table 4 and text for details). Overall, there does not seem to be a simple correlation between IOM and estimated water H isotopic compositions. There is a tendency for the meteorites with the most D-rich IOM to also have the most D-rich estimated water compositions, but this could simply be due to the fact that the generally D-rich soluble organics were not subtracted when estimating the water compositions. Only the estimated water compositions of Al Rais and Bells approach those of cometary ices, in this case Halley which is the most accurately known ($\delta D = 975 \pm 212$‰: Bockelée-Morvan et al., 2004).

IOM in anhydrous IDPs were so similar to IOM in the CRs and Bells, yet the isotopic enrichments in the IOM of these chondrites formed during parent body alteration.

5.2.3. Why such modest D enrichments in the water?

If, as seems almost unavoidable, significant amounts of H_2 were generated during the alteration of the C1–2s and there probably was some isotopic exchange with IOM, why is it that the estimated water compositions are not more D-rich? One explanation is that the fraction of water that was consumed by oxidation of Fe was fairly modest. Most CM2s are relatively reduced (containing tochilinite rather magnetite), perhaps explaining why their water is not highly enriched in D. However, the presence of Ni-rich metal and Fe^{3+}-bearing cronstedtite in CMs does suggest that they experienced some oxidation. There may also have been exchange between the water and D-rich IOM. Both oxidation and exchange may at least partially explain why the H isotopic compositions of the water in CMs are much more D-rich than the estimated bulk solar value (roughly −840‰). If the heavier estimated water compositions in the more oxidized meteorites Bells and Essebi are due to Fe oxidation and H_2 loss, assuming an initial composition of −200‰ (slightly lighter than the lightest measured CM water composition in Table 4) and temperatures of 0–200 °C, Bells would have to have lost ~60–75% of its water and Essebi ~35–50% of its water. The CRs in Table 4 and Tagish Lake would have to have experienced water losses in the same range as Bells and Essebi.

The CIs are arguably the most oxidized of all the C1–2s. If their pre-alteration mineralogy was like that of anhydrous IDPs (Fe-metal, FeS and Mg-rich silicates), then all the O in their Fe-oxides, sulfates and carbonates must have ultimately come from water. Using conservative assumptions, Alexander (2005) estimated that the initial water content of the CIs was at least 35 wt%. This compares with about 14 wt% water in CIs at the present time. Thus, it seems that CIs probably lost at least half their water through oxidation, which would result in a D enrichment of ~400–700‰ if there was Rayleigh loss of H_2 at 0–200 °C. This would mean that the water in the CIs was initially much lighter than the water now present in them (Table 4), and fairly close to the bulk solar value.

It is worth noting that only the estimated water compositions of Bells and Al Rais approach the D enrichments estimated for comets (Fig. 8), even if no correction is made for the isotopic fractionations that probably accompanied H_2 production and loss during alteration. There will have been a radial gradient in the isotopic compositions of nebular ices at the midplane, D enrichments in ices should have increased with increasing radial distances. This gradient would have been the result of temperature dependent equilibrium and kinetic isotope effects associated with the isotopic exchange between H_2O and H_2 (Lécluse and Robert, 1994), as well as the possible preservation of presolar ices in the outer nebula. If H_2 loss and exchange with initially D-rich IOM does not account for much of the range of measured and estimated water compositions, one would have to come to the counter intuitive conclusions that: (1) the water accreted by the OCs formed much further from the Sun than any water in C1–2s and (2) the order of ice formation distance in the C1–2s was CR > Tagish Lake > CI > CM. It seems much more likely that the water in all the chondrites has been enriched in D to varying degrees by H_2 loss and exchange with IOM, and that the ices accreted by the chondrites formed much closer to the Sun than the ices in the three measured comets. This conclusion is not as self-evident as it might first appear because: (i) there has been speculation that the CIs, at least, are fragments of extinct comets (e.g., Ehrenfreund et al., 2001; Gounelle et al., 2006, 2008) and (ii) transport of considerable amounts of ice with large $\Delta^{17}O$ values from the outer to the inner Solar System has been proposed to explain the O isotopic composition of inner Solar System bodies (Yurimoto and Kuramoto, 2004; Lyons and Young, 2005; Ciesla and Cuzzi, 2006).

It is true that, as judged from the O isotopic compositions of secondary magnetites, the water in OCs (Choi et al., 1998) and Rs (Greenwood et al., 2000) had higher $\Delta^{17}O$ values than water in CCs (Rowe et al., 1994; Choi et al., 1997, 2000, 2008; Choi and Wasson, 2003), and it is the OCs and Rs that contain the most D-rich water (Deloule and Robert, 1995; Grossman et al., 2000, 2002; McCanta et al., 2008). However, for the reasons discussed above it is unlikely that the current δD values for water in chondrites are primordial, and the modest range of $\Delta^{17}O$ values (−3‰ to 5‰) recorded in the magnetites may simply reflect varying exchange with silicates prior their formation.

