The origin and evolution of chondrites recorded in the elemental and isotopic compositions of their macromolecular organic matter

C.M.O'D. Alexander [a,*], M. Fogel [b], H. Yabuta [b], G.D. Cody [b]

[a] *Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Road, NW, Washington, DC 20015, USA*
[b] *Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road, NW, Washington, DC 20015, USA*

Abstract

Extraterrestrial organic matter in meteorites potentially retains a unique record of synthesis and chemical/thermal modification by parent body, nebular and even presolar processes. In a survey of the elemental and isotopic compositions of insoluble organic matter (IOM) from 75 carbonaceous, ordinary and enstatite chondrites, we find dramatic variations within and between chondrite classes. There is no evidence that these variations correlate with the time and/or location of chondrite formation, or with any primary petrologic or bulk compositional features that are associated with nebular processes (e.g., chondrule and volatile trace element abundances). Nor is there evidence for the formation of the IOM by Fischer–Tropsch-Type synthesis in the nebula or in the parent bodies. The elemental variations are consistent with thermal maturation and/or oxidation of a common precursor. For reasons that are unclear, there are large variations in isotopic composition within and between chondrite classes that do not correlate in a simple way with elemental composition or petrologic type. Nevertheless, because of the pattern of elemental variations with petrologic type and the lack of any correlation with the primary features of the chondrite classes, at present the most likely explanation is that all IOM compositional variations are the result of parent body processing of a common precursor. If correct, the range of isotopic compositions within and between chondrite classes implies that the IOM is composed of several isotopically distinct components whose relative stability varied with parent body conditions. The most primitive IOM is found in the CR chondrites and Bells (CM2). Isotopically, the IOM from these meteorites resembles the IOM in interplanetary dust particles. Chemically, their IOM resembles the CHON particles of comet Halley. Despite the large isotopic anomalies in the IOM from these meteorites, it is uncertain whether the IOM formed in the interstellar medium or the outer Solar System, although the former is preferred here.
© 2007 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Recently, there has been a renewal of interest in the organic matter in meteorites and interplanetary dust particles (IDPs). This resurgence has been motivated by the development of new analytical techniques, as well as by the potential information the organic matter can provide about processes in the interstellar medium (ISM) and early Solar System. The organic matter is generally divided into solvent soluble (1–25%) and insoluble (75–99%) fractions (Gilmour, 2003). The insoluble organic matter (IOM) is thought to be macromolecular, and composed of small aromatic moieties held together by short highly branched aliphatic chains and ether linkages (e.g., Hayatsu et al., 1977; Cody et al., 2002; Remusat et al., 2005; Sephton et al., 2005). The soluble organic matter is a complex mixture that includes carboxylic acids, amino acids and nucleic acids.

Based on significant D and ^{15}N enrichments, it has been suggested that the IOM is largely interstellar in origin

---

(Robert and Epstein, 1982; Yang and Epstein, 1983, 1984), or at least formed from interstellar precursors. A presolar origin would be consistent with the presence of presolar circumstellar grains in meteorites and IDPs (e.g., Nittler, 2003; Zinner, 2003). More recently, similarities in their 3–4 μm IR (Pendleton et al., 1994) and 200–250 nm UV spectra (Bradley et al., 2005) have strengthened the case for a direct link between the IOM and refractory organics in the diffuse ISM. Alexander et al. (1998) also argued for a presolar origin of the IOM based on the relatively constant ratio between the IOM and presolar grains in all chondrites.

The interstellar origin of the IOM and soluble organic matter rests largely on their D and ^{15}N enrichments, but recent models predict that very large D enrichments will develop in simple gas phases molecules (e.g., CH_4, HCN, NH_3, H_2CO and H_2O) in protoplanetary disks at radial distances of $\geqslant 25$ AU (Aikawa and Herbst, 2001; Aikawa et al., 2002). The models have yet to be extended to smaller radial distances. At these large radial distances, the amount of organic C in the gas phase is relatively small. It is unclear whether the enrichments in the gas phase material can be transferred in significant quantities to the much more abundant condensed organics trapped in ices, or in fact what fraction of ISM organics survive formation of the Solar System. Nevertheless, Remusat et al. (2006) have proposed that the D enrichments in IOM are the result of exchange with D-rich H_3^+ in the outer Solar System. At the very least, these models mean that assigning an interstellar origin to organic matter based on isotopic compositions alone is no longer justified.

Chondrites, IDPs (from outer main belt asteroids and/or comets) and comets will all have accreted at different times and places in the solar nebula. Astrophysical models suggest that there could be extensive radial mixing of dust in disks (Bockelèe-Morvan et al., 2002; Gail, 2004). Also, the thermal structure of the solar nebula and the extent of radial mixing will have changed with time. It is possible that some dust cycled through the hot inner nebula destroying the interstellar organics in the process, and that as it was transported outward again new organic matter formed (Nuth et al., 2000). It has also been suggested that the volatile element fractionations in chondrites result from heating of dust in the nebula at temperatures of from ~400 °C to 700 °C or more (Huss et al., 2003). At these temperatures IOM would be significantly modified or destroyed. If, as these models suggest, the organics found in meteorites, comets, etc. are variable mixtures of material synthesized and/or thermally processed in the ISM and Solar System, this should be reflected in IOM abundances, compositions and functional group chemistries.

Comets (Kissel and Krueger, 1987) and IDPs (Schramm et al., 1989; Thomas et al., 1993) contain roughly 3–4 times as much refractory organic matter than the matrix in even the most primitive meteorites, such as the CIs (Robert and Epstein, 1982; Yang and Epstein, 1983; Alexander et al., 1998). Despite this, there is considerable similarity between the most primitive IOM from chondrites and that in IDPs (Flynn et al., 2003; Keller et al., 2004; Busemann et al., 2006). It is possible, that all chondrites accreted the same primitive IOM component (Alexander et al., 1998; Alexander, 2005b). In this case, all variations in the functional group chemistry, and elemental and isotopic compositions must be consistent with evolution from a common precursor that was presumably synthesized in the outer Solar System or in the ISM.

It is apparent that the IOM retains important information about processes that occurred in the ISM and/or in the solar nebula. Historically, studies of chondrites have tended to ignore the IOM, but its origin is inextricably linked to the formation of its host meteorite. Before the IOM can be used to constraint nebular and chondrite formation processes, the effects of parent body processes (aqueous alteration and metamorphism) and terrestrial weathering must be understood. Indeed, the IOM may provide new insights into the conditions that prevailed during parent body processing. To try to establish the origin(s) of chondritic IOM, as well as how it was modified in the solar nebula, on meteorite parent bodies and on Earth, we report the results of the most extensive and complete survey of the elemental and isotopic compositions of IOM conducted to date. In total, we have analyzed 75 chondrites taken from all major chondrite classes and with a range of petrologic types. We find that parent body processes can effect dramatic elemental and isotopic changes in the IOM. There is no evidence that the IOM formed or was modified in the inner solar nebula. At present, it seems likely that all the IOM in chondrites formed from a common precursor material that formed in the outer Solar System and/or in the ISM.

2. SAMPLES AND METHODS

2.1. Sample selection and petrology

Parent body processing has affected all meteorites and the IOM in them, and the conditions under which this processing occurred varied from parent body to parent body. Hence, the meteorites analyzed here were selected to cover the range of chondrite classes and petrologic types within a class (Table 1). In Tables 1 and 2, meteorites within a class are listed in rough order of increasing aqueous alteration (CMs and CRs) and thermal metamorphism (heated CMs, OCs, CVs, and COs)—little is known of the relative metamorphic grades of the ECs studied and the CIs are completely altered. Several chondrite classes were not studied either because they have no large, unweathered low type 3 members (e.g., Rs and CKs), or because their IOM contents are too low for this study given the sample sizes available (e.g., CHs and CBs). More details of the petrology of the selected meteorites are provided in the Electronic Annex EA-1. Large samples (>1 g) were obtained whenever possible to minimize the potential complications of sample heterogeneity, sample loss during preparation and contamination. Relatively large meteorites were always chosen so that samples could be taken well away from the fusion crust where heating during atmospheric entry might modify the IOM. Except for the enstatite chondrites (ECs), meteorites with petrologic types >3.6–3.7 were not analyzed because IOM C contents in these meteorites are very low (Yang and Epstein, 1983; Grady et al., 1989; Alexander et al.,

Table 1
The meteorites analyzed, along with their classification, shock and weathering stages, abundances of matrix and bulk meteorite insoluble C contents determined in this study

Summary	Fall/find	Classification	Shock	Weath.	Matrix[c] (vol%)	C (wt%)
CI						
Orgueil	Fall	CI1			100	2.00
Ivuna	Fall	CI1			100	2.25
CM						
Bells	Fall	CM2	S1		81.7	0.96
Kivasvaara	Find	CM2				0.97
Murchison	Fall	CM2	S1-2, br		63.6	0.83[d]
Mighei	Fall	CM2	S1		60.7	0.94
Murray	Fall	CM2	S1		58.8	0.96
DOM03183	Find	CM2				0.87
Cold Bokkeveld	Fall	CM2	S1		74.2	0.85
ALH83100	Find	CM1/2		Be		0.76
MET01070	Find	CM1		Be		0.98
CM heated						
LEW85311	Find	CM heated		Be		0.91
Y793321	Find	CM heated				1.31
PCA91008	Find	CM heated		B		0.74
Y86720	Find	CM heated				0.51
CR						
MET00426	Find	CR2		B		0.46
QUE99177	Find	CR2		Be		0.34
EET92042	Find	CR2		B	28.9	0.46
GRA95229	Find	CR2		A		0.68
Al Rais	Fall	CR2	S1		52.9	1.34
GRO95577	Find	CR1		B		0.78
LEW85332	Find	CR?		B/C		0.20
CVox						
Kaba	Fall	CV3 oxB	S1		50.7	0.68
Mokoia	Fall	CV3 oxB	S1, br		39.8	0.54
MET00430	Find	CV3 oxA/B		B		0.51
Bali	Fall	CV3 oxB	S2		50.0	0.35
Allende	Fall	CV3 oxA	S1		38.4	0.18
ALH84028	Find	CV3 oxA	S1	Ae		0.12
CVred						
Leoville	Find	CV3 red	S3		35.1	0.61
Vigarano	Fall	CV3 red	S1-2, br		34.5	0.61
Eframovka	Find	CV3 red	S4		35.7	0.49
MET01017	Find	CV3 red				0.38
CO						
ALH77307	Find	CO3.0	S1	Ae	33.7	0.48
Colony	Find	CO3.0	S1		29.0	0.14
Y81020	Find	CO3.0	S1			0.44
Kainsaz	Fall	CO3.1	S1		30.0	0.43
Y791717	Find	CO3.3	S1			0.10
ALHA77003	Find	CO3.5	S1, br	Ae		0.16
ALH83108	Find	CO3.5	S1	A		0.044
Isna	Find	CO3.7	S1		28.7	0.051
OC						
Semarkona	Fall	LL3.0	S2		15.6	0.36
QUE97008	Find	L3.05	S2	A		0.25
MET00526	Find	L3.05	S2			0.21
MET00452	Find	H3.5		B/Ce		0.27
Bishunpur	Fall	L/LL3.15	S2		13.9	0.25
LEW86018	Find	L3.1		Be		0.25
GRO95502[a]	Find	L3.2	S2	B		0.19
GRO95504[a]	Find	L3.2	S2	A/B		0.24
GRO95505[a]	Find	L3.4		B		0.16
MET96503[b]	Find	L3.1	S2	B	9.9	0.15

Table 1 (*continued*)

Summary	Fall/find	Classification	Shock	Weath.	Matrix[c] (vol%)	C (wt%)
MET96515[b]	Find	L3.1	S2	A/B	9.9	0.19
Krymka	Fall	LL3.2	S3		13.6	0.15
WSG95300	Find	H3.3		A/B		0.25
ALH83010	Find	L3.3		B		0.14
Chainpur	Fall	LL3.4	S1		16.1	0.10
MET00506	Find	H3.4		B		0.21
Tieschitz	Fall	H/L3.6	S3		10.3	0.19
MET00489	Find	L3.6		A/B		0.071
QUE93030	Find	H3.6		B/C		0.002
EH						
GRO95517	Find	EH3		C		0.16
PCA91238	Find	EH3		Be		0.24
ALH77295	Find	EH3		B		0.19
EET87746	Find	EH3		Ce		0.19
Indarch	Fall	EH4	S4		12.5	0.26
EL						
PCA91020	Find	EL3		Ce		0.27
MAC02837	Find	EL3		C		0.26
Ungrouped						
Tagish Lake	Fall	C2			80	2.00[d]
WIS91600	Find	C2		A/Be	85	2.26
Adelaide	Find	C3			35	0.72
MAC87300	Find	C3		B		0.72
Acfer 094	Find	C3			42	0.37
CR weath						
El Djouf	Find	CR2				0.049
Acfer 059	Find	CR2				0.035
Acfer 186	Find	CR2				0.069
Acfer 209	Find	CR2				0.031

Within a chondrite class, the meteorites are listed roughly in order of increasing aqueous alteration or thermal metamorphism.

[a] GRO95502, GRO95504 and, possibly, GRO95505 are paired.

[b] MET96503 and MET96515 are paired.

[c] Sources: Birjukov and Ulyanov (1996), Brearley (1991, 2004a), Huss and Lewis (1995), Huss et al. (1981, 2003), McSween (1977a,b, 1979), Rubin et al. (1985), Weisberg et al. (1993).

[d] IOM C abundance from for Tagish Lake Grady et al. (2002) and for Murchison from Yang and Epstein (1983).

1998). When possible, observed falls were selected. Failing that, the least weathered Antarctic meteorites were preferred. In rare cases, non-Antarctic finds were analyzed— Kivesvaara (CM2) from Finland, Colony (CO3.0) from Oklahoma (USA), Adelaide (ungrouped) from south Australia and Acfer 094 (ungrouped) from Algeria. In these meteorites, the effects of weathering are a concern.

To understand what weathering does to the IOM, we analyzed 4 CR chondrite finds from Algeria—El Djouf 001, and the Acfer meteorites 059, 186, and 209. A previous study of bulk samples of these meteorites suggested that the organic matter in them had been severely affected by weathering (Ash and Pillinger, 1995). CRs were chosen because the large isotopic enrichments in their IOM make it easier to detect isotopic changes associated with weathering, and because the CRs exhibit a fairly uniform degree of parent body alteration.

2.2. Residue preparation

All residues were prepared by demineralization of the bulk meteorites using a CsF–HF (1.6–1.7 g/cc and pH 5–7) technique (Cody et al., 2002; Cody and Alexander, 2005), with all steps carried out at room temperature. The bulk meteorites were crushed to a grain size of <106 μm, treated with ∼2 N HCl to remove Fe, Ni-metal and most sulfide, and then rinsed first with milliQ water and subsequently with dioxane. After this, the samples were treated with two immiscible liquids—dioxane and an aqueous CsF–HF solution (1.6–1.7 g/cc and pH 5–7). The IOM liberated by this treatment collects at the interface between the CsF–HF solution and the dioxane. After centrifugation, the IOM is pipetted off and rinsed several times in ∼2 N HCl, and then rinsed sequentially in 1 N HCl and 9 N HF, ∼2 N HCl, milliQ water and dioxane before being dried down in air at <30–50 °C. In many meteorites, micrometer-sized sulfides remain trapped in the residue. Some of these sulfides gradually oxidized in air so that they can be removed by repeated treatment, at intervals of at least several days, with HCl followed by rinsing in milliQ water and dioxane, and drying.

