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Investigating the variations in carbon and nitrogen isotopes in carbonaceous chondrites

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Abstract—The carbonaceous chondrites contain significant amounts of carbon- and nitrogen-bearing components, the most abundant of which is organic matter. Stepped combustion data of whole rock and HF/HCl residues of carbonaceous chondrites reveal that the organic material can be subdivided operationally into three components: (1) free organic matter (FOM), which is readily extractable from whole-rock meteorites and is enriched in ^{13}C and ^{15}N; (2) labile organic matter (LOM), which has a macromolecular structure but is liberated by hydrous pyrolysis; LOM is the parent structure for some FOM and is also enriched in ^{13}C and ^{15}N; and (3) refractory organic matter (ROM), which is also macromolecular but is virtually unaffected by hydrous pyrolysis and is relatively depleted in ^{13}C and ^{15}N. The macromolecular entities (LOM and ROM) are by far the most abundant organic components present, and as such, the relative abundances of the ^{13}C- and ^{15}N-enriched LOM and the ^{13}C- and ^{15}N-depleted ROM will have a major influence on the overall isotopic composition of the whole-rock meteorite. Laboratory experiments designed to simulate the effects of parent body aqueous alteration indicate that this form of processing removes LOM from the macromolecular material, allowing ROM to exert a stronger influence on the overall isotopic compositions. Hence, aqueous alteration of macromolecular materials on the meteorite parent body may have a significant control on the stable isotopic compositions of whole-rock carbonaceous chondrites. The enstatite chondrites are also carbon rich but have been subjected to high levels of thermal metamorphism on their parent body. Stepped combustion data of HF/HCl residues of enstatite chondrites indicate, that if they and carbonaceous chondrites inherited a common organic progenitor, metamorphism under reducing conditions appears to incorporate and preserve some of the ^{13}C enrichments in LOM during graphitisation. However, when metamorphism is at its most extreme, the ^{15}N enrichments in LOM are lost. *Copyright © 2003 Elsevier Science Ltd*

1. INTRODUCTION

Carbonaceous chondrites are fragments of asteroids relatively unchanged since the formation of the solar system. As such, these primitive objects contain a record of the early solar system environment and the materials from which the solar system was constructed. An important part of this record is preserved within carbon- and nitrogen-bearing components that vary widely in structure and provenance (Table 1). These entities include organic matter, carbonate, diamond, silicon carbide, and graphite. It is thought that the relatively abundant organic matter was assembled from interstellar precursors and then modified during parent body aqueous and thermal processing (Cronin and Chang, 1993). Carbonate appears to have been precipitated during aqueous alteration on meteorite parent bodies, although an origin by nonaqueous reactions in circumstellar shells is also a possibility (Kemper et al., 2002). Diamonds are thought to be circumstellar condensates from carbon stars, whereas silicon carbide has originated mostly from red giant stars (e.g., Anders and Zinner, 1993). Extensive graphite sheets can result from the thermal metamorphism of organic matter on meteorite parent bodies, whereas graphite grains may have several stellar sources, i.e., novae, red giants, and Wolf-Rayet stars (e.g., Anders and Zinner, 1993).

Stable isotopes are valuable tools when attempting to decipher the record present in the carbon- and nitrogen-bearing components in meteorites. Isotopic information can be used as an indicator of both source and alteration history, and because bulk $\delta^{13}C$ and $\delta^{15}N$ values can be dissimilar in different meteorites, there is much potential for translating chemical information into plausible reconstructions of early solar system environments.

The first comprehensive survey of carbon, nitrogen, and hydrogen isotopic compositions of carbonaceous chondrites was performed by Kerridge (1985), who attempted to detect systematic patterns of secondary processing. The carbonaceous chondrite data set for carbon and nitrogen displayed significant intra- and intermeteorite heterogeneity but did not reveal any clear patterns that could be related to parent body alteration.

One early explanation for the observed heterogeneities in the stable isotopic compositions of carbonaceous chondrites was that the bulk isotopic values were reflecting variations in the relative proportions of isotopically distinct components (Boato, 1954). Subsequently, a further level of complexity was added when it was established that the individual components themselves can show internal isotopic variability. For example, the organic macromolecular material is the major carbon- and nitrogen-containing component in carbonaceous chondrites and is therefore key to understanding variations in their bulk isotopic compositions. To investigate isotopic variability within the macromolecular material in the Murchison (CM2) and Allende (CV3) carbonaceous chondrites, stepped heating experiments were used that distinguished between carbon phases by their susceptibility to combustion or pyrolysis (e.g., Halbout et al., 1986; Kerridge et al., 1987; Swart et al., 1982a, 1982b). On the basis of carbon, nitrogen, and hydrogen data, significant

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Table 1. Characteristics of some carbon- and nitrogen-bearing components in carbonaceous chondrites. The table was compiled from the following references: Alexander et al. (1998), Anders (1988), Grady et al. (1988), Kerridge (1985), Robert and Epstein (1982), Russell et al. (1996), Smith and Kaplan (1970), Swart et al. (1982a).

	Abundance (wt. %)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	Combustion T (°C)	Pyrolysis T (°C)
Whole rock	—	0 to –25	–50 to +335	—	—
Organic matter	2.0	–13 to –21	+25 to +150	250 to 450	300 to 1300
Carbonate	0.2	+20 to +80	—	400 to 700	400 to 700
Diamond	0.04	–38	–350	400 to 500	1000
Graphite	0.005	–50 to +340	—	500 to 700	700
Silicon carbide	0.009	+1430	–500	1200 to 1400	1200 to 1400

isotopic variability and a number of isotopically distinct components were discovered at the temperatures at which organic carbon combusts.

Carbon and nitrogen isotopic variability within carbonaceous chondrite macromolecular material was exploited by Alexander et al. (1998) to gain insight into the accretion and parent body alteration history of chondritic organic matter. A relatively constant ratio of interstellar nanodiamonds to organic macromolecular material suggested that all carbonaceous chondrites accreted a common organic progenitor, much of which was presolar. It was proposed that the organic progenitor exhibited an enrichment in the heavy isotopes of carbon, nitrogen, and hydrogen and that these were progressively lost during increasing parent body aqueous and thermal processing. If this hypothesis is correct, then the level of alteration to which a carbonaceous chondrite has been subjected can be assessed by establishing the preservation state of its stable isotopic enrichments.

Other work has cast light on the mechanisms by which isotopic enrichments may be removed from macromolecular material during parent body alteration. Carbon isotopic measurements of fragments of the Murchison macromolecular material produced by hydrous pyrolysis confirmed that aqueous processing can remove heavy isotope–enriched organic components and leave a lighter residue (Sephton et al., 1998). Furthermore, it appeared that isotopic heterogeneity within macromolecular material in carbonaceous chondrites and its major components extends down to the level of individual aromatic units (Sephton et al., 1998, 2000), and consequently, the effects of parent body alteration on the isotopic constitution of chondritic macromolecular materials may be subtle and complex.

Recently, the carbon and nitrogen stable isotope geochemistries of four whole-rock carbonaceous chondrites have been studied (Grady et al., 2002), and in part, their differences may be related to the effects of varying levels and types of parent body alteration on the relatively abundant organic macromolecular material. To assess the extent to which any differences observed in whole-rock carbonaceous chondrites are reflecting the alteration state of organic matter, we have isolated the Murchison macromolecular material from its inorganic matrix by using hydrofluoric (HF) and hydrochloric (HCl) acids (e.g., Amari et al., 1994) and studied it before and after aqueous processing experiments in the laboratory. The residues of the Murchison experiments were also compared to a HF/HCl residue from the Orgueil (CI1) meteorite, which is known to have been subjected to extensive natural aqueous alteration on its

parent body (Zolensky and McSween, 1988). Relying on the hypothesis that carbonaceous and enstatite chondrites inherited a common organic progenitor (Alexander et al., 1998), the consequences of another important parent body process, reductive thermal metamorphism, were studied using HF/HCl residues of three enstatite chondrites that are believed to represent good examples of this type of alteration. The outcomes of this research improve our ability to read the record of solar system evolution in extraterrestrial carbon- and nitrogen-containing material.

2. EXPERIMENTAL

2.1. Stepped Combustion

The samples were analysed by stepped combustion using two separate static mass spectrometer systems. One system (Finesse), comprised one quadropole and one magnetic sector mass spectrometer joined to the same extraction line and was used to determine the amounts of carbon (in the form of CO_2), helium, and nitrogen and the isotopic composition of nitrogen (Wright et al., 1988; Verchovsky et al., 1997). On another instrument (MS86), amounts of carbon and its isotopic composition were measured (Wright and Pillinger, 1989). Both machines were completely automated and provided a highly reproducible protocol for high-resolution, multistep analysis. One combustion step consisted of 30 min of heating with an oxygen pressure of 10 mbar, followed by a 20-min period in which oxygen was resorbed by CuO.

The abundances of stable isotopes are expressed using the δ notation. These indicate the difference (in ‰) between the relevant ratio in the sample and the same ratio in an international standard as follows:

$$\delta‰ = (R_{sample} - R_{standard}/R_{standard}) \times 1000,$$

where $R = {}^{13}C/{}^{12}C$ for carbon and $R = {}^{15}N/{}^{14}N$ for nitrogen; standards are Pee Dee belemnite for carbon and air for nitrogen. The precision for isotope analyses was ±1‰ for carbon in samples > 4 ng and ±3‰ for nitrogen in samples > 5 ng. Typical sample weight was 1 to 3 mg. Procedural blank was > 1 ng for nitrogen and 5 to 10 ng for carbon.