5.2.4. Whence the isotopic variations in CI–CM–CRs and Tagish Lake IOM?

The intra-group variations in IOM compositions in the CMs and amongst the Tagish Lake clasts are almost

certainly the result of parent body processes. Since these variations cover almost the entire range seen in the C1–2s, a reasonable assumption, adopted in the remainder of this paper, is that all C1–2s had a common D- and ^{15}N-rich IOM precursor like that found in the CRs and the most primitive IDPs. If this was the case, what where the mechanisms that produced the observed IOM compositional variations?

There is a general decrease in D enrichment in IOM from CRs to CIs to CMs to Tagish Lake (Alexander et al., 2007). From NMR studies, Cody and Alexander (2005) noted that there is a parallel decrease in the fraction of aliphatic C in the IOM. Cody and Alexander (2005) suggested that this decrease in aliphatic C was due to oxidation of the IOM very early in the alteration process, with the degree of oxidation being moderated by the abundance of metal in the meteorites at the beginning of alteration. An implicit conclusion of this model is that the aliphatic component carries the most D-rich material. The same conclusion was reached from degradative studies of IOM (Remusat et al., 2006; Huang et al., 2007) and observations of IDPs (Aléon et al., 2001; Keller et al., 2004).

However, the non-linear correlation between the reduction in δD value and the loss of aliphatic carbon belies such a simplistic interpretation. Furthermore, it does not explain the large intra-group variations in the bulk δD (and δ^{15}N) values of the IOM from CMs—solid state ^{13}C NMR analyses reveal that there is almost no variation in the aliphatic/aromatic C ratio in CMs, including Bells (Cody et al., 2008b). Nor does it explain the apparent correlation of IOM elemental and isotopic composition with degree of alteration amongst three Tagish Lake clasts (Herd and Alexander, 2009).

An alternative explanation for the elemental and isotopic variations in IOM is suggested by the hydrous pyrolysis (i.e., hydrothermal) experiments of Yabuta et al. (2007), in which purified Murray (CM2) IOM and water were heated together at 300 °C and 100 MPa for several days. Solid state ^{13}C NMR analyses of the residues revealed that the hydrothermal treatment resulted in a dramatic increase in the aromatic/olefinic C content of the IOM from 60% to 80%. Only about 13% of the C was lost from the IOM during the experiment. This would appear to require that some of the aliphatic C was converted to aromatic/olefinic material. The large variation in H/C ratio without much change in IOM C abundance in three Tagish Lake clasts also seems to require conversion of aliphatic material to aromatic material (Herd and Alexander, 2009).

The solid state ^{13}C NMR spectrum of the product in the Yabuta et al. (2007) experiments was superficially similar to that of previously studied samples of Tagish Lake IOM (Pizzarello et al., 2001; Cody and Alexander, 2005), but there are significant differences in the remaining aliphatic components of the two materials. Accompanying the increased aromaticity was the remarkable decrease in the δD value of the IOM (from 792‰ to −41‰) discussed earlier. Similarly large reductions in δD values were observed in the experiments of Oba and Naraoka (2009). Conversion of aliphatic to aromatic/olefinic C will necessarily reduce the bulk H/C. The C–D bond is stronger than the C–H bond, so that either kinetic or equilibrium isotope fractionation should selectively enrich the IOM residue with D as H is eliminated, whereas the opposite is observed experimentally and in Tagish Lake. Thus, the changes in the IOM H isotopic compositions in the hydrothermal experiments must reflect some combination of the loss of deuterated aliphatics and exchange with the water in the experiments.

Gourier et al. (2008) and Remusat et al. (2009) have suggested that the D enrichments in IOM are associated primarily with benzylic C radicals that are highly clustered, explaining the D hotspots. Benzylic radicals are very reactive and are expected to isotopically exchange relatively easily through the tropylium rearrangement (e.g., the formation of cycloheptatriene from a toluyl benzylic cation). This process is likely to be much faster than the exchange of aromatic H in naphthalene, for instance.

The presence of reactive benzylic radicals are not required to explain facile H isotopic exchange during hydrothermal alteration of IOM. Indeed, the abundance and types of functional groups present in IOM (Cody et al., 2002; Cody and Alexander, 2005) would suggest that numerous different ionic exchange reactions would be possible under either low or high pH aqueous conditions (Sessions et al., 2004; Schimmelmann et al., 2006). The fact that IOM exchanges H on similar timescales to naphthalene seems inconsistent with highly exchangeable D-rich benzylic radicals in the IOM being the sole D-rich moieties.