The 1–2 N HCl was prepared from concentrated HCl produced by bubbling high purity HCl gas through milliQ water. Doubly distilled concentrated HF was used in

Table 2
The C contents, elemental ratios (100×) and isotopic compositions of the meteorite residues

	C (wt%)	H/C (at.)	N/C (at.)	O/C (at.)	S/C (at.)	δ^{13}C (‰)	δ^{15}N (‰)	δD (‰)	δ^{18}O (‰)
CI									
Orgueil	67.0 ± 0.7	67.3 ± 1.4	3.49 ± 0.01	18.1 ± 0.2	2.8 ± 1.4	−17.05 ± 0.04	30.7 ± 0.2	972 ± 2	14.5 ± 0.6
Ivuna	65.8	72.3	3.52	15.4		−16.97	31.9	978	15.2
CM									
Bells	62.8 ± 0.7	68.5 ± 0.8	3.37 ± 0.02	20.9 ± 0.3	5.0 ± 1.4	−34.20 ± 0.16	415.3 ± 1.6	3283	14.1 ± 0.2
Kivasvaara	52.2 ± 0.2	73.1 ± 0.3	3.42 ± 0.01	22.6 ± 0.9		−17.13 ± 0.05	2.7 ± 0.2	707 ± 7	7.9 ± 0.9
Murchison	66.5 ± 0.6	58.8 ± 1.6	3.27 ± 0.03	18.3 ± 0.3	1.8 ± 1.2	−18.91 ± 0.01	−1.0 ± 0.4	777 ± 27	13.2 ± 0.6
Mighei	62.5	67.7 ± 3.3	3.42 ± 0.01	17.2 ± 0.1	3.3 ± 1.0	−18.33 ± 0.23	0.5 ± 1.1	803	11.5 ± 0.4
Murray	61.6 ± 1.0	67.7 ± 1.1	3.69 ± 0.01	17.2 ± 1.2	6.0 ± 2.3	−18.05 ± 0.18	7.5 ± 0.1	893	11.5 ± 0.4
DOM03183	69.7 ± 0.4	63.8 ± 0.4	2.57 ± 0.08	10.8 ± 0.3	7.8	−17.45 ± 0.15	−1.9 ± 0.5	639 ± 5	10.4 ± 0.3
Cold Bokk	62.3 ± 0.2	57.6 ± 1.5	3.35 ± 0.01	18.9 ± 0.1	3.0 ± 1.0	−18.63 ± 0.10	−2.0 ± 0.1	734 ± 26	12.5 ± 0.6
ALH83100	61.2 ± 0.7	64.8 ± 1.3	3.22 ± 0.01	19.1 ± 1.0	3.0 ± 1.8	−17.86 ± 0.15	−6.7 ± 0.8	723 ± 11	10.1
MET01070	64.7 ± 0.7	68.0 ± 0.8	2.99 ± 0.03	15.7 ± 0.5	2.9 ± 1.5	−18.17 ± 0.01	−8.5 ± 0.3	693	9.4 ± 0.3
CM heated									
LEW85311	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
Y793321	67.2 ± 0.3	42.2 ± 0.7	3.00 ± 0.06	15.9 ± 0.3	3.2	−8.39 ± 0.07	35.1 ± 0.7	95 ± 7	9.2 ± 0.1
PCA91008	62.5 ± 0.4	34.7 ± 0.5	2.85 ± 0.02	20.0 ± 0.3	3.6	−11.38 ± 0.09	26.0 ± 0.2	244 ± 7	7.8 ± 0.1
Y86720	66.7 ± 0.2	14.8 ± 1.6	1.86 ± 0.01	15.1 ± 0.1	1.9 ± 0.8	−19.86 ± 0.25	29.5 ± 0.6	496 ± 36	10.5
CR									
MET00426	69.0	78.3	3.39	14.4	n.m.	−20.32	176.8	3054	12.6
QUE99177	67.8	80.3	3.65	14.6	n.m.	−20.83	187.4	3139	13.0
EET92042	66.5 ± 0.6	75.7 ± 2.0	3.83 ± 0.02	16.6 ± 0.2	3.2 ± 1.1	−22.19 ± 0.1	184.1 ± 1.4	3002 ± 12	14.2 ± 0.3
GRA95229	63.0	68.9	4.39 ± 0.64	22.0	3.1	−21.61 ± 0.90	153.4 ± 6.7	2909	12.1
Al Rais	61.4	80.6	3.21	16.2	7.4	−24.20	161.8	2619	15.2
GRO95577	75.5	78.6	3.16	11.4	0.7	−26.58	233.2	2973	15.0
LEW85332	56.7	71.9	3.19	20.4	n.m.	−23.70	309.0	3527	10.6
CVox									
Kaba	65.1	31.3	1.29	30.3		−15.44	−26.2	209	17.8
Mokoia	68.9 ± 1.0	20.4 ± 0.3	0.88 ± 0.01	13.2 ± 0.2		−15.04 ± 0.17	−36.3 ± 1.2	341	8.4 ± 0.4
MET00430	*49.1 ± 2.0*	*32.4 ± 2.4*	*0.65 ± 0.01*	*19.0 ± 1.4*		*−18.35*	*−65.6 ± 2.9*	*62 ± 10*	*6.9 ± 0.7*
Bali	56.7	37.4	0.46	13.6	n.m.	−18.00	−47.5	160	9.5
Allende	57.6 ± 1.2	17.4 ± 1.0	0.48 ± 0.03	12.5 ± 0.5		−17.03 ± 0.19	−51.2 ± 0.6	194 ± 13	5.1 ± 0.4
ALH84028	*43.0 ± 0.2*	*18.2 ± 0.2*	*0.62 ± 0.01*	*30.4 ± 0.2*		*−15.89 ± 0.08*	*−41.4 ± 0.1*	*239 ± 10*	*4.9 ± 0.1*
CVred									
Leoville	73.6 ± 0.2	16.4 ± 0.2	1.15 ± 0.08	9.0 ± 0.1		−13.09 ± 0.28	−17.5 ± 2.4	1361 ± 52	11.5 ± 0.4
Vigarano	73.1 ± 0.1	17.6	0.82 ± 0.02	10.7 ± 0.2		−12.05 ± 0.17	−21.3 ± 0.5	839	9.3 ± 0.2
Eframovka	72.3	21.5	0.67	9.7	n.m.	−13.11	−25.7	714	6.8
MET01017	89.5 ± 0.8	8.4 ± 0.4	0.10 ± 0.07	4.6 ± 1.5		−6.79 ± 0.07	−31.4 ± 4.1	−57	7.9 ± 0.9
CO									
ALH77307	65.5	12.9	2.04	15.0	7.7	−8.29	3.0	314	8.2
Colony	54.0	32.7	2.01	29.0		−8.68	17.7	749	10.9
Y81020	64.0	41.6	1.06	18.3	2.3	−8.17	3.3	402	6.8
Kainsaz	68.9	16.3	0.60	11.9		−13.92	−16.4	435	7.1
Y791717	40.1	*49.2*	*0.60*	*28.7*		*−7.13*	*−19.4*	*340*	*2.6*
ALH77003	51.7 ± 0.1	23.8 ± 0.6	0.67 ± 0.01	26.4 ± 0.4		−7.72 ± 0.01	−27.1 ± 4.7	132 ± 9	6.5 ± 0.2
ALH83108	64.5	9.0	0.53	13.5		−4.47	−29.7	417	5.5
Isna	32.0					*−8.50*			
OC									
Semarkona	56.3	47.6	1.49	28.9	7.4	−23.67	26.9	2322	12.6
QUE97008	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
MET00526	66.2 ± 1.8	25.3 ± 0.7	1.65 ± 0.01	18.3 ± 0.5		−15.94 ± 0.09	−4.2 ± 0.1	4526	8.7
MET00452	71.5	42.3	1.43	15.5		−16.05	−7.2	2678	7.9
Bishunpur	57.7	25.1	1.49	22.8		−16.65	12.1	2749	11.2
LEW86018	59.3	26.0	0.74	20.6		−15.88	36.3	2531	4.5
GRO95502[a]	61.2	25.3	0.71	18.5		−11.90	−3.7	3297	8.8
GRO95504[a]	59.7	22.4	0.89	18.4		−10.42	5.3	3174	10.7
GRO95505[a]	60.8	21.8	0.85	18.2		−15.81	−34.4	4009	7.7

Table 2 (*continued*)

	C (wt%)	H/C (at.)	N/C (at.)	O/C (at.)	S/C (at.)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	δD (‰)	$\delta^{18}O$ (‰)
MET96503[b]	62.1	24.6	1.88	20.5		−13.60	−11.3	3984	10.8
MET96515[b]	70.2	22.6	1.50	14.6		−13.36	−8.7	3997	12.0
Krymka	70.7	34.8	0.97	14.8 ± 0.2	3.4	−17.38	−10.7	1917	12.2 ± 0.4
WSG95300	64.0	19.0	0.56	14.1		−12.00	−38.5	6181	6.1
ALH83010	*46.1*	*17.4*	*0.30*	*34.3*		*−14.81*	*−46.9*	*346*	*7.7*
Chainpur	*44.8*	*29.6*	*1.70*	*31.5*		*−16.86*	*8.2*	*2708*	*13.1*
MET00506	63.1	26.1	1.49	15.8		−13.13	−11.3	3908	9.3
Tieschitz	66.5 ± 1.8	16.0 ± 0.4	1.01 ± 0.01	13.6 ± 0.4		−12.31 ± 0.09	7.2 ± 0.1	5558	13.1
MET00489	*28.3*					*−18.82*			
QUE93030	*7.9*					*−16.04*			
EH									
GRO95517	83.8	17.5	0.67	4.6	n.m.	−7.75	27.4	−115	12.8
PCA91238	*47.2 ± 0.1*	*14.8 ± 0.8*	*b.d.*	*5.1*	n.m.	*−7.14 ± 0.04*	*b.d.*	*−160 ± 1*	*12.0*
ALH77295	73.5	23.4	0.38	4.5	n.m.	−7.36	32.5	−23	9.7
EET87746	82.0	24.4	0.58	13.2	n.m.	−7.16	6.9	299	9.1
Indarch	67.2	9.9	0.20	4.1		−8.73	−20.9	−82	11.9
EL									
PCA91020	74.6 ± 1.1	12.4 ± 0.2	0.69 ± 0.01	7.6	n.m.	−8.21	17.8 ± 1.6	−119 ± 3	20.0 ± 0.3
MAC02837	80.9	13.0	0.69	2.4	n.m.	−7.06	14.4	−109	12.8
Ungrouped									
Tagish Lake	67.2 ± 0.3	33.7 ± 1.0	4.28 ± 0.02	16.9 ± 1.4		−14.17 ± 0.13	73.0 ± 1.5	596 ± 4	12.5 ± 0.5
WIS91600	71.1 ± 1.9	41.5 ± 1.3	3.40 ± 0.08	12.1 ± 0.5	3.3	−11.19 ± 0.03	62.8 ± 0.1	349 ± 39	13.1 ± 0.5
Adelaide	77.5	38.4	1.54	13.8		−8.32	10.1	434	15.2
MAC87300	76.1	39.5	1.12	10.6		−7.95	0.8	437	8.5
Acfer 094	*35.1 ± 0.1*	*95.3*	*6.45 ± 0.05*	*62.3*		*−18.47 ± 0.09*	*20.9 ± 0.1*	*39*	*11.1*
CR weath.									
El Djouf	39.7	*44.9*	*6.39*	*51.2*	n.m.	−23.18	*44.5*	*223*	*12.5*
Acfer 059	34.6 ± 1.9	*52.8 ± 2.9*	*5.29*	*57.4 ± 3.2*	n.m.	−23.55	*33.6*	*120*	*9.7*
Acfer 186	46.4	*40.7*	*4.08*	*37.7*	n.m.	−20.36	*90.9*	*428*	*15.0*
Acfer 209	31.7	*51.3*	*6.11*	*66.1*	n.m.	−25.00	*16.7*	*171*	*12.8*

Errors are based on the range of compositions obtained for two or more analyses. Meteorites in italics have C contents in their residues of <50% and their compositions should be treated with more caution because of the potential for greater levels of contamination. b.d., below detection; n.m., not measured.

[a] GRO95502, GRO95504 and, possibly, GRO95505 are paired.

[b] MET96503 and MET96515 are paired.

making the CsF–HF and HF–HCl solutions. All solutions were stored in sealed Teflon bottles and consumed within days to weeks of preparation.

2.3. Elemental and isotopic analysis

To minimize the amount of absorbed water that the residues may contain, prior to analysis the samples were placed in tin or silver capsules of known weight and stored in a dry N_2 flushed oven at 50 °C for at least 12 h. The samples were weighed just prior to analysis. The results of the analyses are summarized in Table 2.

2.3.1. C and N analysis

The bulk C and N elemental and isotopic compositions were determined on the same samples (typically ∼0.2–0.5 mg) loaded into tin capsules. The analyses were conducted using a CE Instruments NA 2500 series elemental analyzer (EA) linked to a Finnigan MAT Delta[plus]XL mass spectrometer by a molecular sieve gas chromatographic (GC) column (Wooller et al., 2004; Wang et al., 2005). Samples were introduced directly from an autosampler (A2100)

into the EA where they were combusted with ultra pure O_2 at 1020 °C in a quartz oxidation column containing chromium(III) oxide and silvered cobalt(II, III) oxide. The resulting gases (CO_2 and N_2), mixed with zero-grade He as the carrier gas, were purified and separated in the GC prior to entering a Finnigan Conflo III interface. Both N_2 and CO_2 samples were analyzed relative to internal working gas standards. Acetanilide (C_8H_9NO) was analyzed at regular intervals to monitor the accuracy of the measured isotopic ratios and elemental compositions.

2.3.2. H and O analysis

The bulk H and O elemental and isotopic compositions of IOM were determined on separate samples using a Thermo Finnigan thermal conversion elemental analyzer (TC/ EA) also coupled to the Thermo Finnigan MAT Delta[plus]XL mass spectrometer via the GC interface. The H and O in the IOM samples and standards (∼0.2–0.5 mg in silver capsules) were converted to H_2 and CO in a pyrolysis reactor (made of glassy C and graphite) held at 1450 °C. Helium (UHP 5.5 grade) was used as a carrier gas to introduce the H_2 and CO into the GC. Reference gases with

known δD values were injected via the dual inlet into the IRMS before and after the samples for the computation of the isotopic compositions of the samples. Standards of known elemental and isotopic composition were analyzed at regular intervals between samples. A H_3^+ correction applied to the H measurements was determined periodically throughout the day.

2.3.3. S contents and ash weights

The S contents in the residues were not determined directly, but were estimated by difference after summation of the H, C, N, and ash weight fractions. The ash weights were determined by heating aliquots of the residue in Pt buckets at 600 °C in air for one hour. This approach depends upon the absence of oxidizable phases (e.g., sulfides that may form sulfates) and volatile material that is free of H, C, N, and O. Totals of greater than 100 wt% are common, except in the CI, CM, and CR chondrites. This implies oxidizable phases are present in many residues. However, those samples with <100 wt% totals provide an estimate of the S contents in the IOM.

3. RESULTS

3.1. Uncertainties and comparison with previous studies

There are three sources of uncertainty in the IOM abundances and compositions listed in Tables 1 and 2: those associated with the analytical techniques, heterogeneity in the meteorites, particularly breccias, and heterogeneity at the sub-milligram scale in the residues. As discussed in more detail in the Electronic Annex EA-1, the major sources of uncertainty in this study are associated with heterogeneity of the residues and the meteorites. For instance, measurements of paired meteorites in this study suggest an uncertainty in the IOM abundances in Table 1 of 10–15%. This is similar to the range of IOM abundances reported by different studies for the same meteorites. On the other hand, the elemental and isotopic compositions of IOM from paired meteorites in this study are generally much more reproducible, as can be seen from Table 2. The uncertainties in Table 2 are based on replicate analyses of the residues and strictly reflect the precision of the measurements, weighing errors and the heterogeneity of the residues. In general, the errors should also reflect the accuracy of the measurements. However, for the H isotopes uncertainties associated with the H_3^+ correction and the possibility of a small memory effect (not corrected for) mean that the H isotopic compositions are the least accurate, with 1σ errors of ∼10‰ for approximately terrestrial ratios and larger errors for the most D-rich compositions.

The analytical techniques used here are different to those used in many previous studies. A detailed comparison of our results with previous studies is provided in the Electronic Annex EA-1. The abundances and isotopic composition of IOM C is similar in all studies. The same is true for H isotopic compositions, except for the OCs for which we find much larger D enrichments. We believe that

this is largely due to the much higher purity of our residues—the presence of H- and O-bearing silicates, fluorides and partially oxidized/hydrated sulfides would have a significant influence on the measured compositions. For example, partial oxidation/hydration in air of small sulfides in some residues compromised many of our early measurements. Reduction of oxides could potentially compromise the O analysis, but in general for the purer residues there is no correlation between ash weight and O/C ratio. To minimize the potential for compromised analyses from contamination, reduction, etc., where possible we will only consider the results for residues with C contents of ⩾50 wt%. Only C abundances and isotopic compositions are reported for residues with <40 wt% C. For reasons that are unclear, studies that use elemental analysis, including this one, report systematically higher H and N elemental abundances in IOM than stepped pyrolysis and combustion studies.

3.2. Effects of weathering

Our analyses of the weathered Algerian CRs El Djouf and Acfer 059, 186, and 209 (Table 2) are entirely consistent with the previous study of these meteorites (Ash and Pillinger, 1995). The IOM contents of these meteorites are an order of magnitude lower than in less weathered meteorites (Table 2). The elemental and isotopic compositions of the remaining IOM are quite different from those of the less weathered CRs. The D and ^{15}N enrichments that are so characteristic of IOM in the less weathered CRs (δD = 2600–3000‰ and $\delta^{15}N$ = 153–233‰) are greatly reduced in the weathered meteorites (δD = 120–428‰ and $\delta^{15}N$ = 17–91‰), although the C isotopic compositions appear to be largely unaltered ($\delta^{13}C$ = −20‰ to −25‰). For the elemental ratios, the H/C ratios are lower (0.4–0.53 vs. 0.75–0.81), while the N/C (0.041–0.064 vs. 0.032–0.041) and O/C (0.38–0.66 vs. 0.11–0.22) ratios are higher in the weathered IOM compared to those from the unweathered CRs.