2.2. Hydrous Pyrolysis

Insoluble organic material in the Murchison meteorite was isolated by digesting the inorganic matrix with cycles of HF and HCl acids (Murchison K procedure until post-HF/HCl step; Amari et al., 1994). Several inorganic nitrides, carbides, and oxides are resistant to HF/HCl treatment, and although they represent only a very small portion of the residue, they may have extreme isotopic compositions (e.g., Zinner, 1998a). Silicon carbide (SiC) was removed with sodium polytungstate density separation, and any free organic compounds were removed by solvent extraction (93:7 DCM/MeOH). Aqueous alteration of the HF/HCl residue was undertaken using the standard hydrous pyrolysis technique for meteorite samples (Sephton et al., 1999). In brief, milligram-sized samples of HF/HCl residue were placed in a 1-mL stainless steel insert with 0.4 mL of high-purity water. The insert was purged with nitrogen gas, sealed, and placed into a 71-mL, stainless steel, high-pressure reactor (series 4740, Parr Instrument Co.), which was
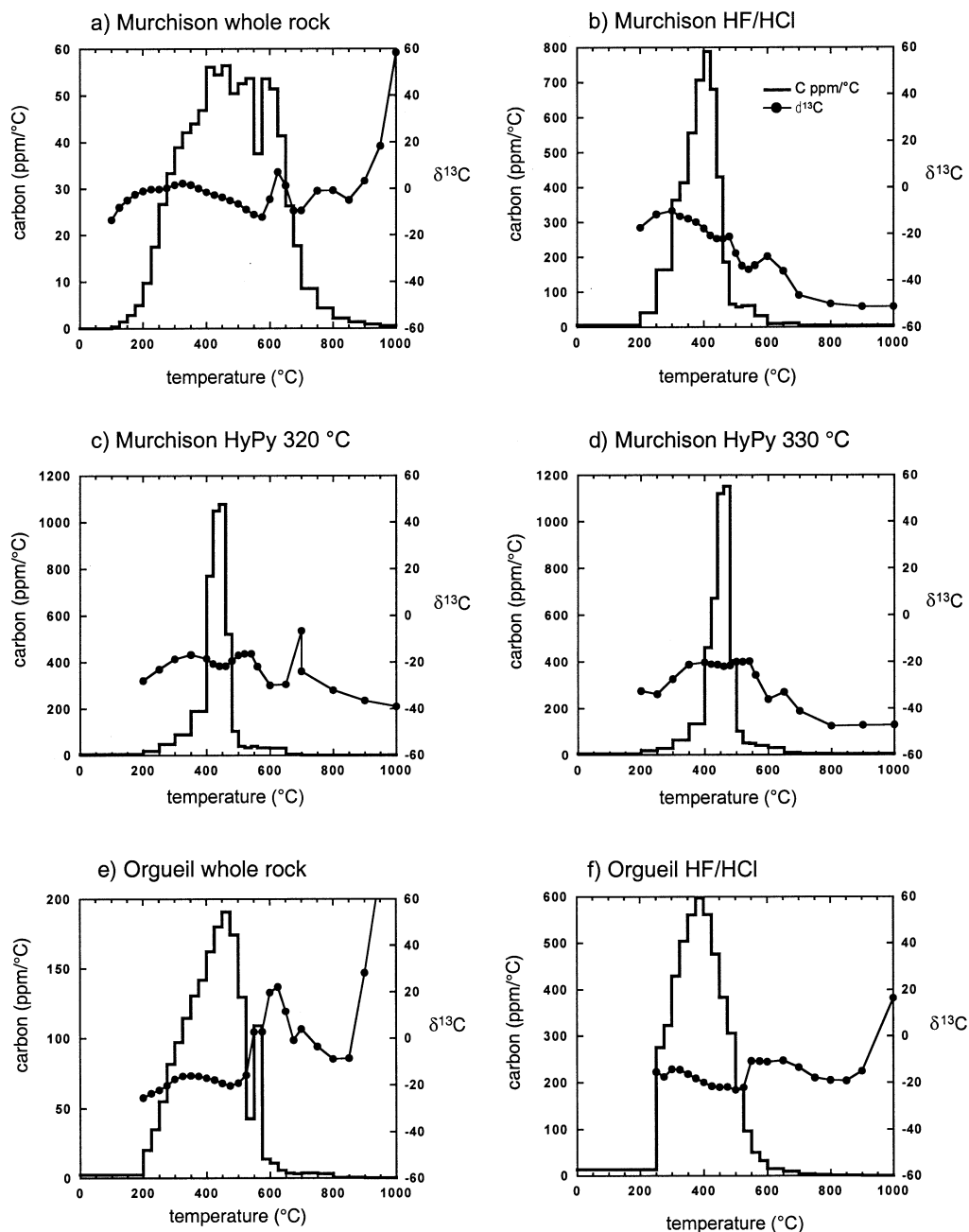
Fig. 1. Carbon yield (—) and δ^{13}C‰ (—●—) profiles for (a) whole-rock Murchison, (b) Murchison HF/HCl residue, (c) 320°C hydrously pyrolysed (HyPy) Murchison HF/HCl residue, (d) 330°C hydrously pyrolysed Murchison HF/HCl residue, (e) whole-rock Orgueil, and (f) Orgueil HF/HCl residue.

filled with 20 mL of water to minimise pressure differentials. The whole arrangement was heated to 320 or 330°C in a muffle furnace for 72 h. When cool, any pyrolysis products were removed by the same extraction procedure as above (93:7 DCM/MeOH), and the residue was analysed by stepped combustion.

3. RESULTS AND DISCUSSION

3.1. Whole-Rock Samples

Stepped combustion data for whole-rock samples of Murchison and Orgueil have been described in detail elsewhere (Grady et al., 2002). A brief description of the combustion profiles follows for whole-rock Murchison (Figs. 1a and 2a) and Orgueil (Figs. 1e and 2e). The stepped combustion plots represent carbon and nitrogen released from a compilation of a number of isotopically distinct components (Table 1) that are present in various amounts in each sample.

The carbon profiles display gently rising δ^{13}C values between 200 and 450°C that correspond to the major carbon release and reflect the combustion of organic matter. The lower temperature steps have slightly more negative δ^{13}C values due
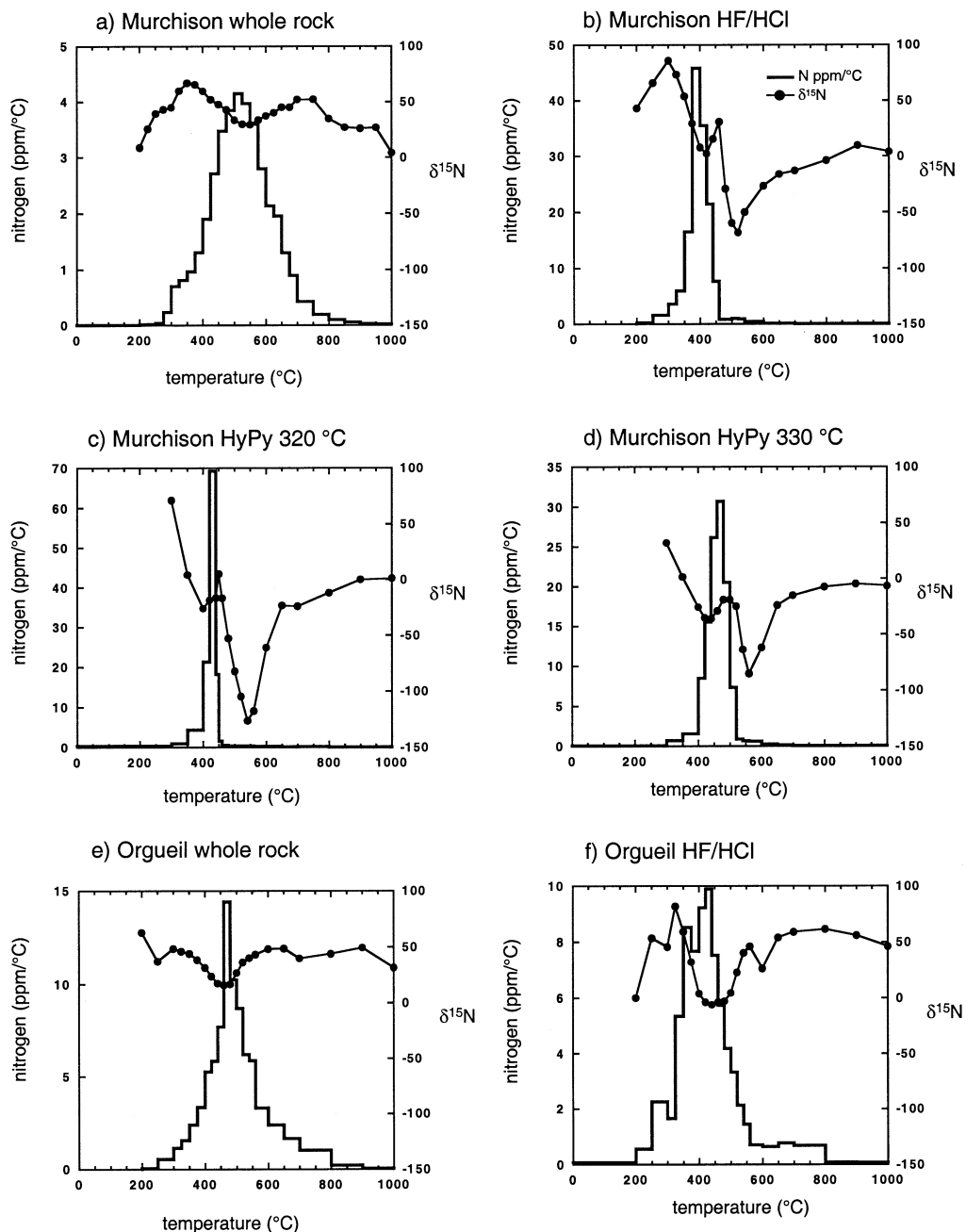
Fig. 2. Nitrogen yield (—) and δ^{15}N‰ (—●—) profiles for (a) whole-rock Murchison, (b) Murchison HF/HCl residue, (c) 320°C hydrously pyrolysed (HyPy) Murchison HF/HCl residue, (d) 330°C hydrously pyrolysed Murchison HF/HCl residue, (e) whole-rock Orgueil, and (f) Orgueil HF/HCl residue.