The meteorites studied by Gourier et al. (2008) and Remusat et al. (2009), Murchison and Orgueil, have IOM with much lower bulk D (and ^{15}N) enrichments than in Bells and the CRs. It is, therefore, possible that the IOM in Murchison and Orgueil has already exchanged their most labile D-rich sites with parent body fluids. However, there is no evidence that the IOM H (or N) isotopic compositions in the CRs are a function of the extent of aqueous alteration (Alexander et al., 2007), or that the CR IOM exchanges more readily than CMs when isolation protocols involve treatments with hot (60–100 °C), concentrated acids (Robert and Epstein, 1982). On the other hand, aliphatic moieties distal from unsaturated functional groups (e.g., carbonyl and olefinic) exchange H very slowly. Thus, if the D-rich material is primarily aliphatic the relatively rapid isotopic exchange observed in the hydrous pyrolysis experiments supports the idea that aliphatic C exits as predominantly short and highly branched chains proximal to unsaturated moieties (Hayatsu et al., 1977; Gardinier et al., 2000; Cody et al., 2002; Cody and Alexander, 2005).

In the hydrothermal experiments of Yabuta et al. (2007), the N isotopic composition of the IOM changed from $\delta^{15}N = 17‰$ to $-7‰$ without significantly changing the N/C ratio. In general, the N/C ratios in C1–2 IOM do not vary that much even though there is a considerable range in δ^{15}N (Table 2 and Alexander et al., 2007). The behavior of the N isotopes in these meteorites is clearly complex and apparently disconnected from D–H systematics. The behavior of N in the meteorites and experiments could be explained by: (1) loss of a minor IOM component with a very ^{15}N-rich composition (Alexander et al., 1998) and/or (2) isotopic exchange. In the meteorites, exchange with ammonia through deamination–amination equilibria

involving olefins should be quite rapid under moderate hydrothermal reactions (Cody et al., 2001). However, in the hydrothermal experiments there was no ammonia added to the solutions. The solutions were deoxygenated by bubbling N_2 through them, but it is unlikely that there would have been enough N_2 dissolved in the solutions to achieve the degree of N isotopic exchange observed in the Yabuta et al. (2007) experiments, nor is it clear how such exchange would occur. The N isotopic compositions of the three Tagish Lake clasts analyzed by Herd and Alexander (2009) are modest and do not vary significantly ($\delta^{15}N = 50$–$60‰$), even as the H/C ratios and δD values do. Thus, N isotope exchange, if it occurred at all in the parent body, is not obviously correlated with loss and isotopic exchange of H.

The experiments of Yabuta et al. (2007) and Oba and Naraoka (2009) showed that the C isotopic composition of the IOM can also be modified under hydrothermal conditions—both studies reported that the $\delta^{13}C$ decreased by ~3‰. As C isotope exchange reactions are much less likely than H and N exchange, this reduction probably reflects the loss from the IOM of isotopically heavier C ($\delta^{13}C \approx 3$–$4‰$ based on mass balance considerations). We note that the total range in C isotopic compositions in C1–2s is ~20‰ (Alexander et al., 2007), which is much greater than that observed in the hydrothermal experiments. In the case of the CMs, the variation in $\delta^{13}C$ is not accompanied by any distinct differences in molecular structure as determined via solid state ^{13}C NMR (Cody et al., 2008b).

The experiments of Yabuta et al. (2007) and Oba and Naraoka (2009) have shown that hydrothermal alteration is able to achieve most of the modifications of IOM (isotopic exchange, conversion of aliphatic to aromatic material, etc.) needed to explain the intra- and the inter-group variations in C1–2 IOM compositions. However, in detail the range of behavior observed in C1–2 IOM is much more varied than observed in the experiments. This is not entirely surprising because the experiments have only explored a very limited range of conditions. It is possible that the response of the IOM to hydrothermal alteration was a sensitive function of the conditions (e.g., temperature, fO_2, pH, solute compositions and concentrations, and mineralogy).

If hydrothermal alteration is the explanation for the variation in IOM compositions in C1–2s, we can draw some straightforward conclusions. With their very isotopically anomalous and aliphatic-rich compositions, the CRs appear to have been altered under the most benign conditions. The CIs experienced more severe alteration of their IOM than the CRs, but less than most CMs. The correlation of D enrichments with low degrees of alteration in CMs could simply reflect limited IOM–water isotopic exchange due to variations in conditions, such as temperature, pH and/or IOM/water ratios. Why Bells retained its primitive IOM isotopic composition so much better than other CMs is unclear, but could be related to the more oxidizing conditions it experienced or, perhaps, near neutral pH in its altering fluid. The recent analyses of the three clasts suggest that the Tagish Lake parent body experienced the widest range of hydrothermal conditions. In the most severely altered clast, the low H/C ratio of the IOM suggests that most of the aliphatic material has been converted to aromatic/olefinic material. Associated with this conversion of aliphatic to aromatic material was a dramatic decrease in D enrichment of the bulk IOM.