3.3. Intra- and inter-class variations

During diagenesis/metamorphism, the elemental compositions of terrestrial kerogens, such as coals, follow a well-defined evolutionary path—initially a rapid decrease in C/O, followed by a more gradual decline in H/C and later N/C (Van Krevelen, 1993; Jiang et al., 2002). The meteoritic IOM also exhibits some systematic variations. In plots of H/C vs. N/C (Fig. 1a), the IOM from petrologic type 1 and 2 meteorites form a group with higher ratios, and the type 3s form another group with lower ratios. The heated CMs form a trend beginning in the CM field that is sub-parallel to the trend of the type 3s. The only meteorite that does not belong to one or other group is Tagish Lake, an anomalous C2. WIS91600, which may be related to Tagish Lake, falls closer to the intermediately heated CMs. In the plot of H/C vs. O/C (Fig. 1b), there is a similar grouping, except that in this case Tagish Lake falls within the type 3 field. Some type 3 meteorites have higher O/C ratios than the main group of type 3s. These include Semarkona (LL3.0), Kaba (CV), and ALH77003
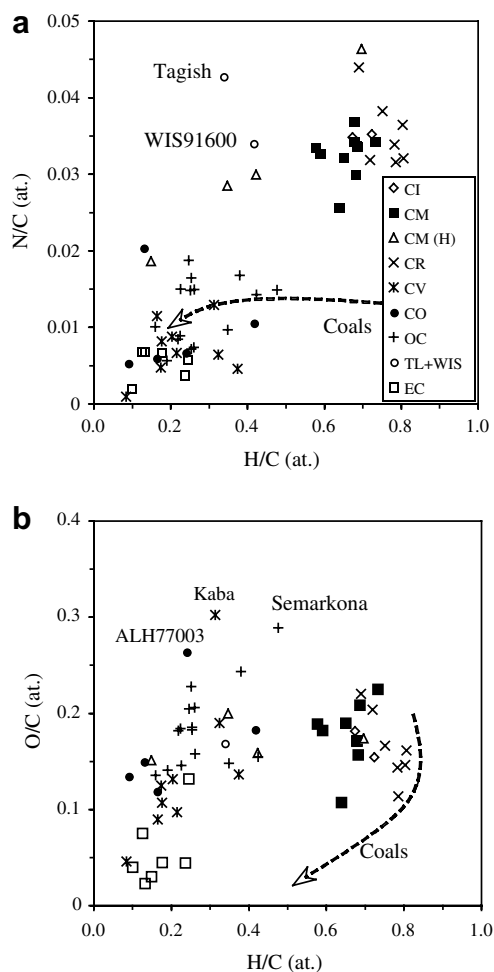
Fig. 1. The atomic H/C vs. N/C and O/C ratios for the IOM isolated from the various chondrites. The chondrites seem to fall into two groups: (1) types 1 and 2, and (2) type 3s. The heated CMs form trends that are either sub-parallel to (Fig. 1a) or the same as (Fig. 1b) the trends/groupings in the other meteorites, suggesting that the range in compositions reflects the differing thermal histories of the chondrites. The apparent evolution of the IOM does not parallel the evolution seen for terrestrial kerogens, such as coals (dashed line: Van Krevelen, 1993; Jiang et al., 2002). The difference in behavior in: (i) Fig. 1a suggests that much of the N functionality in IOM is in a more labile form (e.g., amines) than in coals (pyridinic), and (ii) Fig. 1b suggests that oxidation was an important process during parent body processing.

(CO3.5). The presence of ALH77003 in this group suggests that the high O/C ratios are not simply characteristic of low petrologic grade, but may also be a function of the purity of the residues and/or weathering. The estimates of S/C ratios appear to show no pattern, except a general decline with decreasing H/C. The IOM in Acfer 094 is not considered in detail because it appears to be badly weathered—low matrix-normalized abundance and elemental composition like the weather CRs—so only its C isotopic composition is likely to resemble its preterrestrial composition.

Terrestrial kerogens evolve along a path that is quite distinct from the distribution of chondritic IOM compositions (Fig. 1). Unlike terrestrial kerogens, the IOM H/C and N/C

ratios are correlated and the H/C ratio decreases before the O/C ratio. To determine whether there is a significant loss of C associated with the decrease in H/C (e.g., loss of CH_4, or CO_2 and H_2O), in Fig. 2 the H/C ratio is plotted vs. the matrix-normalized abundance of IOM C in the bulk meteorites. Alexander et al. (1998) and Alexander (2005b) observed that, like presolar grains (Huss and Lewis, 1995), the matrix-normalized IOM abundances in the most primitive chondrites are similar. Thus, the matrix-normalization makes it possible to compare the different meteorite classes and to look for trends that might be common to all. The matrix abundances used are as given in Table 2, except for the CMs which are all set 50 vol% (Huss et al., 2003; Alexander, 2005b), and if not measured are set to typical values for their class (CR = 30%, CV = 35%, CO = 30%, OC = 13%, EC = 13%). There is considerable scatter in the data, reflecting errors in the measured or estimated primitive matrix abundances, variability in the IOM yields, sample heterogeneity and, perhaps, terrestrial contamination. Nevertheless, there seems to be a general trend in the data. The type 1–2 chondrites (except Tagish lake) have high H/C ratios and roughly CI-like matrix-normalized IOM C abundances. Amongst the type 3s, H/C ratios initially decrease significantly (0.5–0.3) with increasing type, while IOM C abundances decrease only moderately. With further decreases in H/C, the IOM C abundance starts to decrease more rapidly. The change in N/C ratio parallels that of the H/C ratio (Fig. 1a), while the O/C ratio remains fairly constant until the H/C falls below ∼0.3.

Alexander et al. (1998) found that in the OCs the IOM N content and N isotopic composition both tended to
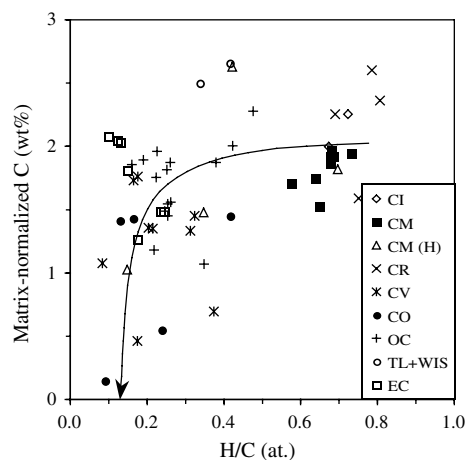

Fig. 2. The atomic H/C ratios vs. the matrix-normalized abundances of C in IOM. It seems that the initial matrix-normalized IOM abundances may have been quite similar in all chondrites, and that they decreased with increasing degree of thermal metamorphism. IOM is all but absent in petrologic types >3.6. The inferred evolution of the IOM during metamorphism is indicated schematically by the line. The heated CMs also roughly follow the line. The ECs tend to have higher IOM abundances than predicted, suggesting that oxidation may have played an important role in the destruction of the IOM during metamorphism in all but the highly reduced ECs. See Table 2 and text for the matrix abundances used.

decrease with increasing petrologic grade. Fig. 3a shows the N/C vs. δ^{15}N values of the IOM samples analyzed here. There is a weak correlation between N/C and isotopic composition in most meteorites, despite the systematic differences in N content and isotopic composition in IOM measured here and in previous studies (Electronic Annex EA-1). However, the most striking features in Fig. 3a are the large δ^{15}N enrichments in Bells and the CR chondrites.

Fig. 3b, compares the H/C and δD values for the IOMs studied here. There is a suggestion of three separate trends in this figure. One trend would extend from the CIs and CMs (except Bells) through Tagish Lake to the CVs, COs, the heated CMs, and ECs. The second trend would extend from Bells and the CRs, through the most primitive OCs to Indarch. The third only involves the OCs, with a general increase in δD values with increasing petrologic type and decreasing H/C.

There is a suggestion of a correlation between H/C and the bulk carbon isotopic compositions of the IOM (Fig. 3c)—the type 2 meteorites tend to have lighter C isotopic compositions than the type 3s. There is little difference

between the C isotopic composition of most CMs and the heated CM, despite the very different H/C ratios. Bells has a much lighter C isotopic composition than the other CMs, or indeed any other chondrite we have measured. Within the type 3s, there is a general correlation between H/C and C isotopic composition trending towards Bells, with Semarkona having the lightest isotopic composition. There are no obvious correlations between O/C and δ^{18}O (Fig. 3d).

Fig. 4a compares the C and H isotopic compositions of the IOM. Except for the OCs, the different chondrite classes tend to form discreet clusters. The oxidized and reduced CVs seem to be separate from one another, although the number of samples analyzed is small. MET01017, the most metamorphosed reduced CV, has a C isotopic composition that resembles those of the ECs and COs. Apart from Bells, the CMs form a very tight cluster. The C and H isotopes of the heated CMs are more variable - H isotopic compositions decrease with increased heating, but the C isotopes are uncorrelated. If the more metamorphosed OCs are excluded, there is an overall inverse correlation between H
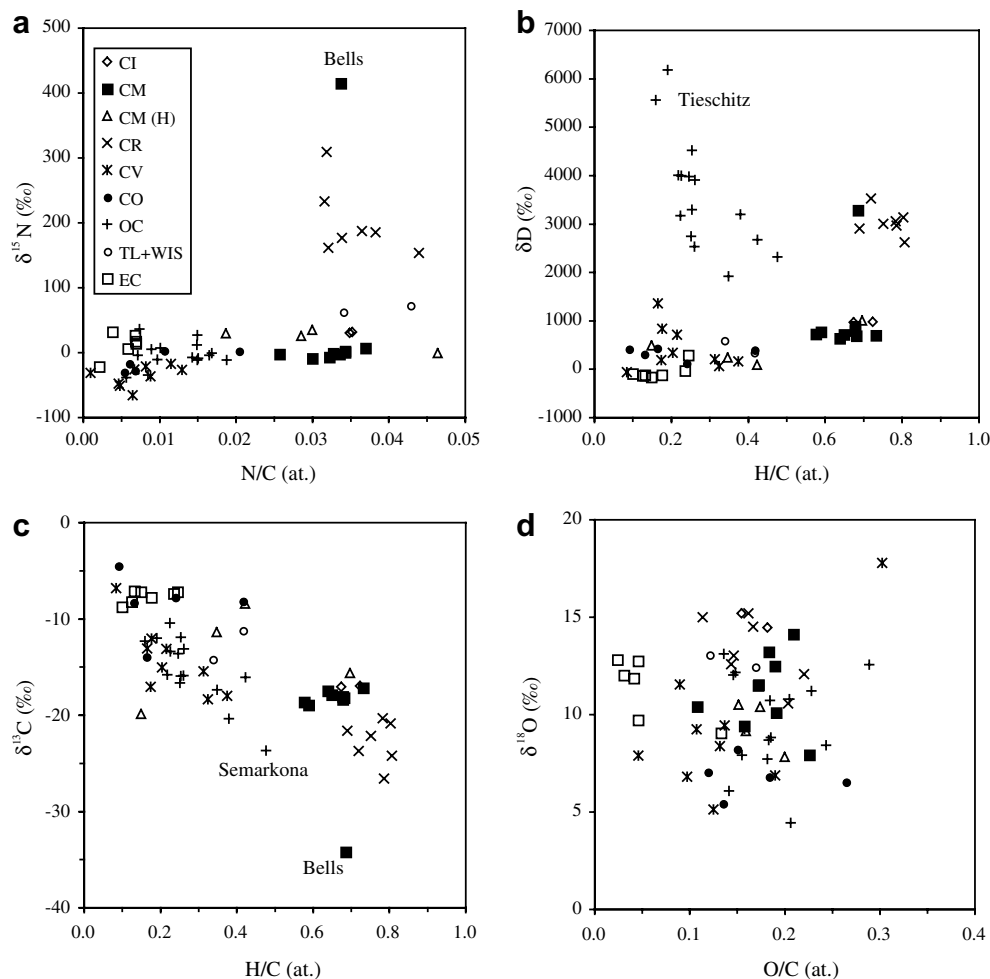
Fig. 3. The elemental ratios vs. the isotopic compositions of C, N, H, and O. There do not appear to be any simple systematic trends between elemental ratio and isotopic composition, except perhaps a rough inverse correlation between δ^{13}C and H/C (Fig. 3c), and a weak correlation between δ^{15}N and N/C in type 3 chondrites (Fig. 3a).
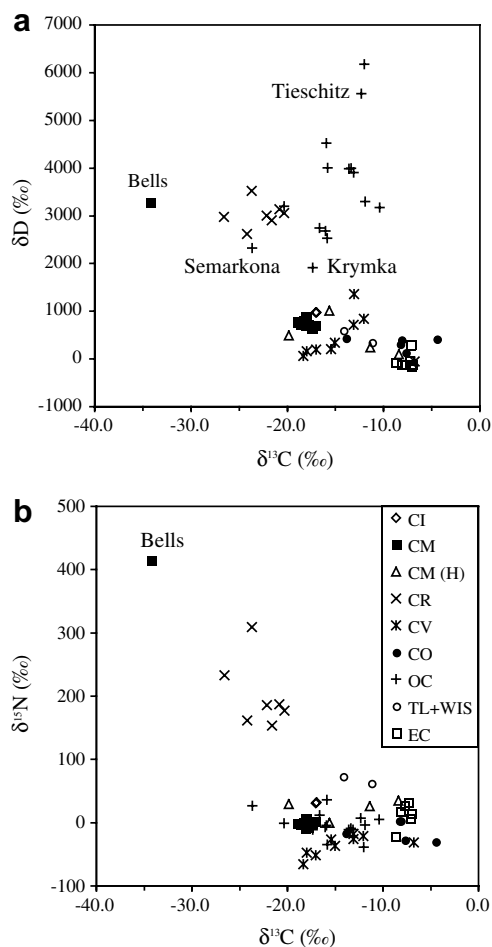
Fig. 4. The C vs. H and N isotopic compositions. Except for the OCs, the different chondrite classes tend to form fairly discreet clusters, including the oxidized and reduced CVs. Bells sits apart from the other tightly clustered CMs, and the heated CMs have more varied C, N, and H isotopic compositions from the CM cluster. There appears to be a general inverse correlation between C and N isotopic compositions. The spread in compositions amongst the CRs is in the same direction as the overall trend, but in the CVs the variation is almost perpendicular to it.

and C isotopes. However, the variations within the chondrite classes are not in the direction of this trend. This is particularly true of the OCs, but is also the case for the CVs and COs.

There is a similar clustering of meteorites from each class in plots of $\delta^{13}C$ vs. $\delta^{15}N$, as well as an overall inverse correlation between C and N isotopic compositions (Fig. 4b). The spread in compositions in the CRs is in the same direction as the overall correlation, but the variation in the CVs is almost perpendicular to the overall trend. The OCs are not tightly clustered but, unlike in Fig. 4a, the C isotopic compositions are the principal reasons for the scatter.

There are no obvious correlations between the isotopic compositions of O and the other elements. It is possible that the IOM from the different meteorites acquired their O isotopic compositions during parent body processing (aqueous

alteration and metamorphism) under mildly oxidizing conditions, in which case their compositions should be correlated with the O isotopic compositions of the bulk meteorites, their matrices, or products of the alteration such as carbonates and sulfates. There is no simple correlation between the IOM O isotopic compositions and those of the bulk meteorites (Fig. 5a). There are fewer O isotopic measurements of matrix than of bulk meteorites, but those that are available are compared with the IOM compositions in Fig. 5b. The matrix and IOM O isotopic compositions are very similar in the CMs and Tagish Lake, and a reasonable correspondence for the CIs and the CR Al Rais. However, when the CR EET92042, the CVs and OCs are included, the IOM O isotopic compositions are nearly independent of the matrix compositions. The IOM O isotopic compositions do not clearly correlate with those of the carbonates (except perhaps Semarkona) and sulfates that also formed during aqueous alteration, although the sulfate compositions more closely resemble the IOM than the carbonate.

4. DISCUSSION

The range and complexity of IOM compositions within and between chondrite classes is striking. The general assumption in meteoritics is that each meteorite class comes from a single parent body, and that each parent body formed from a uniform nebular reservoir. If this is correct, and there have been no errors in the classification of any meteorites, the elemental and isotopic variations that are present in the IOM, particularly in the CMs and OCs, indicate that parent body processes can dramatically modify the IOM. For instance, the elemental composition of Bells IOM is very similar to those of the other CMs, but the H, N, and C isotopic compositions of Bells IOM are dramatically different. The H isotopic compositions of the IOM from the most primitive OCs are comparable to those of IOM from the CRs and Bells. However, the H isotopic compositions of IOM from OCs of higher petrologic grade are more D-rich than any other meteorites analyzed. The C isotopic compositions of the IOM from the OCs also exhibit a range ($\sim 13\permil$) that is second only to the CMs. Metamorphism in the reduced CVs has produced an IOM composition in MET01017 that resembles the IOM of the ECs. The intra-class variations mean that IOM compositions may be useful in helping establish relative petrologic grades within a class, but cannot in general be used for determining the affinities of ungrouped chondrites. Nevertheless, the similarity of Adelaide and MAC87300 to one another and to the COs, for instance, would be consistent with all of them being related.