to an increased contribution from isotopically light terrestrial organic contamination. Between 400 and 625°C, the decrepitation of isotopically heavy carbonate occurs. Within this range, the carbon release displays two maxima, at 525 and 600°C, that reflect contributions from Fe, Mg carbonate, and calcite, respectively (Grady et al., 2002). At ~500 to 550°C, negative deflections are superimposed on the δ^{13}C profiles and reflect isotopically light carbon from diamond. Above 700°C, graphite combustion dominates until 1000°C, at which extremely positive δ^{13}C values for silicon carbide are observed.

The nitrogen profiles form broad M shapes, interpreted as the superimposition of two components (Alexander et al., 1998). One component has a narrow combustion range between 400 and 600°C and is depleted in ^{15}N. Data from pure nanodiamonds (Russell et al., 1996) indicate that they have δ^{15}N values of ~ −350‰ and a typical abundance of 0.04 wt.%. Subtracting this component from the whole-rock 400 to 600°C data indicates that nanodiamonds can account for only up to ~10% of the nitrogen released. Thus, most of the nitrogen released between 400 and 600°C is not associated with nanodiamonds

Table 2. Bulk compositions of the meteorite samples analysed in this study. All values are based on Finesse data, except $\delta^{13}C$, which is from MS86. HyPy indicates hydrous pyrolysis.

Sample		[C] (wt.%)	[N] (wt.%)	N/C	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
Orgueil	Whole rock	4.5	0.207	0.046	−16	32.2
	HF/HCl	9.1	0.18	0.020	−18.5	20.6
Murchison	Whole rock	2.2	0.0968	0.044	−2.7	40.6
	HF/HCl	8.2	0.3327	0.040	−19.2	15.8
	320°C HyPy	9.5	0.25	0.027	−21.6	−12.7
	330°C HyPy	8.4	0.24	0.029	−23.4	−25.4
LEW87223	HF/HCl	17.88	0.93	0.005	−7.0	−7.3
Indarch	HF/HCl	30.80	0.12	0.004	−10.6	−7.5
Yilmia	HF/HCl	17.92	0.11	0.006	−5.6	−26.5

and is probably organic in nature. The remaining nitrogen, which is isotopically heavy, dominates between 200 and 400°C and 600 and 1000°C and is considered to represent a relatively constant background assemblage of organic materials with varying resistance to combustion (Alexander et al., 1998).

3.2. HF/HCl Residues

3.2.1. Carbon in HF/HCl Residues

Figure 1b shows carbon stepped combustion data (Appendix 1) for a HF/HCl residue from the Murchison meteorite. The acid demineralisation process results in a narrower combustion range for the main carbon release and a general shift to more negative $\delta^{13}C$ values when compared to the whole-rock sample (Fig. 1a). These data are consistent with the loss of ^{13}C-enriched carbonate carbon and acid-soluble free organic mol-

ecules to leave a residue composed primarily of organic macromolecular material and other acid-resistant phases. Published work on Murchison reveals average $\delta^{13}C$ values of +43‰ for carbonate and +5‰ for whole solvent extracts (Cronin and Chang, 1993). Studies on Antarctic carbonaceous chondrites have shown that the presence of isotopically heavy carbonate and free organic matter (FOM) has a significant effect on whole-rock $\delta^{13}C$ values (Naraoka et al., 1997).

Aqueous processing of the Murchison HF/HCl residues by hydrous pyrolysis (Figs. 1c and 1d) appears to remove carbon, which combusts between 200 and 350°C and has $\delta^{13}C$ values up to −10‰. The residue remaining after the highest temperature hydrous pyrolysis experiment contains carbon with $\delta^{13}C$ values down to ~−20‰ in the combustion temperature range of 350 to 500°C. The $\delta^{13}C$ value of the bulk HF/HCl residue after the highest temperature hydrous pyrolysis procedure is −23‰ (Table 2). These data are in harmony with published stepped combustion data (Halbout et al., 1986; Kerridge et al., 1987) that reflect two organic components within the macromolecular material that combust within the 200 to 500°C temperature range: an isotopically heavy, low-temperature component and an isotopically lighter, higher temperature component.

Hence, the isotopic effects observed during stepped combustion of whole-rock, HF/HCl, and hydrously pyrolysed HF/HCl samples reflect the presence of three types of organic matter (Fig. 3):

● FOM is present within the whole-rock meteorite and is easily removed with organic solvents. FOM consists of a wide variety of organic compounds, and published analyses of bulk solvent extracts indicate $\delta^{13}C$ values of ~+5‰ (Cronin and Chang, 1993). During stepped combustion of whole-rock meteorites, FOM is released at the lowest temperatures (<250°C).
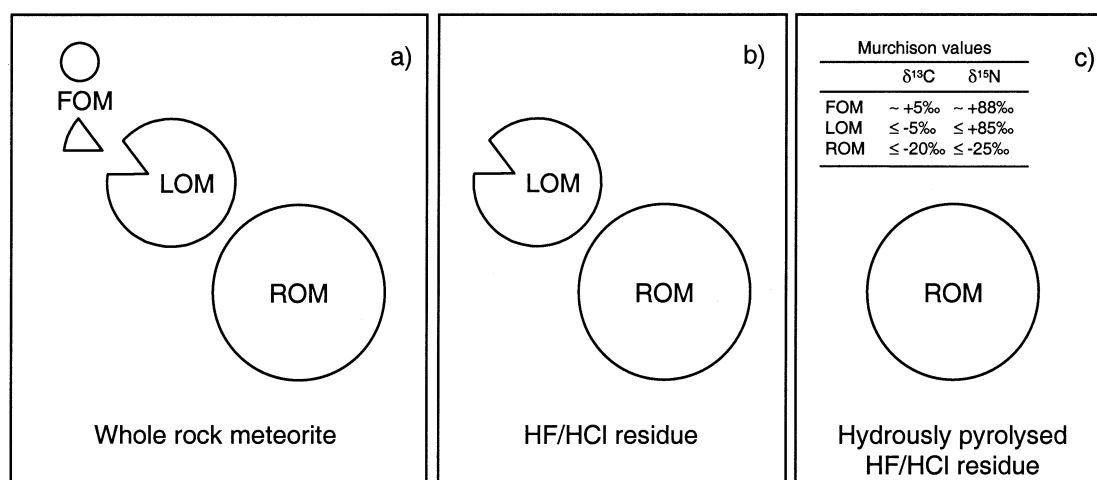

Fig. 3. Schematic representation of the main types of organic matter in a) whole rock carbonaceous chondrites, b) solvent-extracted HF/HCl residues, and c) hydrously pyrolysed HF/HCl residues. FOM is free organic matter, which is extractable with common organic solvents. The circle and segment shapes reflect how some FOM may be genetically related to part of the insoluble organic matter, but some may not. LOM is labile organic matter, which is macromolecular, insoluble in solvents and resistant to HF/HCl treatment but can be liberated by hydrous pyrolysis. ROM is refractory organic matter, which is macromolecular and relatively unaffected by solvents, HF/HCl treatment, and hydrous pyrolysis. The relative abundances of these components are not to scale. Typical $\delta^{13}C$ and $\delta^{15}N$ values for FOM, LOM, and ROM in the Murchison meteorite are listed (compiled from Cronin and Chang, 1993; Sephton et al., 1998; and this paper).

- Labile organic matter (LOM) has a macromolecular structure. This component is not removed by solvent extraction or HF/HCl treatment but is released by hydrous pyrolysis. LOM has been characterised by gas chromatography mass spectrometry and gas chromatography isotope ratio mass spectrometry and consists partly of aromatic units with individual $\delta^{13}C$ values between -25 and $-5‰$ but a bulk fraction $\delta^{13}C$ value of $-5‰$ (Sephton et al., 1998, 2000; Sephton and Gilmour, 2000, 2001). During stepped combustion of HF/HCl residues, LOM is released between 250 and 350°C.