Temperature estimates for alteration assuming either thermodynamic or isotopic equilibrium between phases (see review of Brearley, 2006), or that measure the temperatures of carbonate formation (Guo and Eiler, 2007) are much lower than those of the IOM hydrothermal experiments (270–330 °C). Temperature estimates for the CM2s are ⩽80 °C, with most estimates being ⩽30 °C. CM1s may have experienced higher temperatures (~120 °C), but there is no evidence that their IOM is more aromatic than most CM2s (Cody et al., 2008b), and the δD values of the IOM only decrease modestly from the least to the most altered CMs (from ~1200‰ to ~700‰, excluding Bells and Essebi). Most temperature estimates for CI alteration are similar to those for CM1s, but the IOM in CIs is less aromatic than in CMs (Cody and Alexander, 2005) and slightly more D-rich (Alexander et al., 2007). The temperature estimates for the CRs (50–150 °C), which have the most aliphatic and isotopically anomalous IOM, are too uncertain for comparison with the CIs and CMs. The fact that there is no obvious systematic behavior of the functional group chemistry or isotopic composition of the IOM with alteration temperature estimates, even for CMs and CIs, is puzzling if the diversity of IOM compositions in C1–2s is the result of the hydrothermal modification of a common, less aromatic precursor. Perhaps the meteorites do not record in their current mineralogies the peak temperatures they experienced, and/or other parameters were just as important as temperature (e.g., duration of hydrothermal activity, pH and mineralogy) in controlling the extents of aliphatic to aromatic transformation and isotopic exchange.

6. SUMMARY AND CONCLUSIONS

Very large variations in H and N isotopic compositions are observed in IOM from primitive meteorites. In the OCs, the D enrichments increase with increasing degree of metamorphism, with the most enriched sample having a δD of nearly 12,000‰. A similar behavior is not seen in the CVs and COs. In the OCs, CVs and COs, there is a general trend of increasingly heavy C isotopic compositions with decreasing H/C ratio, a proxy for metamorphic degree, as might be expected for thermal cleavage of C–C bonds. Here we suggest that the large H isotopic fractionations in the OCs occurred at low temperatures (<200 °C) when Fe-metal, as well as Fe in sulfides and silicates, was oxidized by water, and the resulting H_2 was lost from the parent bodies. At low temperatures, there is a very large equilibrium isotopic fractionation between H_2 and H_2O. The residual water remaining as oxidation proceeded would have become increasingly isotopically heavy, and could have isotopically exchanged with the IOM. Isotopic fractionations associated with oxidation of Fe by H_2O and dehydrogenation of the IOM would have led to similarly D-rich IOM in CVs and COs. The fact that the pattern of D enrichments seen in OC IOM are not found in CV and CO IOM is probably due to proportionately less water having been consumed in the

CVs and COs, and the remaining water buffered the H isotopic composition of the IOM despite progressive dehydrogenation.

The OC results demonstrate that large isotopic anomalies alone cannot be taken as unambiguous evidence of a record of nebular or interstellar chemistry. Given this and the fact that generation of H_2 should have occurred during aqueous alteration, we explored whether the D enrichments of IOM in the CIs, CMs and CRs could also be secondary. The loss of H_2 should lead to more oxidizing conditions. Thus, if the IOM D enrichments are secondary there should be a correlation with degree of oxidation in the bulk meteorites and the remaining water should have at least comparable D enrichments to the IOM. Both within the CMs and between the CIs, CMs and CRs there is a general tendency for the more oxidized meteorites to have the more D-rich IOM. In the CMs, but not the CRs, there is also a tendency for the least altered meteorites to have more D-rich IOM. However, while quite uncertain, estimates of the bulk water composition in various chondrites suggest that the δD values of the water in CIs, CMs and CRs are always much lower than in the IOM. At present, there is no mechanism for producing the ^{15}N enrichments found in the IOM, particularly in Bells and the CRs, via parent body processes. So-called isotopic hotspots do not contribute significantly to the bulk IOM isotopic compositions. Nevertheless, the H and N isotopic compositions of the hotspots roughly correlated with the bulk IOM isotopic compositions. The isotopic compositions of the most extreme hotspots are so large that they almost certainly cannot be explained by a parent body mechanism. Hence, the correlation between hotspot and bulk IOM isotopic compositions suggests that the most isotopically anomalous IOM in CIs, CMs and CRs is the most primitive. Perhaps most compelling of all, the IOM in anhydrous IDPs that exhibit little or no evidence for aqueous alteration have bulk IOM and hotspot isotopic compositions that are very similar to the IOM in Bells and the CRs. At present, it seems likely that IOM in Bells and the CRs have isotopic compositions that most closely resemble the primordial IOM, and the IOM in the CRs is closest in its functional group chemistry to the primordial IOM.

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