While it is clear that parent body processes can affect dramatic changes in the elemental and isotopic composition of IOM, there are significant differences in IOM composition even between the most primitive members of the various chondrite classes. Two alternative explanations for this are explored in detail below. First, local nebular processes and conditions where the chondrites formed—e.g., some combination of local IOM synthesis, mixing of two or more IOM components and thermal/chemical modification—
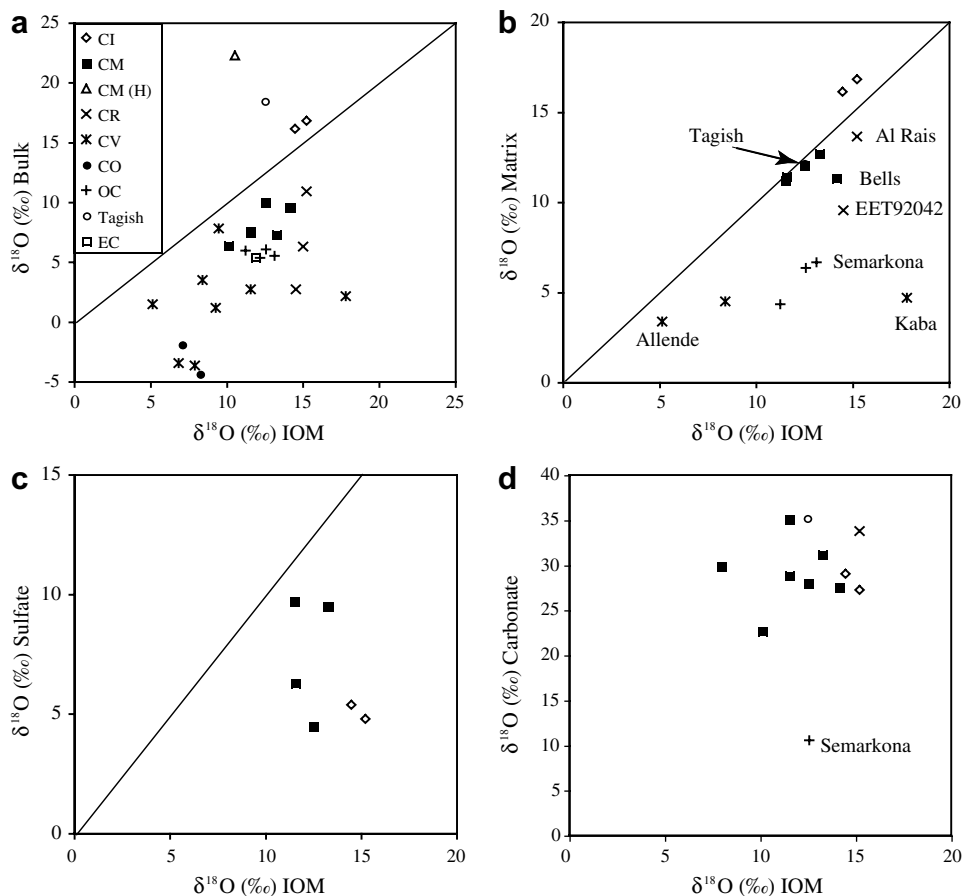
Fig. 5. Comparison of the O isotopic composition of the IOM with that of: (a) the bulk meteorites, (b) the bulk matrix, (c) secondary sulfates, and (d) secondary carbonates. The IOM compositions of most, but not all, of the meteorites roughly parallel those of the bulk meteorites. There is a slightly closer correspondence between the compositions of the IOM and matrix, particularly for the CM chondrites and Tagish Lake. There is very little correlation between the IOM and either the sulfate or carbonate compositions.

could mean that the chondrite classes accreted different IOM materials. Alternatively, given the intra-class range it is possible that the entire range of IOM compositions, even in the most primitive chondrites, is the result of parent body modification of a common IOM precursor under different conditions.

The simplest way to test these two explanations would be to compare the IOM compositions at the time of accretion. Unfortunately, it cannot be guaranteed that even the IOM from the most primitive members of each class have remained unmodified since the time of accretion. Nevertheless, for the purposes of the forthcoming discussion, it is useful to rank the IOM compositions of the most primitive meteorites from each class. This is done for several properties of the IOM in Table 3, where they are also compared to the rankings of various properties of their host meteorites.

4.1. IOM in chondrites, IDPs and comets: A common origin?

Chondritic porous (CP)-IDPs are generally thought to be the most primitive Solar System objects available to us for study. Similarly, the IOM in CP-IDPs has long been considered the most primitive IOM available based on large

Table 3
The order of the IOM compositions, the degrees of alteration, the volatile abundances and the formation ages and distances from the Sun for the various chondrite classes analyzed

IOM

δD	Bells > CR > OC > CV_r > CI > CM > CO > CV_o > EH
$\delta^{13}C$	Bells < CR ≈ OC < CM < CI < CV_r < CV_o < CO ≈ EH
H/C	CR > Bells ≈ CM ≈ CI > OC > CV_o ≈ CV_r ≈ CO > EH

Chondrules

CI < CM = Bells < CV_o = CV_r ≈ CO ≈ CR < OC < EH

CAIs

CI < OC ≈ EH < CR < CM ≈ Bells < CO ≈ CV_o ≈ CV_r

Alteration

CI > CM ≈ Bells > CR > CV_o > OC > CV_r > CO > EH

Volatiles

Zn/Cr	CI > CM = Bells > CV_o = CV_r> CO > CR > OC
P1	CI ≈ CM = Bells ≈ OC > CV_r = CV_o ≈ CR ≈ CO
P3	CI ≈ CM = Bells > OC > CO > CV_r = CV_o > CR

Formation

Age	CR < CO ≈ OC < Bells = CM < CV_r = CV_o
Dist.	CI > CM = Bells > CR > CV_r = CV_o ≈ CO > OC > EH

See text for more details.

D and ^{15}N excesses, particularly in so-called hotspots. Recently, a study of aliquots of several of the primitive meteorite IOM samples described here found D and ^{15}N hotspots in them with similar enrichments to those in IDPs (Busemann et al., 2006). The highest observed abundances of these hotspots are in the IOM of the CRs and Bells. Nevertheless, the abundances of resolvable hotspots ($\sim$1%) are not high enough to contribute significantly to the bulk compositions of the IOM. As in the IDPs, the D and ^{15}N hotspots do not always correlate with one another. The bulk H and N isotopic compositions of IOM from the CRs and Bells are comparable to the average compositions of the most primitive IDPs.

There seems to be a genetic link between the IOM in at least some chondrites and IDPs. It has been argued that the most primitive IDPs are from comets (Joswiak et al., 2000). There is a striking resemblance between the bulk elemental compositions of comet Halley CHON particles, $C_{100}H_{80}N_4O_{20}S_2$ (Kissel and Krueger, 1987), and the meteoritic IOM with the most anomalous isotopic compositions (e.g., EET92042—$C_{100}H_{75}N_4O_{17}S_3$, GRO95577—$C_{100}H_{79}N_3O_{11}S_1$, and Bells—$C_{100}H_{69}N_3O_{21}S_5$). Comet Halley is an Oort cloud comet, but it may have formed at $\geqslant$30 AU (Mumma et al., 2002). If IDPs do come from comets, they are most likely to have come from Kuiper Belt comets (Flynn, 1989) that would have formed at distances of >35 AU. Samples of comet 81P/Wild 2 returned by the Stardust mission have higher N and O contents, as well as more modest D and ^{15}N enrichments, compared to IOM in IDPs and primitive meteorites (Sandford et al., 2006), but issues of modification (possibly even synthesis) during capture and contamination have yet to be fully explored.

The IOM in the CRs, Bells, IDPs and, probably, comets could either be one component that was added in different amounts to the IOM in the various chondrite classes, or it is the common precursor from which all IOM evolved due to nebular and/or parent body processes.

4.2. Local sources of IOM?

Formation of the IOM in the ISM has long been favored, but at present the evidence for and against ISM or nebular origins is equivocal. Formation in the ISM or in the outer solar nebula alone does not explain the range of IOM compositions we observe since both sources would be expected to deliver relatively uniform IOM to the inner Solar System. On the basis of stepped combustion isotopic studies, Alexander et al. (1998) and Sephton et al. (2003) proposed that the IOM might be composed of at least two components. They suggested that the less abundant of the two is relatively labile and ^{15}N-rich. Whether the two components are in physically distinct materials that formed independently, or are just different functional groups within the IOM is not known.

It is interesting to note that TEM observations have found two major physical forms of carbonaceous material in IOM residues. The less abundant form ($\leqslant$10%: Garvie and Buseck, 2006) is composed of roughly spherical grains (globules) that are often hollow (Garvie and Buseck, 2004; Nakamura-Messenger et al., 2006), and in Tagish Lake they seem to be ^{15}N-rich (Ashley et al., 2005; Nakamura-Messenger et al., 2006). At present, it is not clear whether the globules formed in the ISM, in the nebula or on the parent bodies (Garvie and Buseck, 2006), or if these two physical forms are in any way linked to the chemical components of Alexander et al. (1998) and Sephton et al. (2003).

Whatever its physical form, loss of the labile ^{15}N-rich component alone cannot, for instance, explain the rough inverse correlation between bulk IOM N and C isotopic compositions (Fig. 4b) because in stepped combustion experiments the ^{15}N-rich component does not appear to be associated with isotopically light C (<-35‰) (Alexander et al., 1998; Sephton et al., 2003). The difference in N isotopic compositions between Bells and the other CMs, and what seem to be vestiges of a ^{15}N-rich component in OCs like Semarkona and Inman, and even in ECs (Alexander et al., 1998), suggest that all chondrites accreted at least some ^{15}N-rich material.

Given the uncertainties in the source(s) of the IOM and how it would have reacted to nebular and parent body processes, below we explore whether the range of IOM compositions we observe in chondrites can be understood in terms of local nebula synthesis of some or all the IOM in the formation regions of the various chondrite groups.

4.2.1. IOM synthesis in the nebula—FTT synthesis?

If the IOM in chondrites formed in the nebula via a common process, the evidence for this should be found in all chondrites. Fischer–Tropsch (FTT) synthesis ($CO + H_2 \rightarrow CH_4$, C_2H_6, etc. $+ H_2O + CO_2$) on catalytic mineral surfaces (e.g., magnetite, Fe–Ni-metal, silicate smokes, etc.) has often been invoked as a plausible mechanism for producing the IOM in the nebula (Hayatsu and Anders, 1981; Christoffersen and Buseck, 1983; Bradley et al., 1984; Brearley, 1990; Ferrante et al., 2000; Johnson et al., 2007). FTT synthesis does not produce large H and N isotopic anomalies, but it is, perhaps, conceivable that either: (1) some simple, isotopically anomalous organic molecules were mixed with FTT products forming in the region of the asteroid belt, or (2) FTT products exchanged with highly fractionated material elsewhere in the nebula. IOM is highly aromatic (Gardinier et al., 2000; Sephton et al., 2000, 2004; Cody et al., 2002; Cody and Alexander, 2005) and does not resemble the typical low temperature aliphatic hydrocarbon products of FTT synthesis. A sustained reheating of low temperature FTT products (Studier et al., 1972) or FTT synthesis at higher temperatures (Johnson et al., 2004) might produce a more aromatic material that better resembles the IOM, but this has yet to be demonstrated.

Kinetic chemical models predict that FTT synthesis would have been most efficient in the asteroid belt region (Kress and Tielens, 2001), although recent experiments (Sekine et al., 2006) show that Kress and Tielens (2001) significantly overestimated the rate of FTT synthesis under nebular conditions. In the models, FTT synthesis would have occurred primarily on metal grains (Kress and Tielens,

2001). In experiments conducted under nebula-like conditions at 473 K, the percentage of CO converted to hydrocarbons in 1000 h was relatively low (0.01–0.05%) and the products were all volatile (Llorca and Casanova, 2000). The experimental temperatures were close to the temperature ($\sim$500 K) at which reaction rates should peak under nebular conditions (Kress and Tielens, 2001). The inefficiency of FTT synthesis in producing condensable organic matter is problematic. Alexander (2005b) estimated the percentages of the total solar C in IOM in chondrites, IDPs and comets to be 7–8%, $\sim$35%, and 30–100%, respectively. Nebular timescales would have been much longer than the experimental ones, but the surface area of metal available in the nebula may have been much lower as the metal particle sizes in the experiments were $\sim$10 nm across. These sizes are much smaller than is typical for metal particles in chondrites, and most fine-grained metal in IDPs is in GEMS rather than occurring as isolated grains with surfaces that were readily accessible to the nebular gas.

A prediction of FTT synthesis is that the IOM should always be associated with mineral catalysts and, if the synthesis happened in the nebula, one would expect the same mineralogical associations to occur in all chondrites and IDPs. However, to date no consistent, ubiquitous petrologic relationship between the IOM and Fe–Ni-metal, or any other mineral, has been reported. Other minerals that would be expected to be associated with FTT synthesis are Fe–Ni-carbides. Fe–Ni-carbides are important products of FTT synthesis on Fe–Ni-metal (Llorca and Casanova, 1998, 2000), and their development tends to poison the metal catalyst.

In IDPs, fine grained (10s of nm) Fe–Ni-metal and carbide grains are found in the IOM, and some carbide grains have thin (10s of Å) graphitic rims (Christoffersen and Buseck, 1983; Bradley et al., 1984). The origin of the carbide remains unresolved, but the bulk of the IOM is not associated with them or the metal grains. Similarly sized carbide grains have been reported in the matrices of the relatively unaltered CMs Murchison and Y791198 (Brearley, 2003, 2004b), in the CR2 EET92042 (Abreu and Brearley, 2005), and in the LL3 Semarkona (Keller, 1998). The grains in the CMs and CRs (but not in Semarkona) are commonly associated with carbonaceous material, typically as $\sim$5 nm thick rims. In Semarkona and some other OCs where they have been found, all carbide-bearing assemblages appear to be the result of parent body processes (Hutchison et al., 1987; Krot et al., 1997; Keller, 1998). Brearley (1990) described carbon–metal aggregates in three OCs that may have been produced by FTT synthesis. The fact that these aggregates have only been found in three ordinary chondrites suggests that they are not the products of a widespread nebular or parent body process.

Metal and carbides are susceptible to oxidation or even sulfidization on parent bodies. No association of Fe-oxides and carbonaceous material has been reported. Zolensky et al. (2002) describe pentlandite grains in Tagish Lake that are 10s of nm across and like the carbide grains some of these have thin carbonaceous rims. In EET92042 (CR2), pentlandite grains in an anhydrous chondrule rim are commonly associated with carbonaceous material, but sulfides

in the typical matrix and in dark inclusions are not (Abreu and Brearley, 2005). In neither of these meteorites are the rimmed sulfide concentrations high enough to explain the observed IOM abundances (Table 1).

In conclusion, FTT synthesis (or any other mineral catalyzed synthesis) cannot be the primary mechanism of IOM formation.

4.2.2. IOM synthesis in the nebula—other mechanisms?

Were there as yet unrecognized mechanisms for making the IOM in the nebula, particularly in the region of the asteroid belt? Conditions in the solar nebula, especially the inner nebula (<5 AU), would have changed with time and radial distance (e.g., Bell et al., 1997). Thus, if most of the IOM formed in the inner nebula, one might expect to see systematic variations in the abundance and composition of the IOM with the formation ages and/or formation locations of the chondrite parent bodies.

The accretion ages for chondrites are unknown, but each chondrite class has a chemically, isotopically and physically distinct chondrule population. Turbulent diffusion in the nebula would have rapidly homogenized the chondrules in the asteroid belt unless the chondrites accreted soon after their chondrules formed (Alexander, 2005a). Thus, the absolute or relative ages of the chondrules in each chondrite group may provide a guide to their relative accretion ages. In Table 3 the chondrule/chondrite ages are ordered based on the absolute ages for the CV and CR chondrules ages (4566.7 ± 1.0 and 4564.7 ± 0.6 My, respectively) (Amelin et al., 2002, 2004) and the oldest ^{26}Al relative ages, of CO and OC chondrules ($\sim$1–1.5 My after CAIs) (Tachibana et al., 2003; Kurahashi et al., 2004). The ages of CM chondrules are not known, but Mn–Cr ages for carbonates suggest that alteration of the CMs occurred within $\sim$1 My of CAI formation (Brearley et al., 2001). The CM chondrules must have formed before this and, therefore, are probably older than the CO and OC chondrules. In summary, the relative order (oldest to youngest) of chondrite formation seems to be CV > CM > CO + OC > CR. If this is the correct order, there is no apparent correlation between accretion time and IOM composition or matrix-normalized IOM abundance (Table 3).