- Refractory organic matter (ROM) is not removed by solvents, HF/HCl treatment, or hydrous pyrolysis and probably consists of a more condensed, aromatic macromolecular structure with a high proportion of covalent bonding. Analyses of hydrously pyrolysed HF/HCl residues suggest average $\delta^{13}C$ values of $\sim -20‰$ (Sephton et al., 1998). During stepped combustion of HF/HCl residues ROM is released between 350 and 500°C.

It has been known for many years that the bulk $\delta^{13}C$ value of the Murchison macromolecular material is $\sim -16‰$ (Cronin and Chang, 1993). From the work presented here, it is apparent that ROM has $\delta^{13}C$ values of $\sim -20‰$. Hence, the $\delta^{13}C$ value of the bulk macromolecular material represents a mixture of LOM ($\delta^{13}C \leq -5‰$) and ROM ($\delta^{13}C = -20‰$). A simple mass balance calculation using the end-member $\delta^{13}C$ values of $-5‰$ for LOM and $-20‰$ for ROM gives us an LOM/ROM ratio of ~ 0.25, but this is a gross oversimplification because LOM displays a range of isotopic compositions (Sephton et al., 1998; Sephton and Gilmour, 2001).

It is the influence of the ^{13}C-depleted ROM component on the $\delta^{13}C$ of bulk macromolecular material (LOM and ROM combined) that led to the paradoxical situation in which many free aromatic hydrocarbons ($\delta^{13}C$ up to $-5‰$) were isotopically heavier than the parent structures from which they were probably released ($\delta^{13}C = -16‰$) (Cronin and Chang, 1993; Gilmour and Pillinger, 1994). Kinetic isotope effects during bond destruction would lead to the opposite isotopic relationship. This paradox was finally resolved when compound-specific $\delta^{13}C$ values were obtained for some FOM aromatics in Murchison and their structurally identical LOM counterparts liberated by hydrous pyrolysis (Sephton et al., 1998). The similarity between the $\delta^{13}C$ values of FOM aromatics and LOM aromatics suggested a genetic relationship. Furthermore, close inspection of the cases in which $\delta^{13}C$ values were available for both FOM aromatics and LOM aromatics revealed a consistent enrichment in ^{12}C in the FOM compounds. This indicated that the FOM aromatic compounds have been released from the LOM aromatic fraction in a preterrestrial generation event. Hence, to some extent, FOM and LOM can be considered as two solubility fractions of a single component.

Compound-specific isotope measurements of FOM and LOM aromatic units reveal large fractionations in $\delta^{13}C$ for sizable compounds that differ by only one or two carbon atoms, which suggests molecule production at the low temperatures (~ 10 K) found in interstellar environments (Sephton and Gilmour, 2000). Deuterium enrichments in FOM and LOM are characteristic of interstellar material and support this interpretation (Kerridge et al., 1987; Krishnamurthy et al., 1992). ROM also contains significant amounts of deuterium (Kerridge et al.,

1987), but compound-specific $\delta^{13}C$ measurements for its structural units have not been obtained. Hence, it is presently unknown whether LOM and ROM share a common origin. It is possible that they represent two end-members of the same structure, with higher molecular weight entities becoming progressively depleted in ^{13}C and ^{15}N. Alternatively, LOM and ROM may be two separate fractions.

3.2.2. Nitrogen in HF/HCl Residues

Figure 2b shows nitrogen data (Appendix 2) for a HF/HCl residue from the Murchison meteorite. The HF/HCl residue clearly shows the presence of isotopically light and heavy components observed in the whole-rock samples, but with greater resolution because the shielding effect of some ^{15}N-enriched solvent and acid-soluble FOM has been removed. Published work on whole solvent extracts of FOM reveals $\delta^{15}N$ values up to $+88‰$ (Cronin and Chang, 1993).

Below 350°C, there is a release of nitrogen, with $\delta^{15}N$ values up to $\sim +85‰$. This nitrogen is removed progressively by hydrous pyrolysis (Figs. 2c and 2d) until $\delta^{15}N$ values approaching 0‰ are reached. Hence, by comparing the nitrogen data with the carbon data discussed above, it becomes apparent that both isotopically heavy, low-temperature carbon and nitrogen corresponding to LOM are removed by aqueous processing.

Above 350°C, the region with low $\delta^{15}N$ values (mostly 400 to 600°C) in the whole-rock sample is resolved into two components. This observation supports our earlier conclusion, based on the Murchison whole rock data, that diamonds alone can account for only up to 10% of the nitrogen released in this range.

The first and most abundant isotopically light component has $\delta^{15}N$ values of $-36‰$ in the HF/HCl residue from the highest temperature hydrous pyrolysis experiment. This component combusts between 400 and 500°C, the temperature range in which most of the planetary noble gases are released (Verchovsky et al., 2002). Hence, we must consider the possibility that the isotopically light nitrogen is derived from the carrier of the planetary noble gases (or so-called Q phase). However, the negative $\delta^{15}N$ values are not observed in more thermally metamorphosed meteorites. such as the enstatite chondrites Yilmia (EL6), which still contains its Q noble gases but releases practically no nitrogen between 400 and 500°C (Verchovsky et al., 2002). Therefore, an alternative source must be sought. Crucially, the isotopically light nitrogen component released at 400 to 500°C (Fig. 4) coincides with the release of significant amounts of carbon, suggesting that it may be a portion of the relatively abundant organic macromolecular material. N/C ratios of ~ 0.02 for the 400 to 500°C combustion range are consistent with this suggestion because they are reasonably similar to the N/C ratio of 0.012 determined for the bulk macromolecular material in Murchison by pyrolytic release studies (Appendix 2; Zinner, 1988). Quantitatively, this portion of the macromolecular material must account for 90% or so of the nitrogen released between 400 and 600°C, which cannot be attributed to diamonds. Comparing the nitrogen and carbon data therefore indicates that both isotopically light, high-temperature carbon ($\delta^{13}C$ approaching $-30‰$) and nitrogen ($\delta^{15}N$ down to $\sim -35‰$) corresponding to ROM remain after aqueous processing.
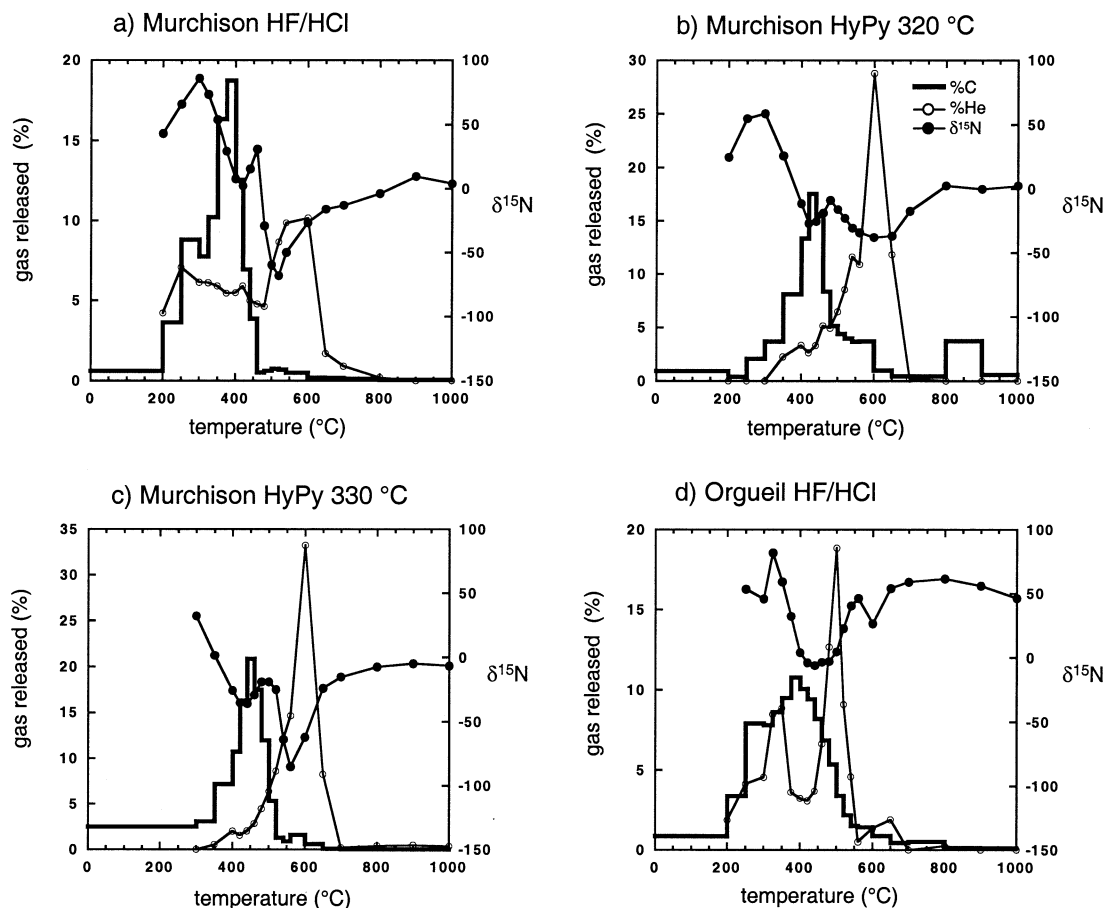
Fig. 4. Carbon yield (——), helium yield (—○—), and $\delta^{15}N‰$ (—●—) profiles for (a) Murchison HF/HCl residue, (b) 320°C hydrously pyrolysed (HyPy) Murchison HF/HCl residue, (c) 330°C hydrously pyrolysed Murchison HF/HCl residue, and (d) Orgueil HF/HCl residue.

The recognition of isotopically heavy, low-temperature and isotopically light, higher temperature organic nitrogen components released between 250 and 500°C is consistent with published stepped combustion data (Robert and Epstein, 1982; Halbout et al., 1986; Kerridge et al., 1987; Alexander et al., 1998). Figures 2b to 2d indicate that hydrous pyrolysis of the HF/HCl residues progressively removes nitrogen, which combusts below 350°C and has $\delta^{15}N$ values > +50‰. The residue remaining after hydrous pyrolysis combusts mostly between 350 and 500°C and has a bulk $\delta^{15}N$ value of ~ −25‰ (Table 2). The nitrogen data appear, generally, to mirror the carbon data in the 200 to 500°C combustion range and imply that these two elements reside in common sources.

The carbon and nitrogen isotope data from the stepped combustion of whole-rock, HF/HCl, and hydrously pyrolysed HF/HCl samples allow us to further constrain the isotopic characteristics of our three types of organic matter. FOM (which combusts below 250°C) is enriched in both ^{13}C and ^{15}N ($\delta^{13}C \sim$ +5‰; $\delta^{15}N \sim$ +88‰). LOM (which combusts between 250 and 350°C) is also enriched in both ^{13}C and ^{15}N ($\delta^{13}C \leq$ −5‰; $\delta^{15}N \leq$ +85‰). The similar carbon and nitrogen isotopic characteristics of FOM and LOM reflect in part a genetic relationship. ROM (which combusts between 350 and 500°C) appears isotopically distinct from the two other

organic fractions and is depleted in both ^{13}C and ^{15}N ($\delta^{13}C \leq$ −20‰; $\delta^{15}N \leq$ −25‰).

At ~425°C in Figures 2b to 2d, relatively positive $\delta^{15}N$ values are encountered. Kerridge et al. (1987) recognised a similar response during stepped combustion for a Murchison HF/HCl residue and attributed these values to a third nitrogen-bearing component. Although this release has no corresponding response in the carbon stepped combustion data (Figs. 1b to 1d), Kerridge et al. (1987) suggested that this ^{15}N-enriched component was organic and buried deeply within the aromatic backbone of the organic matter. An extrapolation of Alexander et al.'s (1998) interpretations would assign the ^{15}N-enriched component to part of the broad background release of organic materials with varying resistance to combustion, on to which ^{15}N-depleted components are superimposed. Currently, it is not possible to discriminate between the hypotheses of a single component (Kerridge et al., 1987) and of multiple background components (Alexander et al., 1998).

At ~550°C, the second isotopically light ^{15}N component is encountered. $\delta^{15}N$ values down to ~ −125‰ correspond to a small amount of nitrogen released from diamonds, which in pure form have a $\delta^{15}N$ value of −350‰ (Russell et al., 1996). Traditionally, the presence of diamonds in acid-insoluble residues of meteorites is unequivocally identified by the selective

chemical destruction of other combustible phases. This "burning down the haystack to find the needle" approach, although key to the discovery of diamonds, renders large amounts of precious acid residue unavailable for study (Zinner, 1998b). Figure 4 displays an alternative means of distinguishing between diamond and other combustible phases using a combination of stepped combustion, nitrogen isotopes, and helium abundances. In primitive meteorites, diamonds have $\delta^{15}N$ values of −350‰ (Table 1) and are the main carrier of helium, where it forms part of the P3 and HL noble gases (Huss and Lewis, 1994). The other helium carrier is the Q phase, but this combusts separately at lower temperatures (Verchovsky et al., 2002). Hence, the characteristic combination of relatively low $\delta^{15}N$ values and an increased release of helium in Figure 4 pinpoints the contribution from diamonds at 550 to 600°C.

3.3. Aqueous Alteration

The responses of the Murchison HF/HCl residue to hydrous pyrolysis provide a valuable insight into how parent body processes affect the overall carbon and nitrogen isotopic composition of carbonaceous chondrites. It has already been suggested that progressive aqueous processing results in the loss of ^{13}C- and ^{15}N-enriched LOM components from the macromolecular material and, hence, a gradual depletion in overall $\delta^{13}C$ and $\delta^{15}N$. This effect is clearly seen in the cumulative plots for processing experiments, in which the removal of FOM and LOM leaves a residue that contains an increasing proportion of ROM and therefore becomes progressively isotopically lighter (Fig. 5). It follows that the isotopic composition of the organic matter in total is controlled by the relative concentration of the ^{13}C- and ^{15}N-enriched FOM and LOM and the ^{13}C- and ^{15}N-depleted ROM (i.e., the (FOM + LOM)/ROM ratio).

The cumulative plots for carbon and nitrogen also provide revealing insight as to how these elements are bound within the macromolecular material. Aqueous alteration appears to remove isotopically heavy nitrogen faster than isotopically heavy carbon, suggesting that much of the nitrogen in LOM is present in a hydrolysable, and probably oxidisable, form.

Figures 1f and 2f contain stepped combustion data for the Orgueil HF/HCl residue. Comparing the combustion products in the 200 to 500°C range for the Murchison and Orgueil HF/HCl residues provides us with an opportunity to test the hypothesis outlined above on naturally processed samples. Published petrographic studies indicate that Orgueil has experienced substantially more aqueous alteration than Murchison (Zolensky and McSween, 1988). Both Orgueil and Murchison HF/HCl residues release isotopically heavy carbon at combustion temperatures below 350°C. As combustion temperatures increase, however, differences in the carbon and nitrogen release characteristics become apparent. $\delta^{13}C$ values of < −20‰, representing an increased influence of ROM, are observed when ~60% of the carbon has been released from the Orgueil HF/HCl residue, whereas ~70% of the carbon has to be removed from the Murchison residue before similar values are encountered (Fig. 5a). Furthermore, a minima in $\delta^{15}N$ values, again representing the influence of ROM, is encountered when ~50% of the nitrogen has been released from the Orgueil HF/HCl residue, whereas ~80% of the nitrogen has to

be liberated from the Murchison HF/HCl residue before similar values are observed (Fig. 5b).

If we assume that both Orgueil and Murchison began with the same kind of macromolecular materials in the early solar system, then these data suggest that significant amounts of the isotopically heavy carbon and nitrogen in LOM have already been removed from Orgueil by preterrestrial aqueous alteration. For Orgueil, this has allowed ROM (low $\delta^{13}C$, low $\delta^{15}N$) to appear at lower temperatures during stepped combustion. Moreover, at least 40% of the overall carbon and nitrogen is released from both meteorite HF/HCl residues in the range of 375 to 480°C (Figs. 1b, 1f, 2b, and 2f), with both elements showing roughly similar isotopic compositions in both meteorites. This is consistent with both meteorites containing structurally and isotopically similar ROM in their macromolecular material inventory.

A process that may be equally as effective as aqueous alteration for removing labile organic enrichments in ^{13}C and ^{15}N is oxidative metamorphism, i.e., the reaction of organic matter with oxidised gases, liquids, or minerals at raised temperatures. CV3 and CO3 carbonaceous chondrites have been heated from 400 to 500°C on their parent bodies (Zolensky and McSween, 1988). In the presence of excess oxygen, these temperatures lead to the complete combustion of organic matter. Only small amounts of oxidising agents would be required to cause the partial loss of organic matter on the CV3 or CO3 parent bodies. Presumably, as in the aqueous processing experiments, the more reactive ^{13}C- and ^{15}N-enriched LOM would be lost first, leaving a residue containing more ^{13}C- and ^{15}N-depleted ROM. Published data on the stable isotopic composition of organic matter in type 3 carbonaceous chondrites do reveal relatively depleted $\delta^{13}C$ and $\delta^{15}N$ values (Swart et al., 1982a, 1982b; Halbout et al., 1986).

Inevitably, if the isotopic composition of a meteorite is related to how extensively it has lost its heavy isotope enriched FOM + LOM, then the portion of the asteroid from which the meteorite originated must have been operating as an open system. The aqueous processing experiments reveal how the isotopic composition of the Orgueil HF/HCl residue could have been produced from a Murchison-like precursor by aqueous alteration on the meteorite parent body. Furthermore, because Murchison itself has been subjected to some parent body aqueously processing, its macromolecular material must have originated from a more isotopically enriched starting material. It is also important to note that the carbon content of whole-rock Orgueil is significantly greater than that of Murchison (3 and 2 wt.%, respectively; Kerridge, 1985). Therefore, a mechanism that concentrated aqueously altered organic materials would be required to produce a macromolecular inventory in Orgueil from precursor materials similar to those found in Murchison. In this context it is interesting to consider the recent discovery that meteoritic organic matter is strongly associated with clay minerals, suggesting that these minerals may have had an important trapping and possibly catalytic role during molecular evolution in the early solar system (Pearson et al., 2002). The significant amounts of swelling clays in CI1 meteorites such as Orgueil (Tomeoka and Buseck, 1988) may have facilitated the trapping and accumulation of aqueously altered organic residues. The transport and separation of organic species during aqueous alteration on the meteorite parent body has been in-

Fig. 5. Isotopic composition (in ‰) of (a) carbon and (b) nitrogen released during the stepped combustion of the Murchison and Orgueil samples. HyPy = hydrously pyrolysed.

voked previously to explain the organic assemblages in carbonaceous chondrites (Wing and Bada, 1991).