The radial formation distances of the chondrites from the Sun are even more uncertain than the accretion ages. However, based on the assumption of a radial thermal gradient in the nebula and similarities in the reflectance spectra between chondrites and the radially zoned asteroids, the general assumption has been that the formation distances for the chondrites are EC < OC < CC, and that the more water-rich CCs (CIs, CMs, and CRs) formed further from the Sun than the less altered CCs (CVs and COs).

If we use this crude ordering, there is no obvious correlation between formation distance and either IOM composition or matrix-normalized IOM abundance (Table 3). Of course, the above ordering assumes a static thermal gradient, which would not have been the case. Even allowing for sunward migration of the thermal gradient with time, the similar ages of the COs and OCs present a conundrum. Contrary to what would be expected if the COs formed far-

ther from the Sun than the OCs, the COs appear to have been largely anhydrous, while the evidence for parent body aqueous alteration in the OCs (Alexander et al., 1989b; Grossman et al., 2000) shows that they accreted water, presumably as ice.

The presence and extent of aqueous activity in chondrites are crude indicators of at least the relative accretion temperatures. Determining the extents of aqueous alteration in the CVs and OCs is not easy because of the metamorphic overprint. The only two chondrite classes studied that do not show evidence of significant aqueous activity are the ECs and COs. Their IOMs have the heaviest C isotopic compositions of any of the chondrite classes. Any further comparisons are difficult because of the strong metamorphism all ECs have experienced, and the absence of unweathered, primitive COs. Nevertheless, there is no clear correlation between the extent of alteration and IOM composition (Table 3), but the aqueous alteration itself may have modified the IOM, masking any correlation that was originally present.

Clearly, there are significant uncertainties in both the relative ages and formation locations of the chondrites, but the lack of obvious correlations between estimates of either of these quantities and the properties of the IOM requires that we consider other possible explanations for the variations in IOM compositions.

4.3. Modification of a common precursor

If local synthesis in the inner nebula is not the explanation for the different compositions of IOM in the various chondrite classes, the IOM must have come from the outer nebula or ISM. Either source would be expected to deliver a uniform precursor material to the inner Solar System that could have been modified in the nebula and/or in chondrite parent bodies.

4.3.1. Modification in the nebula?

That there could have been modification in the nebula is suggested by the reported correlations between the abundances of volatile presolar noble gas components and the bulk volatile element fractionations in chondrites (Huss et al., 2003). Huss et al. (2003) explained these correlations as being the result of heating of primordial dust in a nebular-wide thermal gradient to at least 400 °C and probably in excess of 700 °C. At these temperatures, the volatile noble gas components and trace elements would have been partially or wholly lost, and the IOM modified (partially graphitized) or destroyed. To produce the variations in abundances of the volatile materials between the meteorite classes, either the peak temperatures to which material was heated differed, or the relative fractions of dust heated to particular temperatures varied. In either case, the different thermal histories that would have been experienced by material from different chondrite classes would produce differences in the IOM.

Alexander (2005b) has questioned whether the correlation between the noble gas component abundances and volatile element fractionations exist (Table 3 and Fig. 6). For instance, the CR chondrites consistently have the lowest
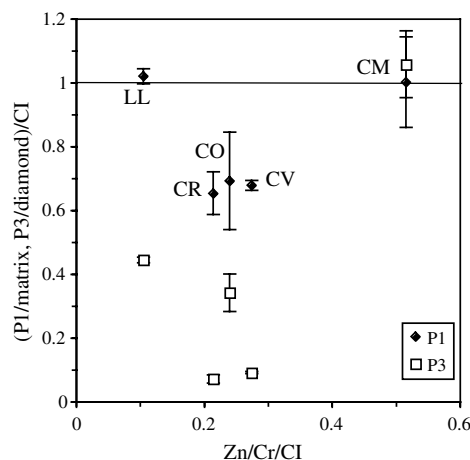

Fig. 6. The CI-normalized Zn/Cr ratios vs. the P1 and P3 noble gas concentrations in matrix and nanodiamond, respectively, from the most primitive members of several chondrite groups (Huss et al., 2003). There is no correlation between the volatile element fractionations and the noble gas abundance variations as would be predicted if both were the products of the same heating event(s) in the nebula.

abundances of the noble gas components and amongst the largest volatile element fractionations. Therefore, they should contain the most thermally processed material. Yet the IOM in the CRs is amongst the most isotopically anomalous and shows little or no evidence of having been heated (Cody and Alexander, 2005; Busemann et al., 2006). Alexander (2005b) suggested that perhaps the loss of the noble gas components is the result of parent body processing.

Chondrule and CAI formation are two alternative heat sources for modifying the IOM. Both formed in short, high temperature (>1400 °C) events. Such high temperatures would almost certainly destroy the IOM. However, on the peripheries of these events, or if unheated material were mixed into the formation regions as they cooled, IOM may be modified but not destroyed. If chondrule or CAI formation did affect the IOM, one would expect an inverse correlation between chondrule or CAI abundance and IOM matrix-normalized abundance or composition. In neither case is there an obvious correlation with IOM properties (Table 3).

4.3.2. Modification in parent bodies

There are a number of processes that might reasonably have occurred on the meteorite parent bodies that could change the bulk compositions of IOM. If present, some isotopic exchange and/or reaction with H_2O, H_2, NH_3, etc., is likely (Yabuta et al., 2007). Thermal metamorphism of the IOM will lead to the loss of labile functional groups and aromatization, and an associated reduction in H/C, N/C, and O/C ratios. Differences in these ratios between the heated and typical CMs are consistent with the compositions of IOM in type 3 chondrites being produced by heating of an originally CI–CM–CR-like IOM (Figs. 1 and 2). Except in the ECs and, perhaps, the reduced CVs, there is little or no IOM in chondrites with petrologic types greater

than ~3.6–3.7 (Table 2). The disappearance of the IOM with increasing petrologic type in CCs and OCs is probably the result of oxidation during metamorphism (Alexander et al., 1989a). The trend in Fig. 2, suggests that initially material with high H/C ratios is driven off (CH₄, H₂O, H₂S, etc.), followed by a period in which destruction/modification of the IOM results in little change in H/C ratio. The fact that, unlike with terrestrial kerogens, the O/C ratio does not change greatly during much of this evolution (Fig. 1b) is consistent with a continuous oxidation process. Evidence for partial oxidation of IOM at the onset of aqueous alteration has also been found (Cody and Alexander, 2005), ultimately producing IOM like that found in Tagish Lake. The fact that, unlike in coals, the N/C and H/C ratios correlate in the IOM suggests that the N in the IOM is in more labile functional groups (e.g., amines) than in coal (pyridines).

The abundances and elemental compositions of IOM in chondrites are broadly understandable in terms of parent body processing of a common precursor material whose elemental composition and matrix-normalized abundance resembled the IOM in CI, CM, and CR chondrites. However, the isotopic compositions seem to belie such a simple picture. For instance, the IOM δD values in the reduced CVs fall with increasing metamorphic grade (from 1361‰ to −57‰), just as they do in the heated CMs (from 1008‰ to 493–95‰), and are uniformly low in the oxidized CVs and COs (62–637‰). Vestiges of a D-rich IOM precursor may even be preserved in the EH chondrite ET87746 (δD = 299‰). On the other hand, the behavior in the OCs is quite different—the most primitive, Semarkona, has a δD of 2322‰ while more processed meteorites like Tieschitz and WSG95300 have compositions of 5558‰ and 6181‰, respectively. The C isotopic compositions are only slightly more systematic. In the OCs, the C isotopic composition of IOM in Semarkona resembles that in the CRs and tends to become heavier with increasing petrologic type. There seems to be a similar behavior in the reduced CVs, but the C isotopes in the IOM of the oxidized CVs, COs, and ECs are essentially independent of metamorphic grade. The C isotopic compositions of the IOM in the heated CMs are much more varied than the unheated ones but do not seem to vary systematically with the degree of heating.

Metamorphism of the IOM is associated with a reduction in H/C ratio as labile material is driven off and, if this occurred in a kinetic regime, it would be associated with increasingly heavy isotopic compositions in the residual IOM. The maximum possible kinetic isotopic fractionations for C and H isotopes would occur via Rayleigh fractionation of CH₄ and atomic H, respectively—Rayleigh fractionation requires that the gas does not exchange with the IOM after it is generated. There is a rough correlation between H/C ratio and δ¹³C in the IOM (Fig. 2c), but there is no simple correlation between matrix-normalized C content and δ¹³C (Fig. 7). Most IOM compositions in Fig. 7 could be explained by the Rayleigh loss of material with masses between methane and benzene, and an initial IOM abundance and composition like that in the CR GRO95577. However, loss of methane
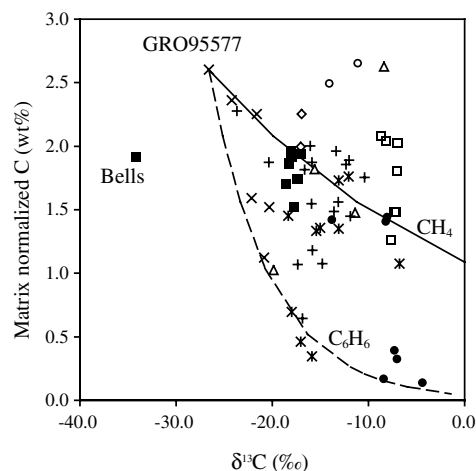

Fig. 7. The C isotopic compositions vs. matrix-normalized C abundances of IOM. The curves show the expected variations if the C was lost as CH₄ and C₆H₆ (or similar mass C-bearing species) under Rayleigh conditions starting from an IOM composition and abundance like that in GRO95577. Most meteorites lie on or between the curves, but Bells IOM, isotopically the most primitive, cannot be explained in this way. If Bells IOM is used as the starting point, most meteorites would lie above the CH₄ curve (the lightest likely C-bearing species) and, therefore, would not be explainable by this mechanism.

(H/C = 4) would rapidly deplete all H (~20% C loss) in the IOM (initial H/C ≈ 0.8), and could only be the explanation if there was an additional source of H. Nor would it explain the composition of Bells IOM, which at least isotopically appears to be the most primitive. Also, the D-rich compositions of the OCs cannot simply be explained by Rayleigh fractionation, even under the most optimistic conditions. Fig. 8 plots the H isotopic compositions vs. the fraction of H lost. The fraction of H lost was calculated assuming that all OCs started off with IOM abundances and D/H ratios like Semarkona and initial H/C ratios like Bells, and that H was lost as atomic H. As can be seen, almost all OCs plot above the Rayleigh line. There are, of course, three OC classes, but there seems to be no systematic differences in IOM compositions between them (Fig. 9), although classification of highly unequilibrated OCs is difficult. Finally, except in the heated CMs, the N isotopic compositions of IOM from more metamorphosed samples are typically lighter, opposite from what one would predict if kinetic isotope fractionation were the principal cause of the range of IOM compositions.

Similar complexity is apparent in the C1 and C2 meteorites that experienced hydrothermal alteration. The overall composition of Bells IOM makes it a good candidate for the most primitive material. If it is close to the composition of the IOM accreted by the CM parent body, then the other CM IOM compositions, with their much lighter H and N isotopic compositions (e.g., Fig. 2a and b), must have been produced without significantly changing the IOM abundance or the H/C or N/C ratios. It is possible that H and N isotopes were exchanged during hydrothermal alteration,
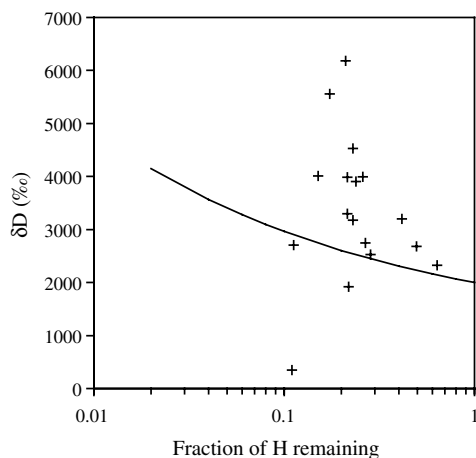
Fig. 8. The H isotopic compositions vs. the fraction of H remaining in the IOM of OCs assuming that all OC IOM: (1) started with an isotopic composition like Semarkona, and (2) had an elemental composition like Bells. The line assumes that the H was lost as atomic H under Rayleigh conditions. Even with these optimal conditions, the large D enrichments seen in the more metamorphosed OCs cannot be explained in this way.
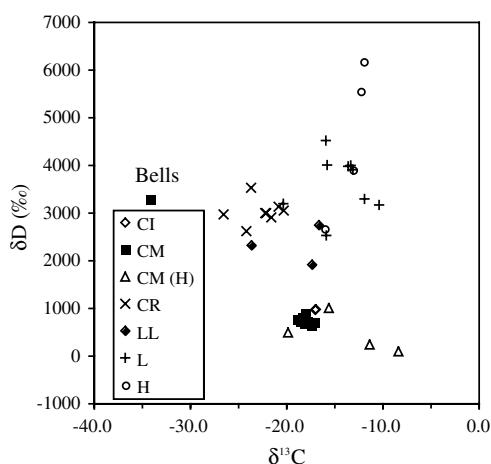

Fig. 9. Comparison of the IOM C vs. H isotopic compositions in the three OC classes with those in CI, CM, and CR chondrites. For reasons that are unclear, the OC IOM seems to become increasingly D-rich with increasing petrologic type. There is no systematic difference in the compositions of the IOM from the three OC classes. There are no LL chondrites with very D-rich compositions, but no LL chondrites with petrologic types $\geqslant 3.2$ were analyzed.

although if the formation temperatures of the carbonates (~20 °C: Clayton and Mayeda, 1984; Benedix et al., 2003; Guo and Eiler, 2006) reflect the peak alteration temperatures, the similarity to the IOM isolation temperature makes such extensive exchange seem unlikely. Alteration in the CRs could not have occurred at much lower temperatures, yet their compositions are much closer to those of Bells. Alteration in CIs is thought to have occurred at higher temperatures than the CMs (~50–150 °C: Clayton and

Mayeda, 1984; Leshin et al., 1997), but they have slightly more anomalous H and N isotopic compositions than most CMs. It is even more difficult to explain the ~10‰ difference in C isotopic compositions between Bells and the other CMs. Extensive C isotopic exchange in macromolecular material, particularly if they are as aromatic as the IOM, is very difficult to achieve.

If there was a common IOM precursor, the range of O/C and O isotopic compositions requires that there has been secondary modification. Cody and Alexander (2005) have suggested that the variations in elemental compositions of IOM in the CM, CI, CR, and Tagish Lake chondrites reflect variable oxidation on the parent bodies. The fact that, unlike with terrestrial kerogens, in IOM from type 3 chondrites the O/C ratios remain fairly constant during metamorphism while H/C ratios and IOM abundances fall (Figs. 1b and 2) is also suggestive of oxidation. In this case, since the O producing the O functionality must be coming from the altering fluids or minerals in the meteorites, there should be some correlation between the O isotopic compositions of the IOM and the bulk meteorites or their components. Much of the spread in $\delta^{18}O$ of the bulk meteorite compositions probably reflects isotopic fractionations associated with hydrothermal alteration and dehydration (Clayton and Mayeda, 1999; Young et al., 1999), but there is not much correspondence between bulk and IOM compositions (Fig. 5a).

Given the intimate association of the IOM and matrix, a comparison between IOM and matrix seems more appropriate. Unfortunately, the database of matrix O isotopic compositions is relatively small. Nevertheless, for Tagish Lake, the CMs and CIs that have been analyzed, matrix and IOM $\delta^{18}O$ compositions are very similar (Fig. 5b). The CIs fall slightly above the 1:1 line, perhaps because of the inclusion of isotopically heavy carbonates (Fig. 5d) in their bulk compositions. It may be significant that the CM that falls furthest from the 1:1 line is Bells, which contains the most isotopically anomalous IOM and experienced rather different alteration conditions to other CMs (Brearley, 1995). The CRs Al Rais and EET92042, like Bells, fall to the right of the 1:1 line in Fig. 5b. Al Rais lies closer to the 1:1 line and its IOM is slightly less anomalous than that of EET92042. Al Rais is also thought to be more altered than EET92042 (or its pair EET87770) (Clayton and Mayeda, 1999). As with the bulk meteorites, the IOM in the less aqueously altered CV and OC chondrites have larger $\delta^{18}O$ values than their matrix compositions. One possible explanation for this is that the distance from the 1:1 line reflects the water/rock ratio during alteration, but the apparently most aqueously altered of these meteorites, Semarkona (LL3) and Kaba (CV3), do not fall closer to the 1:1 line than the other members of their classes. In fact, Kaba plots further away from the 1:1 line than any other meteorite.