The discussion above has a bearing on attempts to identify which type of carbonaceous chondrite contains the most pristine material. Bulk geochemical studies suggest that type 1 meteorites have elemental abundances closest to the sun and represent therefore the most primitive overall chemistry (Anders and Grevesse, 1989). In contrast, petrographic studies suggest that type 3 carbonaceous chondrites contain the least altered minerals (McSween, 1979). Now, the stable isotopic data in this study indicate that for the organic matter at least, it

is type 2 carbonaceous chondrites that contain the most primitive material. The primitive nature of the organic matter in type 2 chondrites has been noted previously (Alexander et al., 1998).

3.4. Thermal Metamorphism

To assess the effects of reductive thermal metamorphism (i.e., the transformation of organic matter at raised temperatures in the absence of oxidising agents) on the LOM ^{13}C and ^{15}N enrichments, we examined HF/HCl residues from three ensta-

a) LEW87223 HF/HCl

b) Indarch HF/HCl
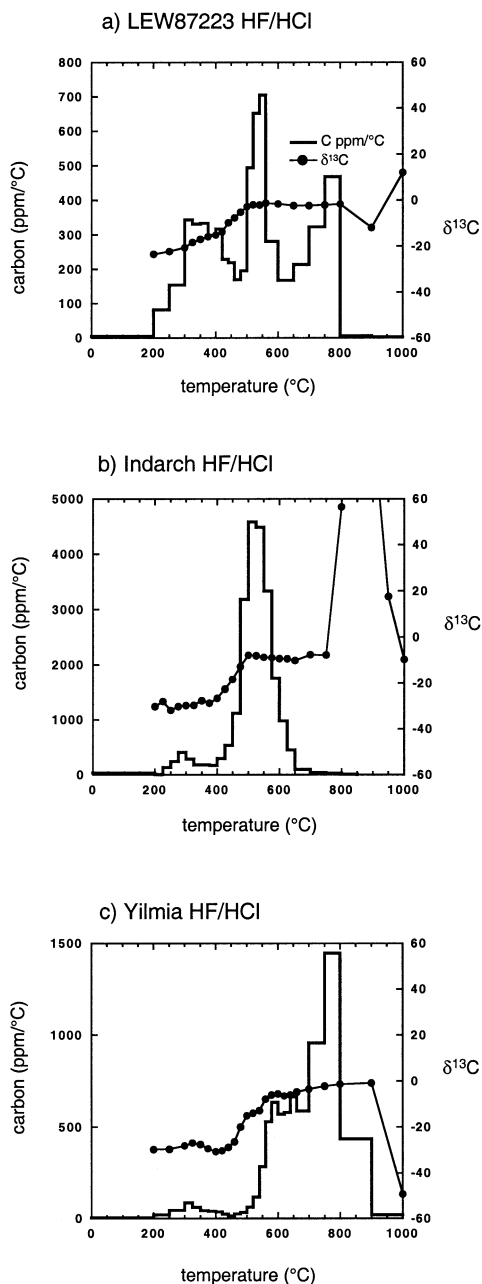
c) Yilmia HF/HCl

Fig. 6. Carbon yield (—) and $\delta^{13}C‰$ (—●—) profiles for enstatite chondrites. (a) LEW 87223 HF/HCl residue, (b) Indarch HF/HCl residue, (c) Yilmia HF/HCl residue.

a) LEW87223 HF/HCl

b) Indarch HF/HCl

c) Yilmia HF/HCl

Fig. 7. Nitrogen yield (—) and $\delta^{15}N‰$ (—●—) profiles for enstatite chondrites. (a) LEW 87223 HF/HCl residue, (b) Indarch HF/HCl residue, (c) Yilmia HF/HCl residue.

tite meteorites that have experienced high temperatures in the natural reducing environment on their parent body (Mason, 1966). The stepped combustion data (Appendices 1 and 3) for these samples were interpreted with the assumption that the carbonaceous and enstatite chondrites inherited a common organic progenitor, which was then processed in different ways on the respective parent bodies (Alexander et al., 1998). Figures 6 and 7 show stepped combustion data for three enstatite chondrites, which form a sequence of increasing parent body metamorphism in the following order: LEW 87223 (E3) < Indarch (EH4) < Yilmia (EL6).

The carbon release profile of LEW 87223 (Fig. 6a) is trimodal. The first release peak at 300°C has a $\delta^{13}C$ value below −20‰ and is probably isotopically light terrestrial contamination. The second and third peaks in carbon release occur at 500 and 750°C, respectively, and both have $\delta^{13}C$ values of ~−2‰. Because the crystalinity of graphite has an effect on combustion temperature, the second and third releases probably reflect two types of graphite, one of which is poorly ordered (500°C) and another of which is more crystalline (750°C). The plots for Indarch (Fig. 6b) and Yilmia (Fig. 6c) also display the release of isotopically light, low-temperature carbon, which peaks at
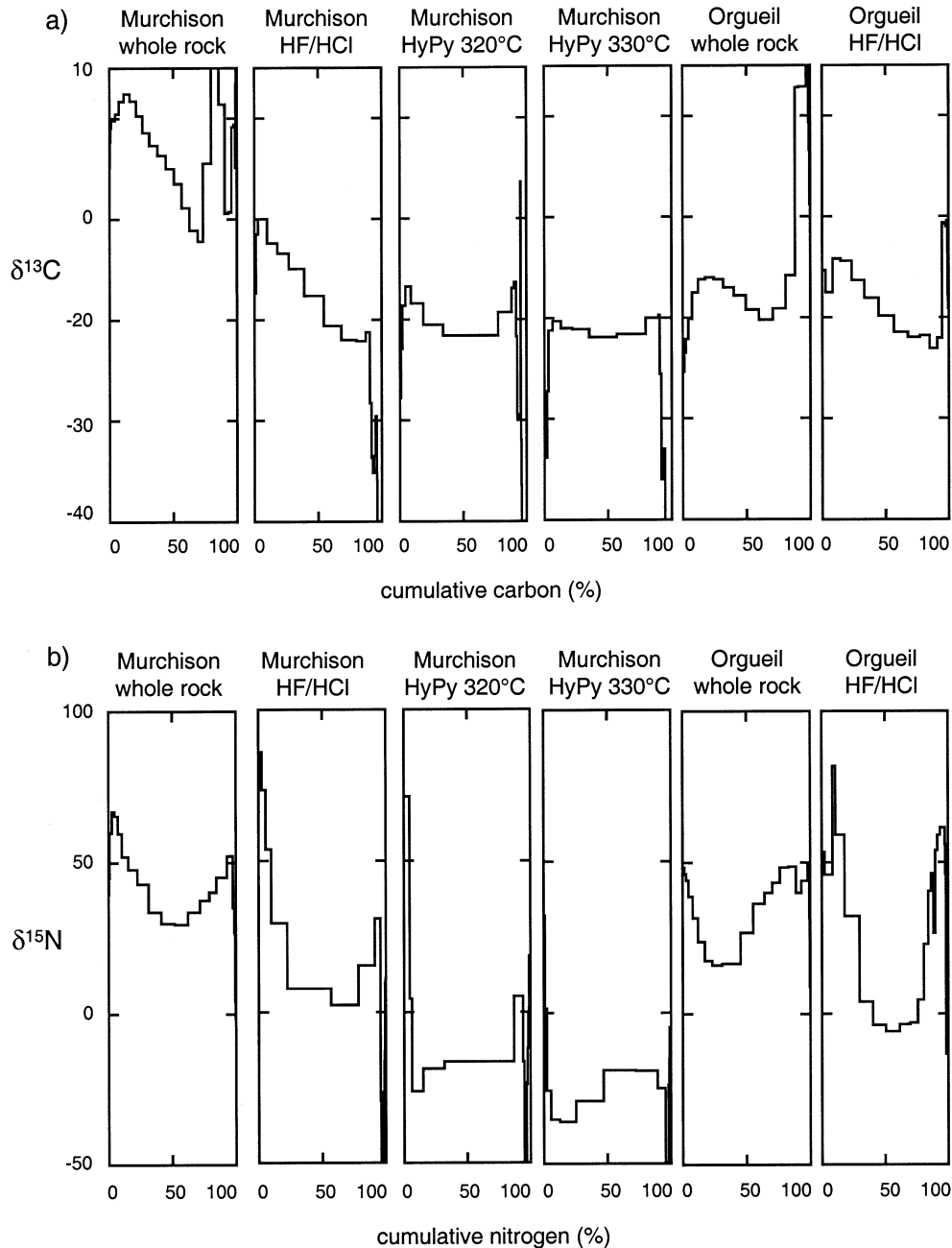
a)