The similarity in the $\delta^{18}O$ values of the IOM and bulk matrix in CIs, CMs, and Tagish Lake suggest that their O functionality is a product of the aqueous alteration or at least that it exchanged with their matrices during the alteration. If correct, it is surprising that in these meteorites, unlike Semarkona, there is no correlation between the O

isotopic compositions of the IOM, or indeed the matrix, and the carbonates and sulfates that formed during the alteration (Fig. 5c and d). Whether kinetic and equilibrium fractionations can explain the lack of correlation is beyond the scope of this paper. Almost complete isotopic equilibration between IOM and matrix is also in conflict with the suggestion that a large fraction of the O functionality is present as unexchangeable phenolic ester linkages between aromatic rings (Hayatsu et al., 1980). Lastly, the C isotopic compositions of the carbonate and IOM are uncorrelated (Fig. 10), suggesting that the CO_2 from which the carbonates formed was not directly derived from the IOM and that the two did not exchange/react much with one another.

The range of intra-class IOM isotopic compositions seem to require processes other than or in addition to exchange and kinetic isotopic fractionation associated with loss of labile components. One possibility is that the IOM contains a number of components or functional groups with a range of isotopic compositions that are more or less refractory depending on the conditions. Obvious candidates for this are the H and N isotopic hotspots. They appear to have similar elemental compositions to the bulk of the IOM, and the fact that H and N isotopic compositions are not always correlated allows for the different behaviors of H and N within and between chondrite classes. However, the spatially resolvable hotspots only make up at most a few area percent of the IOM in Bells an the CRs (Busemann et al., 2006). The bulk of the IOM has a relatively uniform elemental and isotopic composition ($\delta D \approx 2000$–3000 ‰), at least at the spatial resolution of the ion microprobe studies conducted to date (Busemann et al., 2006). Hotspot abundances are lower in other CMs, CIs, and Tagish Lake (Busemann et al., 2006), but mass balance using observed hotspot abundances and compositions suggests that this cannot explain their lower δD and $\delta^{15}N$ values.

In summary, all IOM elemental compositions seem to be part of a continuum that can be explained qualitatively by

thermal metamorphism and oxidation of a common precursor similar to that in CRs and CMs, but the isotopes paint a more complex picture. The IOM is a chemically and isotopically complex material (e.g., isotopic hotspots) and given the range of parent body conditions that existed, it is perhaps not surprising that it has reacted in diverse ways. Even so, the different behaviors of the IOM in the OCs, COs, and CVs during metamorphism is perplexing, particularly the differences in IOM composition between Semarkona (LL3.0) and ALH77307 (CO3.0). Nevertheless, it is clear from the petrology of these meteorite classes, as well as from the differing stability of circumstellar SiC, graphite and nanodiamonds in them (Huss and Lewis, 1995), that there were significant differences in the conditions during metamorphism on their respective parent bodies. The IOM in the very primitive Acfer 094 is weathered, but its C isotopes should be relatively unmodified and they resemble those in the CMs. If Acfer 094 is related to the COs, it seems that the C isotopes in CO IOM were modified at a very early stage (<ALH77307) of parent body processing. The differences between Bells and the other CMs are also difficult to explain, but Bells experienced a rather different style of alteration. Thus, it cannot be ruled out that there was some modification of the IOM in the nebula, but the absence of any correlation with other potential indicators of nebular conditions and the intra-class variations produced by parent body processing suggests that evolution of all IOM from a common precursor is the most likely explanation.

4.4. Site of the D-rich material

Understanding the cause(s) of the isotopic enrichments is central to determining the origin of the IOM. While some of the D and ^{15}N enrichments are carried in hotspots, most appears to be in the bulk IOM (Busemann et al., 2006). In IDPs, Keller et al. (2004) inferred that the D-rich carrier is primarily in an aliphatic component. Remusat et al. (2006) have taken this one stage further. Based on compound specific isotopic analyses of the products of pyrolysis and RuO_4 degradation experiments conducted on Orgueil IOM, they suggested that IOM is composed of three components: two components are aliphatic, Type 1 (CH_2 groups) with $\delta D \approx 1250$‰ and Type 2 (CH and CH_3 groups) with $\delta D \approx 550$‰, and the third component, Type 3, is aromatic with $\delta D \approx 150$‰. Remusat et al. (2006) suggest that the Type 1 isotopic composition was established by exchange of the IOM with H_3^+ formed at ~ 100 K. Such high temperatures are more consistent with environments in the solar nebula rather than interstellar molecular clouds.

Given the importance of this conclusion, we examine the model in the light of our results. The discussion assumes that all chondrites accreted a common precursor. We cannot rule out that each meteorite's IOM composition reflects exchange under different conditions in the nebula. However, previously we showed that there are no systematic variations with estimates of the relative locations and/or times of chondrite formation, and that parent body processes can dramatically alter the composition of IOM. Here and elsewhere (Cody et al., submitted for publication), we
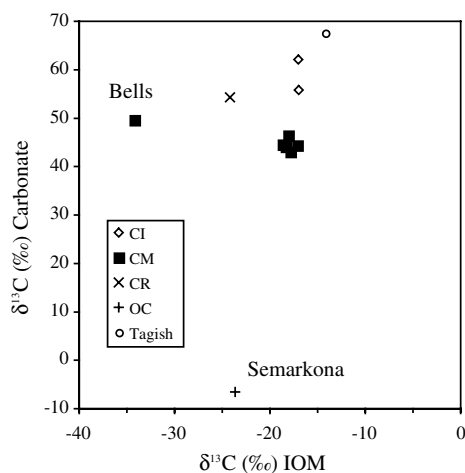

Fig. 10. The C isotopic compositions of IOM and carbonate in various meteorites. There is no obvious correlation between their compositions, suggesting that although the IOM experienced some oxidation (Cody and Alexander, 2005) the oxidized material was not the major source of the C in the carbonate.

have also argued that the variations in composition and structure of IOM amongst chondrites are consistent with evolution during parent body processing from a common precursor like that found in Bells and the CRs.

The bulk compositions of the IOM from Bells and the CR2s are much more D-rich than even the Type 1 component proposed by Remusat et al. (2006). Wang et al. (2005) measured the H isotopic compositions of individual compounds during pyrolysis of EET92042 IOM. Most of the compounds were aromatic and had isotopic compositions of $\delta D \approx 2500$–4400‰, close to that of the bulk IOM, and there was no simple correlation between δD value and degree of substitution—e.g., naphthalene (unsubstituted aromatic) had a $\delta D = 1257 \pm 25‰$ while substituted moieties had lower δD values. These results apparently conflict with the model of Remusat et al. (2006).

There is some question about whether molecular pyrolysates are all fragments of the IOM, or whether some or all formed and/or exchanged H isotope during the pyrolysis experiments. If the aliphatic component carries the D, the Wang et al. results require that either the aromatic compounds form during the experiments from aliphatic material or there must be exchange between pyrolysates. In either case, this calls into question the conclusions of Remusat et al. (2006) since they are based largely on the results of pyrolysis experiments. If the aromatic components are indigenous but have exchanged with D-rich aliphatic material, the composition of the aliphatic material must be higher than the compositions measured by Wang et al. (2005).

A highly simplified model of the IOM can be developed based on NMR estimates of average H/C ratios of the aromatic (0.42) and aliphatic (1.4) moieties, with a constant fraction of C bonded to O (0.11) (Cody and Alexander, 2005). Taking the Remusat et al. (2006) value for the aromatic component ($\delta D \approx 150‰$), to approximately reproduce the compositions of Bells and the CR2 IOM requires that $\delta D \approx 4000$ ‰ for the aliphatic component (Fig. 11). Using the temperature dependent isotopic fractionation factor of Remusat et al. (2006), 4000‰ would require temperatures of $\sim$75 K.

Interestingly, Tagish Lake (and the possibly related WIS91600) falls quite close to the aromatic-aliphatic mixing curve in Fig. 11, consistent with the suggestion that it formed from Bells-/CR-like IOM by the loss of a large fraction of its aliphatic material (Cody and Alexander, 2005). Presumably the lost aliphatic material would have to have been side chains on aromatic moieties or a separate aliphatic component rather than the aliphatic linkages between aromatic moieties, otherwise much of the IOM in Tagish Lake would have become soluble. The lower δD enrichments in most CM and all CI chondrites, compared to Bells and the CRs, might be the result of exchange with water during aqueous alteration, in which case the final composition would reflect the degree of exchange, the water's isotopic composition and the IOM/water ratio.

The 4000‰ estimated above is the average aliphatic H isotopic composition. There is considerable CH and CH$_3$ in the aliphatic material (Cody et al., 2002; Cody and Alexander, 2005). NMR estimates of the fraction of aliphatic H
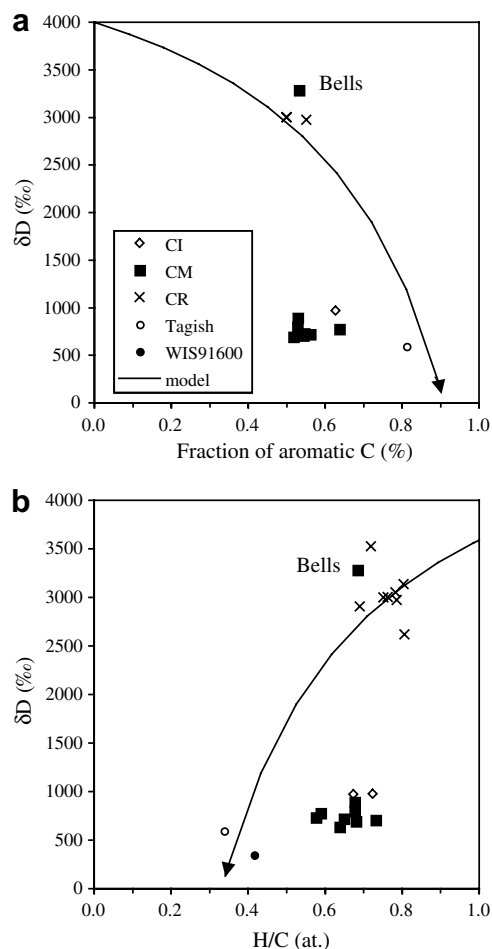

Fig. 11. The IOM H isotopic compositions vs. the fractions of aromatic C (Cody and Alexander, 2005) and the H/C ratios. The curves are mixing lines between aromatic C ($\delta D = 150‰$, H/C = 0.42) and aliphatic C ($\delta D = 4000‰$, H/C = 1.4). Mixing of these two components can roughly reproduce the compositions of the IOM in Bells, the CRs, Tagish Lake and the possibly related meteorite WIS91600, but not the IOM in the CIs and most CMs.

in CH$_2$ range from $\sim$0–50%. If, like Remusat et al. (2006), we assume that the CH$_2$ groups carry most of the D, their average δD value would have to be $\geqslant 8000‰$, requiring reaction temperatures of $\leqslant 65$ K. Even this temperature is an upper limit because it assumes complete exchange of all CH$_2$ groups with H$_3^+$, as well as no exchange during aqueous alteration and isolation of the IOM. At present, the conclusion that the IOM must have a solar origin based on the model dependent temperature estimates is premature.

4.5. Solar or interstellar?

There is no compelling evidence for the formation or modification of the IOM in the inner solar nebula. Variation in IOM composition within meteorite classes shows that parent body processes can sometimes dramatically modify IOM, although the mechanisms for doing this are not understood. At present, it seems likely that the IOM in all chondrites evolved from a common precursor. This, and the fact that

refractory organic matter resembling chondritic IOM appears to be more abundant in comets, suggests that either the IOM formed in the outer Solar System or a higher fraction of interstellar material survived there.

4.5.1. Solar?

If the IOM is solar, an efficient mechanism for making PAHs is required, such as irradiation of condensed aliphatic material (Strazzulla, 1997) or direct formation from the solar gas at high temperature (Morgan et al., 1991). Irradiation of D- and ^{15}N-rich aliphatic material could explain the isotopic compositions of the most primitive IOM, but whether this would produce material that is structurally like the IOM is not known. There is no independent evidence for an intense irradiation of material in meteorite matrices or IDPs. Nor is there any evidence for the preservation of the unirradiated material, requiring a remarkably efficient process. On the other hand, the so-called Q or P1 noble gases are trapped within the IOM (e.g., Huss et al., 1996; Busemann et al., 2000). The current abundance of noble gases is too low to have significantly modified the IOM, but perhaps the noble gases were implanted during an energetic particle irradiation and subsequently most were lost. The combined fractionations associated with acceleration of the irradiating material (proportional to first ionization potential) and the subsequent loss (proportional to the mass/volatility of the elements and isotopes) might explain the large elemental and isotopic fractionations in Q relative to solar. However, if, as seems likely, the noble gases were accompanied by H (more abundant and low ionization potential), it is not clear that the net result of the irradiation would be a material with a lower H/C ratio and higher aromatic fraction.

Efficient synthesis of PAHs from simple linear hydrocarbons (e.g., CH_4, C_2H_2) in a solar gas requires a restricted range of temperatures (1100–900 K) and pressures (10^{-7}–10^{-6} bars), as well as times ($\sim 10^6$ yrs) that are a significant fraction of a disk's lifetime (Morgan et al., 1991). Consequently, this mechanism is an unlikely one for making abundant PAHs in the nebula.

A more likely mechanism is derivation of PAHs by pyrolysis or sputtering of refractory ISM organics. This could happen over a much wider range of conditions and on much shorter timescales. The shocks that appear to have been responsible for the formation of crystalline silicates in IDPs and comets (Alexander et al., 2007), and possibly for making chondrules (e.g., Desch and Connolly, 2002), would pyrolize the ISM organics.

Even if PAHs can be made in this or some other way, somehow they must be converted to IOM. By analogy with the ISM, this presumably requires cycling of dust through denser colder regions and warmer less dense regions (with sublimation/condensation of ices and volatile organics), as well as UV and cosmic ray irradiation. This could be achieved by vertical or radial transport of dust in the disk, although vertical transport will be on shorter timescales—turbulent diffusion timescales are similar in the horizontal and vertical directions, but the vertical scale height of the disk is much smaller than radial distances at least in the outer nebula. At high latitudes in the disk, photochemistry and ion molecule reactions may generate large isotopic fractionations in molecules that could ultimately exchange with (e.g., Remusat et al., 2006) or bond to the forming IOM.

The vertical thermal structure of the disk will have varied with radial distance and time. Thus, IOM that formed at different radial distances and times is likely to have different isotopic compositions. Consequently, unless radial mixing was remarkably efficient, the elemental and isotopic compositions IOM in meteorites and comets should be different, and the IOM compositions should vary between meteorite classes that formed at different times and places. The IOM in the most primitive meteorites and IDPs appears to be very similar, and there is no compelling evidence that the IOM compositional variations we see between meteorite classes either predate parent body processing or correlate with estimates of the relative ages and/or formation locations of the chondrite classes.

There has been a concerted effort to understand the evolution of water in the solar nebula because of its potential role in transferring mass independent O isotopic anomalies generated at the surface of the disk (Lyons and Young, 2005) or in the ISM (Yurimoto and Kuramoto, 2004) into the inner Solar System. The fate of the IOM and the PAHs from which it forms will be tied to the fate of the ice. The amount of cycling a developing IOM grain will experience will depend on the rate at which grains accrete and grow into larger objects—the larger the object the lower its vertical diffusion rate and the higher its inward radial drift. Current models suggest that ice grains tend to aggregate rapidly into meter-sized objects that either form planetesimals or rapidly migrate into the inner Solar System (Ciesla and Cuzzi, 2006; Ciesla et al., 2006). Given that the IOM, PAHs, etc. will be intimately associated with the ice, it seems possible that there will be insufficient time to produce the abundances of IOM found in comets, IDPs and perhaps even chondrite matrices. The alternative source of IOM is the ISM.

4.5.2. Interstellar?

Because conditions in the ISM and outer Solar System would have been quite similar, it may be difficult to definitively demonstrate whether the IOM is solar and/or interstellar. With the isotopic enrichments in D and ^{15}N no longer diagnostic of formation in the ISM, at present the evidence for or against an interstellar origin is largely indirect.

Spectroscopically, the IOM resembles the refractory organics in the ISM (Pendleton et al., 1994; Bradley et al., 2005). The survival of circumstellar grains in meteorites and IDPs demonstrates that some presolar material survived formation of the Solar System and processing of dust in the nebula. The ratio of IOM to presolar nanodiamonds in chondrites is roughly constant (Alexander et al., 1998; Alexander, 2005b), which is consistent with a presolar origin for the IOM. The abundance of nanodiamonds in IDPs is not known. Other types of circumstellar grain seem to be more susceptible to destruction during parent body processing (e.g., Huss and Lewis, 1995), but, like the IOM, the abundance of presolar silicates in IDPs (Floss and Stadermann, 2004) is significantly higher than in meteorite matrices (Marhas et al., 2006).

Interstellar silicates are almost entirely amorphous (⩾97.8%: Kemper et al., 2004, 2005). The detection of crystalline silicates in Oort cloud and Kuiper belt comets (Swamy et al., 1988; Hanner et al., 1999; Harker et al., 2005) clearly shows that significant fractions of cometary material were processed at high temperatures (>1000 K). Such high temperatures would have modified or, more likely, destroyed any interstellar organic matter. Therefore, if the IOM in comets, IDPs and meteorites is interstellar, there should be an inverse correlation between the abundance of crystalline silicates and IOM, and these abundances should be consistent with the estimated initial abundance in ISM dust.