b)
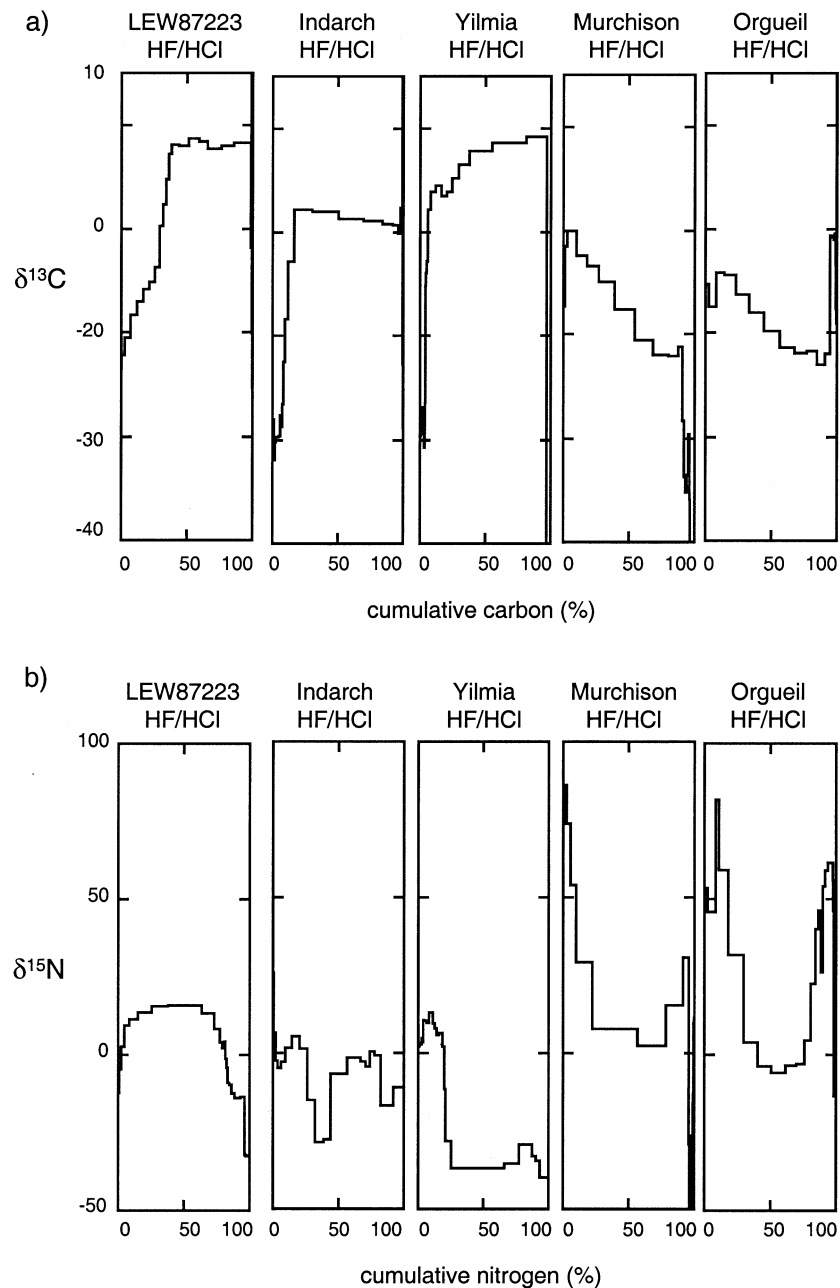
Fig. 8. Isotopic composition (in ‰) of (a) carbon and (b) nitrogen released during the stepped combustion of the Murchison, Orgueil, and three enstatite chondrite HF/HCl residues.

300°C and represents terrestrial contamination. Yet the main release of carbon for Indarch and Yilmia occurs at higher temperatures and is characterised by values of −8‰ and −4‰, respectively. Yilmia exhibits the highest temperature peak carbon release, probably reflecting its extreme level of parent body metamorphism.

The nitrogen release profiles for the enstatite chondrites (Fig. 7) vary significantly. In contrast to the carbon experiments, there appears to be little contribution from nitrogen-bearing terrestrial contamination at ~300°C. The main nitrogen release peaks close to 400°C for LEW 87223 (Fig. 7a), at 500°C for Indarch (Fig. 7b), and above 800°C for Yilmia (Fig. 7c). These

differences in the temperature of the main release of nitrogen are probably a reflection of the level parent body temperatures experienced by the samples. Low-temperature components may have been destroyed or transformed to more stable materials as metamorphism proceeded.

Figure 8 displays the stepped combustion data for the LEW 87223, Indarch, and Yilmia HF/HCl residues on cumulative plots. For carbon, the $\delta^{13}C$ values of all three enstatite chondrites tend to lie close to those for the Murchison HF/HCl residue. There is little compelling evidence of a progressive loss of ^{13}C with increasing parent body temperature, and $\delta^{13}C$ values occupy a relatively small range. If we assume that the

insoluble carbon in both the carbonaceous and enstatite chondrites originated from a common progenitor, then only relatively small amounts of ^{13}C-enriched LOM have been lost during reductive metamorphism on the enstatite chondrite parent bodies. Much of the LOM (and presumably some incorporated FOM) carbon has been preserved during graphitisation.

The cumulative plot for nitrogen indicates that $\delta^{15}N$ values appear much more susceptible to reductive metamorphism than their $\delta^{13}C$ counterparts. There is some evidence of a progressive loss of ^{15}N with increasing parent body temperature, and $\delta^{15}N$ values occupy a much greater range than $\delta^{13}C$ values. Furthermore, the $\delta^{15}N$ values for the highly metamorphosed Indarch and Yilmia samples are significantly lighter than the Murchison HF/HCl residue, and if the carbonaceous chondrite organic matter is analogous to the progenitor of the enstatite insoluble carbon, then significant amounts of ^{15}N-enriched LOM (and initially incorporated FOM) have been lost during extreme parent body metamorphism. The expulsion of nitrogen during the graphitisation of organic matter is a predictable consequence of parent body metamorphism. Carbonaceous material with extremely low N/C ratios has been previously observed in 800 to 1000°C stepped combustion analyses of whole-rock enstatite chondrites (Grady et al., 1986).

4. CONCLUSIONS

1. Stepped combustion data indicate three operationally defined types of organic matter in carbonaceous chondrites. FOM is soluble in organic solvents, combusts below 250°C, and is enriched in ^{13}C and ^{15}N. LOM has a macromolecular structure, is insoluble in solvents and HF/HCl acids, but is released by hydrous pyrolysis. LOM combusts between 250 and 350°C and is enriched in ^{13}C and ^{15}N. ROM is unaffected by solvents, HF/HCl treatment, and hydrous pyrolysis. ROM combusts between 350 and 500°C and is depleted in ^{13}C and ^{15}N.

2. The isotopic similarities between FOM and LOM reflect, at least in part, a genetic link and can be thought of as two solubility fractions of a single component. Hence, the isotopic composition of total organic matter is determined by the (FOM + LOM)/ROM ratio. The macromolecular entities (LOM and ROM) are by far the most abundant organic components present and as such have a major influence of the overall isotopic composition of the whole-rock meteorite.

3. Laboratory alteration experiments indicate that aqueous processing effectively removes the labile ^{13}C- and ^{15}N-enriched LOM from the macromolecular inventory, allowing the more refractory ^{13}C- and ^{15}N-depleted ROM to exert a stronger influence on the overall isotopic composition.

4. Examination of the ^{13}C and ^{15}N enrichments of meteorite macromolecular materials indicate that type 2 carbonaceous chondrites, although partly altered, contain the most pristine organic matter.

5. If the carbonaceous and enstatite chondrites inherited a common organic progenitor, then it appears that reductive thermal metamorphism incorporates and partially preserves FOM + LOM ^{13}C enrichments; the associated ^{15}N enrichments are lost at high levels of metamorphism.

6. The combination of $\delta^{15}N$ profiles and helium release patterns can help distinguish diamond from other combustible phases in meteoritic HF/HCl residues without the need for methods involving selective chemical destruction.

REFERENCES

Alexander C. M. O., 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.

Amari S., Lewis R. S., and Anders E. (1994) Interstellar grains in meteorites—I. Isolation of SiC, graphite, and diamond—size distributions of SiC and graphite. *Geochim. Cosmochim. Acta* **58,** 459–470.

Anders E. (1988) Circumstellar material in meteorites; noble gases, carbon and nitrogen. In *Meteorites and the Early Solar System* (eds. J. F. Kerridge and M. S. Matthews), pp. 927–955. University of Arizona Press, Tucson.

Anders E. and Grevesse N. (1989) Abundances of the elements—Meteoritic and solar. *Geochim. Cosmochim. Acta* **53,** 197–214.

Anders E. and Zinner E. (1993) Interstellar grains in primitive meteorites—Diamond, silicon-carbide, and graphite. *Meteoritics* **28,** 490–514.

Boato G. (1954) The isotopic composition of hydrogen and carbon in the carbonaceous chondrites. *Geochim. Cosmochim. Acta* **6,** 209–220.