Within the uncertainties, Alexander (2005b) has argued that the IOM abundances are consistent with the partial destruction during formation of crystalline silicates from ISM dust. However, the uncertainties are large. In addition, CP-IDP compositions are not solar suggesting that something is missing from our CP-IDP sample (Alexander and Keller, 2006), and the Deep Impact experiment showed that astronomical observations of comets can severely underestimate the crystallinity of their dust (Harker et al., 2005). The least heated CP-IDPs during atmospheric entry are enriched in volatile elements by factors of ∼2–3 (Flynn et al., 2006) and on average are depleted in refractory elements (Schramm et al., 1989; Thomas et al., 1993) relative to CI. Assuming solar (or CI) volatile element/Si abundances, CP-IDPs appear to represent ⩽30–50% of their parent body material, the remainder being volatile-poor material that is perhaps much denser and therefore burns up on atmospheric entry. If this volatile-poor material is also free of IOM, the bulk IOM abundance of the CP-IDP parent body(s) would be much closer to the IOM content of CI chondrites. Assuming that the under represented, volatile-poor materials are high temperature solar products, the IOM abundance in the CP-IDP parent body(s) would still be consistent with an interstellar origin.

The origin of the IOM in IDPs is also intimately tied to the origin of their amorphous silicates (Alexander et al., 2007)—so-called GEMS or glass with embedded metal and sulfide (Bradley, 1994). If GEMS are amorphous interstellar silicates (Bradley, 1994; Bradley et al., 1999), the IOM is probably interstellar because a large fraction of interstellar silicates remain and the abundance of IOM is roughly consistent with the fraction of silicates that have been processed. On the other hand, if GEMS are largely solar condensates (Keller and Messenger, 2004; Keller et al., 2005), the IOM must also be solar because almost all interstellar silicates have been reprocessed at high temperatures in the nebula.

There is considerable uncertainty about the nature and origin of the C-rich dust in the diffuse ISM (Mennella et al., 2002; Pendleton and Allamandola, 2002; Dartois et al., 2004). The IOM in chondrites is composed of 50–60% of small PAHs ($<C_{20}$) and 40–50% short, highly branched aliphatic chains (e.g., Sephton et al., 2004; Cody and Alexander, 2005). Of the models for the refractory organics in the diffuse ISM, this most closely resembles that of Pendleton and Allamandola (2002), although the PAHs in their model are larger (C_{20-200}) and more abundant (∼80%) than in the most primitive IOM.

Pendleton and Allamandola (2002) envisage most of the PAHs having formed in C-star outflows. PAHs, amorphous C and graphite are likely to begin to form in large amounts when C > O + Si, i.e., when all O has been consumed as CO and all Si as SiC. On average, the C at this stage will be isotopically much lighter than the heavier than solar isotopic compositions of circumstellar SiC grains from C-stars. Indeed, circumstellar graphite grains from AGB stars are on average isotopically lighter than the solar C isotopic composition. This is potentially problematic for a C-star origin of the PAHs since the bulk C isotopic composition of the IOM is essentially solar, but large uncertainties remain about the expected composition of PAHs in C-star winds. In stark contrast to the IOM, the H and N isotopic compositions of PAHs from C-stars will be very light. If the PAHs in the IOM are presolar, either they formed in the isotopically well-mixed ISM or they exchanged there.

5. SUMMARY AND CONCLUSIONS

We have found a wide range of IOM elemental and isotopic compositions within and between chondrite classes, even amongst the most primitive meteorites of each class. One possible explanation for these variations is that they were established in the solar nebula prior to accretion. However, the variations do not correlate with estimates of formation times or locations of the chondrites, nor do they correlate with volatile element fractionations in the bulk chondrites. Numerous arguments almost certainly rule out FTT synthesis of most of the IOM either in the nebula or on parent bodies.

On the other hand, intra-class variations, particularly amongst the CMs and OCs, show that parent body processing can dramatically alter the elemental and isotopic composition of the IOM. The general elemental trends in IOM from type 3 chondrites are consistent with a combination of pyrolysis and oxidation of a common precursor with an elemental composition and matrix-normalized abundance like that of IOM in CI–CM–CR chondrites.

There is little systematic variation in the elemental compositions of IOM amongst CMs, despite the range of types analyzed, or between CMs, CIs and CRs even though the extent of alteration in these meteorites are quite different. However, there is evidence that they all experienced some oxidation at the onset of alteration—the degree of oxidation does not increase with increasing degree of alteration of the bulk meteorite.

Such a simple picture of modification of a common IOM material during parent body processing is belied by the variations in isotopic compositions, within and between classes. If there was a common precursor, this variation in IOM behavior suggests that it is composed of several isotopically distinct components whose relative stabilities are sensitive functions of the conditions during parent body processing. The chemically most primitive and isotopically most anomalous IOM seems to be preserved in the CR chondrites and Bells (CM2). The IOM in these meteorites closely resembles that found in CP-IDPs. By comparison, the IOMs even from Semarkona (LL3.0), ALH77307 (CO3.0), Kaba (CV3.0), and Acfer 094 (C3.0) appear to

have been modified by parent body processes and/or terrestrial weathering.

Whether all chondrites accreted the same IOM material cannot be established with certainty because of the overprint of parent body processing and/or terrestrial weathering. However, some members of each chondrite class studied retain what appear to be vestiges of the D- and ^{15}N-rich compositions that characterize IOM in Bells and the CRs.

If all chondrites did accrete the same IOM material, whether the IOM primarily formed in the Solar System or in the ISM remains uncertain. Conditions in the outer Solar System and in the ISM may have been quite similar, and it is likely that there was considerable radial mixing in the disk. The presence of circumstellar grains in chondrites demonstrates that some ISM material is preserved in meteorites, and upper limits on the abundances of refractory interstellar organics that survive, at least in comets and IDPs, are to first order consistent with IOM abundances in them.

Taken together, the presence of large isotopic anomalies in the IOM and the higher abundance of IOM-like material in comets compared to chondrites require that if IOM is solar it formed in the outer rather than the inner Solar System. Two things are required if the IOM formed in the Solar System—formation of simple PAHs and linking of these PAHs by short branched aliphatic chains. Linking of the PAHs may require a similar process to that proposed for producing refractory organics in the ISM—repeated irradiation of organic-rich dust in ice-bearing and ice-free environments, perhaps as a result of vertical and radial convection.

While a solar origin cannot be ruled out, most properties of the IOM are consistent with an ISM origin—isotopic composition, abundance relative to crystalline silicates and nanodiamonds, IR and UV absorption characteristics. Given that circumstellar material survives in meteorites, at present an interstellar origin for the IOM is the most straightforward.

APPENDIX A. SUPPLEMENTARY DATA

This Electronic Annex provides: details of the petrology of the meteorites analyzed, a comprehensive comparison between the elemental and isotopic compositions measured in this and previous studies, as well as discussion of the reproducibility and accuracy of the results, and the potential for isotopic exchange during isolation of the insoluble organic matter from the meteorites. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2007.06.052.

REFERENCES

Abreu N. M. and Brearley A. J. (2005) HRTEM and EFTEM studies of phyllosilicate-organic matter associations in matrix and dark inclusions in the EET92042 CR2 carbonaceous chondrite. *Lunar Planet. Sci.* **XXXVI**, #1826.

Aikawa Y. and Herbst E. (2001) Two-dimensional distributions and column densities of gaseous molecules in protoplanetary disks. II. Deuterated species and UV shielding by ambient clouds. *Astron. Astrophys.* **371**, 1107–1117.

Aikawa Y., van Zadelhoff G. J., van Dishoeck E. F. and Herbst E. (2002) Warm molecular layers in protoplanetary disks. *Astron. Astrophys.* **386**, 622–632.

Alexander C. M. O'D., Arden J. W. and Pillinger C. T. (1989a) Carbonaceous components in ordinary chondrites; implications for metamorphism vs. heterogeneous accretion. *Lunar Planet. Sci.* **XX**, 7–8.

Alexander C. M. O'D., Barber D. J. and Hutchison R. (1989b) The microstructure of Semarkona and Bishunpur. *Geochim. Cosmochim. Acta* **53**, 3045–3057.

Alexander, C. M. O'D. (2005a) From supernovae to planets: the view from meteorites and IDPs. In *Chondrites and the Protoplanetary Disk*, vol. 341 (eds. A. N. Krot, E. R. D. Scott and B. Reipurth). The Astronomical Society of the Pacific, pp. 972–1002.

Alexander C. M. O'D. (2005b) Re-examining the role of chondrules in producing the volatile element fractionations in chondrites. *Meteorit. Planet. Sci.* **40**, 943–965.

Alexander, C. M. O'D., Boss, A. P., Keller, L. D., Nuth, I. J. A. and Weinberger, A. (2007) Astronomical and meteoritic evidence for the nature of interstellar dust and its processing in protoplanetary disks. In *Protostars and Planets V* (eds. B. Reipurth, D. Jewitt and K. Keil). University of Arizona Press, pp. 801–814.

Alexander C. M. O'D. and Keller L. P. (2006) Are there clues to the dust 'annealing' process in protoplanetary disks in IDPs? *Lunar Planet. Sci.* **XXXVII**, #2325.

Alexander C. M. O'D., Russell S. S., Arden J. W., Ash R. D., Grady M. M. and Pillinger C. T. (1998) The origin of chondritic macromolecular organic matter: a carbon and nitrogen isotope study. *Meteorit. Planet. Sci.* **33**, 603–622.

Amelin Y., Krot A. N., Hutcheon I. D. and Ulyanov A. A. (2002) Lead isotopic ages of chondrules and calcium–aluminum-rich inclusions. *Science* **297**, 1678–1683.

Amelin Y., Krot A. N. and Twelker E. (2004) Pb isotopic age of the CB chondrite Gujba, and the duration of the chondrule formation interval. *Geochim. Cosmochim. Acta Suppl.* **68**, 759.

Ash R. D. and Pillinger C. T. (1995) Carbon, nitrogen and hydrogen in Saharan chondrites: the importance of weathering. *Meteoritics* **30**, 85–92.

Ashley J. W., Huss G. R., Garvie L. A. J., Guan Y., Buseck P. R. and Williams L. B. (2005) Nitrogen and carbon isotopic measurements of carbon nanoglobules from the Tagish Lake meteorite by secondary ion mass spectrometry. *Lunar Planet. Sci.*, 2205.

Bell K. R., Cassen P. M., Klahr H. H. and Henning T. (1997) The structure and appearance of protostellar accretion disks: limits on disk flaring. *Astrophys. J.* **486**, 372–387.

Benedix G. K., Leshin L. A., Farquhar J., Jackson T. and Thiemens M. H. (2003) Carbonates in CM2 chondrites: constraints on alteration conditions from oxygen isotopic compositions and petrographic observations. *Geochim. Cosmochim. Acta* **67**, 1577–1588.

Birjukov V. V. and Ulyanov A. A. (1996) Petrology and classification of new Antarctic carbonaceous chondrites PCA91082, TIL91722 and WIS91600. *Antarct. Meteorite Res.* **9**, 8.

Bockelèe-Morvan D., Gautier D., Hersant F., Hurè J. M. and Robert F. (2002) Turbulent radial mixing in the solar nebula as the source of crystalline silicates in comets. *Astron. Astrophys.* **384**, 1107–1118.

Bradley J. P. (1994) Chemically anomalous preaccretionally irradiated grains in interplanetary dust from comets. *Science* **265**, 925–929.

Bradley J. P., Brownlee D. E. and Fraundorf P. (1984) Carbon compounds in interplanetary dust: evidence for formation by heterogeneous catalysis. *Science* **223**, 56–58.

Bradley J. P., Dai Z. R., Erni R., Browning N., Graham G., Weber P., Smith J., Hutcheon I., Ishii H., Bajt S., Floss C., Stadermann F. and Sandford S. (2005) An astronomical 2175 Å feature in interplanetary dust particles. *Science* **307**, 244–247.

Bradley J. P., Keller L. P., Snow T. P., Hanner M. S., Flynn G. J., Gezo J. C., Clemett S. J., Brownlee D. E. and Bowey J. E. (1999) An infrared spectral match between GEMS and interstellar grains. *Science* **285**, 1716–1718.

Brearley A. J. (1990) Carbon-rich aggregates in type 3 ordinary chondrites: characterization, origins, and thermal history. *Geochim. Cosmochim. Acta* **54**, 831–850.

Brearley A. J. (1991) Mineralogical and chemical studies of matrix in the Adelaide meteorite, a unique carbonaceous chondrite with affinities to ALH A77307 (CO3). *Lunar Planet. Sci.* **XXII**, 133–134.

Brearley A. J. (1995) Aqueous alteration and brecciation in Bells, an unusual saponite-bearing, CM chondrite. *Geochim. Cosmochim. Acta* **59**, 2291–2318.

Brearley A. J. (2003) Ubiquitous nanophase Fe,Ni carbides in Murchison fine-grained rims: possible relicts of nebular Fischer–Tropsch reactions. *Meteorit. Planet. Sci. Suppl.* **38**, 5262.

Brearley A. J. (2004a) A unique style of alteration of iron-nickel metal in WIS91600, an unusual C2 carbonaceous chondrite. *Lunar Planet. Sci.* **XXXV**, #1358.

Brearley A. J. (2004b) In situ location and characterization of carbon-bearing phases in carbonaceous chondrites: insights from Yamato 791198, a weakly-altered CM2 chondrite. *Lunar Planet. Sci.* **XXXV**, #1896.

Brearley A. J., Hutcheon I. D. and Browning L. (2001) Compositional zoning and Mn–Cr systematics in carbonates from the Y791198 carbonaceous chondrite. *Lunar Planet. Sci.* **XXXII**, #1458.

Busemann H., Baur H. and Wieler R. (2000) Primordial noble gases in "Phase Q" in carbonaceous and ordinary chondrites studied by closed system stepped etching. *Meteorit. Planet. Sci.* **35**, 949–973.

Busemann H., Young A. F., Alexander C. M. O'D., Hoppe P., Mukhopadhyay S. and Nittler L. R. (2006) Interstellar chemistry recorded in organic matter from primitive meteorites. *Science* **314**, 727–730.

Christoffersen R. and Buseck P. R. (1983) Epsilon carbide – a low-temperature component of interplanetary dust particles. *Science* **222**, 1327–1329.

Ciesla F. J. and Cuzzi J. N. (2006) The evolution of the water distribution in a viscous protoplanetary disk. *Icarus* **181**, 178–204.

Ciesla F. J., Krot A. N. and Lyons J. R. (2006) Water transport in the solar nebula: implications for the mixing of oxygen isotopic reservoirs. *Lunar Planet. Sci.*, #1627.

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

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

Cody G. D. and Alexander C. M. O'D. (2005) NMR studies of chemical structural variation of insoluble organic matter from different carbonaceous chondrite groups. *Geochim. Cosmochim. Acta* **69**, 1085–1097.

Cody G. D., Alexander C. M. O'D. and Tera F. (2002) Solid state (^{1}H and ^{13}C) NMR spectroscopy of the insoluble organic residue in the Murchison meteorite: a self-consistent quantitative analysis. *Geochim. Cosmochim. Acta* **66**, 1851–1865.

Cody, G. D., Alexander, C. M. O'D., Yabuta, H., Kilcoyne, A. L. D., Araki, T., Ade, H., Dera, P., Fogel, M., Militzer, B. and Mysen, B. O. (submitted for publication) Chemical evolution of meteoritc organic matter in the early Solar System. *Earth Planet. Sci. Lett.*

Dartois E., Muñoz-Caro G. M., Deboffle D. and d'Hendecourt L. (2004) Diffuse interstellar medium organic polymers. Photoproduction of the 3.4, 6.85 and 7.25 mum features. *Astron. Astrophys.* **423**, L33–L36.

Desch S. J. and Connolly, Jr., H. C. (2002) A model of the thermal processing of particles in solar nebula shocks: application to the cooling rates of chondrules. *Meteorit. Planet. Sci.* **37**, 183–208.

Ferrante R. F., Moore M. H., Nuth J. A. and Smith T. (2000) NOTE: laboratory studies of catalysis of CO to organics on grain analogs. *Icarus* **145**, 297–300.

Floss C. and Stadermann F. J. (2004) Isotopically primitive interplanetary dust particles of cometary origin: evidence from nitrogen isotopic compositions. *Lunar Planet. Sci.*, #1281.

Flynn G. J. (1989) Atmospheric entry heating: a criterion to distinguish between asteroidal and cometary sources of interplanetary dust. *Icarus* **77**, 287–310.

Flynn G. J., Keller L. P., Feser M., Wirick S. and Jacobsen C. (2003) The origin of organic matter in the solar system: evidence from interplanetary dust particles. *Geochim. Cosmochim. Acta* **67**, 4791–4806.

Flynn G. J., Lanzirotti A. and Sutton S. R. (2006) Chemical compositions of large cluster IDPs. *Lunar Planet. Sci.* **XXXVII**, #1216.

Gail H.-P. (2004) Radial mixing in protoplanetary accretion disks. IV. Metamorphosis of the silicate dust complex. *Astron. Astrophys.* **413**, 571–591.

Gardinier A., Derenne S., Robert F., Behar F., Largeau C. and Maquet J. (2000) Solid state CP/MAS ^{13}C NMR of the insoluble matter of the Orgueil and Murchison meteorites: quantitative study. *Earth Planet. Sci. Lett.* **184**, 9–21.

Garvie L. A. J. and Buseck P. R. (2004) Nanosized carbon-rich grains in carbonaceous chondrite meteorites. *Earth Planet. Sci. Lett.* **224**, 431–439.

Garvie L. A. J. and Buseck P. R. (2006) Carbonaceous nanospheres in chondrites. *Lunar Planet. Sci.* **XXXVII**, #1455.

Gilmour, I. (2003) Structural and isotopic analysis of organic matter in carbonaceous chondrites. In *Meteorites, Comets and Planets*, vol. 1 (ed. A. M. Davis). Elsevier-Pergamon, pp. 269–290.

Grady M. M., Verchovsky A. B., Franchi I. A., Wright I. P. and Pillinger C. T. (2002) Light element geochemistry of the Tagish Lake CI2 chondrite: comparison with CI1 and CM2 meteorites. *Meteorit. Planet. Sci.* **37**, 713–735.

Grady M. M., Wright I. P. and Pillinger C. T. (1989) A preliminary investigation into the nature of carbonaceous material in ordinary chondrites. *Meteoritics* **24**, 147–154.

Grossman J. N., Alexander C. M. O'D., Wang J. and Brearley A. J. (2000) Bleached chondrules: evidence for widespread aqueous processes on the parent asteroids of ordinary chondrites. *Meteorit. Planet. Sci.* **35**, 467–486.

Guo W. and Eiler J. M. (2006) Temperature of aqueous alteration on CM chondrite parent bodies based on carbonate 'clumped-isotope' thermometry. *Lunar Planet. Sci.* **XXXVII**, #2288.

Hanner M. S., Gehrz R. D., Harker D. E., Hayward T. L., Lynch D. K., Mason C. C., Russell R. W., Williams D. M., Wooden D. H. and Woodward C. E. (1999) Thermal emission from the dust coma of comet Hale-Bopp and the composition of the silicate grains. *Earth Moon and Planets* **79**, 247–264.

Harker D. E., Woodward C. E. and Wooden D. H. (2005) The dust grains from 9P/Tempel 1 before and after the encounter with Deep Impact. *Science* **310**, 278–280.

Hayatsu R. and Anders E. (1981) Organic compounds in meteorites and their origins. In *Topics of Current Chemistry*. Springer-Verlag, pp. 1–37.

Hayatsu R., Matsuoka S., Scott R. G., Studier M. H. and Anders E. (1977) Origin of organic matter in the early solar system-VII. The organic polymer in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **41**, 1325–1339.

Hayatsu R., Winans R. E., Scott R. G., McBeth R. L., Moore L. P. and Studier M. H. (1980) Phenolic esters in the organic polymer of the Murchison meteorite. *Science* **207**, 1202–1204.

Huss G. R., Keil K. and Taylor G. J. (1981) The matrices of unequilibrated ordinary chondrites: implications for the origin and history of chondrites. *Geochim. Cosmochim. Acta* **45**, 33–51.

Huss G. R. and Lewis R. S. (1995) Presolar diamond, SiC, and graphite in primitive chondrites: abundances as a function of meteorite class and petrologic type. *Geochim. Cosmochim. Acta* **59**, 115–160.

Huss G. R., Lewis R. S. and Hemkin S. (1996) The "normal planetary" noble gas component in primitive chondrites: compositions, carrier, and metamorphic history. *Geochim. Cosmochim. Acta* **60**, 3311–3340.

Huss G. R., Meshik A. P., Smith J. B. and Hohenberg C. M. (2003) Presolar diamond, silicon carbide, and graphite in carbonaceous chondrites: implications for thermal processing in the solar nebula. *Geochim. Cosmochim. Acta* **67**, 4823–4848.

Hutchison R., Alexander C. M. O'D. and Barber D. J. (1987) The Semarkona meteorite: first recorded occurrence of smectite in an ordinary chondrite, and its implications. *Geochim. Cosmochim. Acta* **51**, 1875–1882.

Jiang Y. J., Solum M. S., Pugmire R. J., Grant D. M., Schobert H. H. and pappano P. J. (2002) A new method for measuring the graphite content of anthracite coals and soots. *Energy Fuels* **16**, 1296–1300.

Johnson N. M., Cody G. D. and Nuth, III, J. A. (2004) Organics on Fe–silicate grains: potential mimicry of meteoritic processes? *Lunar Planet. Sci.* **XXXV**, #1876.

Johnson N. M., Steiner M. E. and Nuth J. A. (2007) Fischer–Tropsch reactions and implications for protostellar systems. *Lunar Planet. Sci.* **XXXVIII**, #2183.

Joswiak D. J., Brownlee D. E., Pepin R. O. and Schlutter D. J. (2000) Characteristics of asteroidal and cometary IDPs obtained from stratospheric collectors: summary of measured He release temperatures, velocities and descriptive mineralogy. *Lunar Planet. Sci.* **XXXI**, #1500.

Keller L. P. (1998) A TEM study of iron–nickel carbides in the matrix of the Semarkona unequilibrated ordinary chondrite. *Meteorit. Planet. Sci.* **33**, 913–919.

Keller L. P. and Messenger S. (2004) On the origin of, GEMS. *Lunar Planet. Sci.* **XXXV**, #1985.

Keller L. P., Messenger S. and Christoffersen R. (2005) GEMS revealed: spectrum imaging of aggregate grains in interplanetary dust. *Lunar Planet. Sci.* **XXXVI**, #2088.

Keller L. P., Messenger S., Flynn G. J., Clemett S., Wirick S. and Jacobsen C. (2004) The nature of molecular cloud material in interplanetary dust. *Geochim. Cosmochim. Acta* **68**, 2577–2589.

Kemper F., Vriend W. J. and Tielens A. G. G. M. (2004) The absence of crystalline silicates in the diffuse interstellar medium. *Astrophys. J.* **609**, 826–837.

Kemper F., Vriend W. J. and Tielens A. G. G. M. (2005) Erratum: The absence of crystalline silicates in the diffuse interstellar medium (2004 ApJ 609, 826). *Astrophys. J.* **633**, 534.

Kissel J. and Krueger F. R. (1987) The organic component in dust from comet Halley as measured by the PUMA mass spectrometer on board Vega 1. *Nature* **326**, 755–760.

Kress M. E. and Tielens A. G. G. M. (2001) The role of Fischer–Tropsch catalysis in solar nebula chemistry. *Meteorit. Planet. Sci.* **36**, 75–92.

Krot A. N., Zolensky M. E., Wasson J. T., Scott E. R. D., Kiel K. and Ohsumi K. (1997) Carbide-magnetite assemblages in type-3 ordinary chondrites. *Geochim. Cosmochim. Acta* **61**, 219–237.

Kurahashi E., Kita N. T., Nagahara H. and Morishita Y. (2004) Contemporaneous formation of chondrules in the ^{26}Al–^{26}Mg system for ordinary and CO chondrites. *Lunar Planet. Sci.* **XXXV**, #1476.

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

Llorca J. and Casanova I. (1998) Formation of carbides and hydrocarbons in chondritic interplanetary dust particles: a laboratory study. *Meteorit. Planet. Sci.* **33**, 243–251.

Llorca J. and Casanova I. (2000) Reaction between H_2, CO, and H_2S over Fe,Ni metal in the solar nebula: experimental evidence for the formation of sulfur-bearing organic molecules and sulfides. *Meteorit. Planet. Sci.* **35**, 841–848.

Lyons J. R. and Young E. D. (2005) CO self-shielding as the origin of oxygen isotope anomalies in the early solar nebula. *Nature* **435**, 317–320.

Marhas K. K., Hoppe P., Stadermann F. J., Floss C. and Lea A. S. (2006) The distribution of presolar grains in CI and CO meteorites. *Lunar Planet. Sci.* **XXXVII**, #1959.

McSween, Jr., H. Y. (1977a) Carbonaceous chondrites of the Ornans type: a metamorphic sequence. *Geochim. Cosmochim. Acta* **41**, 477–491.

McSween, Jr., H. Y. (1977b) Petrographic variations among carbonaceous chondrites of the Vigarano type. *Geochim. Cosmochim. Acta* **41**, 1777–1790.

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

Mennella V., Brucato J. R., Colangeli L. and Palumbo P. (2002) CH bond formation in carbon grains by exposure to atomic hydrogen: the evolution of the carrier of the interstellar 3.4 micron band. *Astrophys. J.* **569**, 531–540.

Morgan, Jr., W. A., Feigelson E. D., Wang H. and Frenklach M. (1991) A new mechanism for the formation of meteoritic kerogen-like material. *Science* **252**, 109–112.

Mumma M. J., DiSanti M. A., Dello Russo N., Magee-Sauer K., Gibb E. and Novak R. (2002) The organic volatile composition of Oort cloud comets: evidence for chemical diversity in the giant-planets' nebular region. *Asteroids, Comets, Meteors – ACM* **2002**, 753–762.

Nakamura-Messenger K., Messenger S., Keller L. P., Clemett S. J. and Zolensky M. E. (2006) Organic globules in the Tagish Lake meteorite: remnants of the protosolar disk. *Science* **314**, 1439–1442.

Nittler L. R. (2003) Presolar stardust in meteorites: recent advances and scientific frontiers. *Earth Planet. Sci. Lett.* **209**, 259–273.

Nuth J. A., Hill H. G. M. and Kletetschka G. (2000) Determining the ages of comets from the fraction of crystalline dust. *Nature* **406**, 275–276.

Pendleton Y. J. and Allamandola L. J. (2002) The organic refractory material in the diffuse interstellar medium: mid-infrared spectroscopic constraints. *Astrophys. J. Suppl.* **138**, 75–98.

Pendleton Y. J., Sandford S. A., Allamandola L. J., Tielens A. G. G. M. and Sellgren K. (1994) Near-infrared absorption spectroscopy of interstellar hydrocarbon grains. *Astrophys. J.* **437**, 683–696.

Remusat L., Derenne S. and Robert F. (2005) New insight on aliphatic linkages in the macromolecular organic fraction of Orgueil and Murchison meteorites through ruthenium tetroxide oxidation. *Geochim. Cosmochim. Acta* **69**, 4377–4386.

Remusat L., Palhol F., Robert F., Derenne S. and France-Lanord C. (2006) Enrichment of deuterium in insoluble organic matter from primitive meteorites: a solar system origin? *Earth Planet. Sci. Lett.* **243**, 15–25.

Robert F. and Epstein S. (1982) The concentration and isotopic composition of hydrogen, carbon and nitrogen in carbonaceous meteorites. *Geochim. Cosmochim. Acta* **46**, 81–95.

Rubin A. E., James J. A., Keck B. D., Weeks K. S., Sears D. W. G. and Jarosewich E. (1985) The colony meteorite and variations in CO3 chondrite properties. *Meteoritics* **20**, 175–196.

Sandford S. A., Aléon J., Alexander C. M. O'D., Araki T., Bajt S., Baratta G. A., Borg J., Bradley J. P., Brownlee D. E., Brucato J. R., Burchell M. J., Busemann H., Butterworth A., Clemett S. J., Cody G., Colangeli L., Cooper G., d'Hendecourt L., Djouadi Z., Dworkin J. P., Ferrini G., Fleckenstein H., Flynn G. J., Franchi I. A., Fries M., Gilles M. K., Glavin D. P., Gounelle M., Grossemy F., Jacobsen C., Keller L. P., Kilcoyne A. L. D., Leitner J., Matrajt G., Meibom A., Mennella V., Mostefaoui S., Nittler L. R., Palumbo M. E., Papanastassiou D. A., Robert F., Rotundi A., Snead C. J., Spencer M. K., Stadermann F. J., Steele A., Stephan T., Tsou P., Tyliszczak T., Westphal A. J., Wirick S., Wopenka B., Yabuta H., Zare R. N. and Zolensky M. E. (2006) Organics captured from comet 81P/Wild 2 by the Stardust spacecraft. *Science* **314**, 1720.

Schramm L. S., Brownlee D. E. and Wheelock M. M. (1989) Major element composition of stratospheric micrometeorites. *Meteoritics* **24**, 99–112.

Sekine K., Sugita S., Shido T., Yamamoto T., Iwasawa Y., Kadono T. and Matsui T. (2006) An experimental study on Fischer–Tropsch catalysis: implications for impact phenomena and nebular chemistry. *Meteorit. Planet. Sci.* **41**, 715–730.

Sephton M. A., Love G. D., Meredith W., Snape C. E., Sun C.-G. and Watson J. S. (2005) Hydropyrolysis: a new technique for the analysis of macromolecular material in meteorites. *Planet. Space Sci.* **53**, 1280–1286.

Sephton M. A., Love G. D., Watson J. S., Verchovsky A. B., Wright I. P., Snape C. E. and Gilmour I. (2004) Hydropyrolysis of insoluble carbonaceous matter in the Murchison meteorite: new insights into its macromolecular structure. *Geochim. Cosmochim. Acta* **68**, 1385–1393.

Sephton M. A., Pillinger C. T. and Gilmore I. (2000) Aromatic moieties in meteoritic macromolecular materials: analyses by hydrous pyrolysis and ¹³C of individual compounds. *Geochim. Cosmochim. Acta* **64**, 321–328.

Sephton M. A., Verchovsky A. B., Bland P. A., Gilmour I., Grady M. M. and Wright I. P. (2003) Investigating the variations in carbon and nitrogen isotopes in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **67**, 2093–2108.

Strazzulla G. (1997) Ion irradiation: Its relevance to the evolution of complex organics in the outer Solar System. *Adv. Space Res.* **19**, 1077–1084.

Studier M. H., Hayatsu R. and Anders E. (1972) Origin of organic matter in early solar system-V. Further studies of meteoritic hydrocarbons and a discussion of their origin. *Geochim. Cosmochim. Acta* **36**, 189–215.

Swamy K. K. S., Sandford S. A., Allamandola L. J., Witteborn F. C. and Bregman J. D. (1988) A multicomponent model of the infrared emission from Comet Halley. *Icarus* **75**, 351–370.

Tachibana S., Nagahara H., Mostefaoui S. and Kita N. T. (2003) Correlation between relative ages inferred from ²⁶Al and bulk compositions of ferromagnesian chondrules in least equilibrated ordinary chondrites. *Meteorit. Planet. Sci.* **38**, 939–962.

Thomas K. L., Blanford G. E., Keller L. P., Klöck W. and McKay D. S. (1993) Carbon abundance and silicate mineralogy of anhydrous interplanetary dust particles. *Geochim. Cosmochim. Acta* **57**, 1551–1566.

Van Krevelen D. W. (1993) *Coal*. Elsevier.

Wang Y., Huang Y., Alexander C. M. O'D., Fogel M. and Cody G. (2005) Molecular and compound-specific hydrogen isotope analyses of insoluble organic matter from different carbonaceous chondrites groups. *Geochim. Cosmochim. Acta* **69**, 3711–3721.

Weisberg M. K., Prinz M., Clayton R. N. and Mayeda T. K. (1993) The CR (Renazzo-type) carbonaceous chondrite group and its implications. *Geochim. Cosmochim. Acta* **57**, 1567–1586.

Wooller M. J., Francis D., Fogel M. L., Miller G. H., Walker I. R. and Wolfe A. P. (2004) Quantitative paleotemperature estimates from δ¹⁸O of chironomid head capsules preserved in arctic lake sediments. *J. Paleolimnol.* **31**, 267–274.

Yabuta H., Williams L. B., Cody G. D., Alexander C. M. O'D. and Pizzarello S. (2007) The insoluble carbonaceous material of CM chondrites: a possible source of discrete organic compounds under hydrothermal conditions. *Meteorit. Planet. Sci.* **42**, 37–48.

Yang J. and Epstein S. (1983) Interstellar organic matter in meteorites. *Geochim. Cosmochim. Acta* **47**, 2199–2216.

Yang J. and Epstein S. (1984) Relic interstellar grains in Murchison meteorite. *Nature* **311**, 544–547.

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

Yurimoto H. and Kuramoto K. (2004) Molecular cloud origin for the oxygen isotope heterogeneity in the Solar System. *Science* **305**, 1763–1766.

Zinner, E. (2003) Presolar grains. In *Meteorites, Comets and Planets*, vol. 1 (ed. A. M. Davis). Elsevier-Pergamon, pp. 17–40.

Zolensky M. E., Nakamura K., Gounelle M., Mikouchi T., Kasama T., Tachikawa O. and Tonui E. (2002) Mineralogy of Tagish Lake: an ungrouped type 2 carbonaceous chondrite. *Meteorit. Planet. Sci.* **37**, 737–761.

Associate editor: Sandra Pizzarello