Cronin J. R. and Chang S. (1993) Organic matter in meteorites: Molecular and isotopic analyses of the Murchison meteorite. In *Chemistry of Life's Origins* (eds. J. M. Greenburg and V. Pironello), pp. 209–258. Kluwer, Dordrecht, the Netherlands.

Gilmour I. and Pillinger C. T. (1994) Isotopic compositions of individual polycyclic aromatic hydrocarbons from the Murchison meteorite. *Mon. Not. R. Astron. Soc.* **269,** 235–240.

Grady M. M., Wright I. P., Carr L. P., and Pillinger C. T. (1986) Compositional differences in enstatite chondrites based on carbon and nitrogen stable isotope measurements. *Geochim. Cosmochim. Acta* **50,** 2799–2813.

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

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.

Halbout J., Mayeda T. K., and Clayton R. N. (1986) Carbon isotopes and light element abundances in carbonaceous chondrites. *Earth Planet. Sci. Lett.* **80,** 1–18.

Huss G. R. and Lewis R. S. (1994) Noble-gases in presolar diamonds—I. Three distinct components and their implications for diamond origins. *Meteoritics* **29,** 791–810.

Kemper F., Jäger C., Waters L. B. F. M., Henning T., Molster F. J., Barlow M. J., Lim T., and de Koter A. (2002) Detection of carbonates in dust shells around evolved stars. *Nature* **415,** 295–297.

Kerridge J. F. (1985) Carbon, hydrogen and nitrogen in carbonaceous chondrites—Abundances and isotopic compositions in bulk samples. *Geochim. Cosmochim. Acta* **49,** 1707–1714.

Kerridge J. F., Chang S., and Shipp R. (1987) Isotopic characterisation of kerogen-like material in the Murchison carbonaceous chondrite. *Geochim. Cosmochim. Acta* **51,** 2527–2540.

Krishnamurthy R. V., Epstein S., Cronin J. R., Pizzarello S., and Yuen G. U. (1992) Isotopic and molecular analyses of hydrocarbons and monocarboxylic acids of the Murchison meteorite. *Geochim. Cosmochim. Acta* **56,** 4045–4058.

Mason B. (1966) The enstatite chondrites. *Geochim. Cosmochim. Acta* **30,** 23–39.

McSween H. Y. Jr. (1979) Are carbonaceous chondrites primitive or processed? A review. *Rev. Geophys. Space Phys.* **17,** 1059–1078.

Naraoka H., Shimoyama A., Matsubaya O., and Harada K. (1997) Carbon isotopic compositions of Antarctic carbonaceous chondrites with relevance to the alteration and existence of organic matter. *Geochem. J.* **31,** 155–168.

Pearson V. K., Sephton M. A., Kearsley A. T., Bland P. A., Franchi I. A., and Gilmour I. (2002) Clay mineral-organic matter relationships in the early solar system. *Meteorit. Planet. Sci.* **37,** 1829–1833.

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.

Russell S. S., Arden J. W., and Pillinger C. T. (1996) A carbon and nitrogen isotope study of diamond from primitive chondrites. *Meteorit. Planet. Sci.* **31,** 343–355.

Sephton M. A. and Gilmour I. (2000) Aromatic moieties in meteorites: Relics of interstellar grain processes? *Astrophys. J.* **540,** 588–591.

Sephton M. A. and Gilmour I. (2001) Pyrolysis-gas chromatography-isotope ratio mass spectrometry of macromolecular material in meteorites. *Planet. Space Sci.* **49,** 465–471.

Sephton M. A., Pillinger C. T., and Gilmour I. (1998) $\delta^{13}C$ of free and macromolecular aromatic structures in the Murchison meteorite. *Geochim. Cosmochim. Acta* **62,** 1821–1828.

Sephton M. A., Pillinger C. T., and Gilmour I. (1999) Small-scale hydrous pyrolysis of macromolecular material in meteorites. *Planet. Space Sci.* **47,** 181–187.

Sephton M. A., Pillinger C. T., and Gilmour I. (2000) Aromatic moieties in meteoritic macromolecular materials: Analyses by hydrous pyrolysis and $\delta^{13}C$ of individual compounds. *Geochim. Cosmochim. Acta* **64,** 321–328.

Smith J. W. and Kaplan I. R. (1970) Endogenous carbon in carbonaceous meteorites. *Science* **167,** 1367–1370.

Swart P. K., Grady M. M., and Pillinger C. T. (1982a) Isotopically-distinguishable carbon phases in the Allende meteorite. *Nature* **297,** 381–383.

Swart P. K., Grady M. M., Wright I. P., and Pillinger C. T. (1982b) Carbon components and their isotopic compositions in the Allende meteorite. *J. Geophys. Res.* **87,** A283–A288.

Tomeoka K. and Buseck P. R. (1988) Matrix mineralogy of the Orgueil CI carbonaceous chondrite. *Geochim. Cosmochim. Acta* **52,** 1627–1640.

Verchovsky A. B., Fisenko A. V., Semjonova L. F., and Pillinger C. T. (1997) Heterogeneous distribution of xenon-HL within presolar diamonds. *Meteorit. Planet. Sci.* **32,** A131–A132.

Verchovsky A. B., Sephton M. A., Wright I. P., and Pillinger C. T. (2002) Separation of planetary noble gases carrier from bulk carbon in enstatite chondrites. *Earth Planet. Sci. Lett.* **199,** 243–255.

Wing M. R. and Bada J. L. (1991) Geochromatography on the parent body of the carbonaceous chondrite Ivuna. *Geochim. Cosmochim. Acta* **55,** 2937–2942.

Wright I. P. and Pillinger C. T. (1989) Carbon isotopic analysis of small samples by use of stepped-heating extraction and static mass spectrometry. In *New Frontiers in Stable Isotopic Research; Laser Probes, Ion Probes, and Small-Sample Analysis* (eds. W. C. ShanksIII and R. E. Criss), pp. 9–34. U. S. Geological Survey, Reston, VA.

Wright I. P., Boyd S. R., Franchi I. A., and Pillinger C. T. (1988) High-precision determination of nitrogen stable isotope ratios at the sub-nanomole level. *J. Phys E Sci. Instrum.* **21,** 865–875.

Zinner E. (1988) Interstellar cloud material in meteorites. In *Meteorites in the Early Solar System* (eds. J. F. Kerridge and M. S. Mathews), pp. 956–983. University of Arizona Press, Tucson.

Zinner E. (1998a) Stellar nucleosynthesis and the isotopic composition of presolar grains from primitive meteorites. *Ann. Rev. Earth Planet. Sci.* **26,** 147–188.

Zinner E. (1998b) Trends in the study of presolar dust grains from primitive meteorites. *Meteorit. Planet. Sci.* **33,** 549–564.

Zolensky M. and McSween H. Y. Jr. (1988) Aqueous alteration. In *Meteorites and the Early Solar System* (eds. J. F. Kerridge and M. S. Mathews), pp. 114–143. University of Arizona Press, Tucson.

Appendix 1. Carbon Yields and Isotopic Compositions for HF/HCl Residues Analysed by Stepped Combustion.

T (°C)	Murchison HF/HCl C (ppm)	δ¹³C (‰)	Murchison HyPy 320°C C (ppm)	δ¹³C (‰)	Murchison HyPy 330°C C (ppm)	δ¹³C (‰)	Orgueil HF/HCl C (ppm)	δ¹³C (‰)	LEW87223 HF/HCl C (ppm)	δ¹³C (‰)	Indarch HF/HCl C (ppm)	δ¹³C (‰)	Yilmia HF/HCl C (ppm)	δ¹³C (‰)
200	1284	−17.3	1010	−27.8	1084	−32.5			926	−23.4	6912	−30.2	725	−29.7
225											115	−28.0		
250	2057	−11.5	912	−22.9	888	−33.9	3331	−15.3	4100	−22.2	3360	−31.9	1024	−29.6
275							6878	−17.5			6028	−30.2		
300	8191	−10.0	2374	−18.6	1406	−27.3	8076	−14.2	7730	−20.5	10,177	−29.7	2279	−28.1
325	9092	−12.4					10,735	−14.4	8587	−18.3	7217	−29.6	2158	−26.9
350	10,337	−13.4	4437	−16.7	3164	−21.2	12,599	−16.3	8306	−17.0	4407	−27.6	1537	−27.5
375	13,893	−14.9					14,017	−18.1	8355	−15.8	4425	−28.7	1089	−29.4
400	17,656	−17.6	9503	−18.4	6671	−20.3	14,929	−19.8	7488	−15.1	4293	−26.6	991	−30.7
420	15,763	−20.6	15,393	−20.5	9223	−21.0			6346	−13.7			715	−30.3
425							14,040	−21.4			7315	−22.5		
440	13,602	−22.0	20,984	−21.6	13,440	−21.1			4569	−9.7			469	−28.8
450							11,906	−22.0			13,331	−18.4		
460	8603	−22.1	21,535	−21.6	22,395	−21.9			4383	−7.6			313	−26.4
475							9589	−21.8			27,977	−12.8		
480	3710	−21.2	10,429	−19.3	23,029	−21.6			3391	−5.2			493	−19.9
500	1304	−28.3	2071	−16.9	8097	−20.0	7651	−23.1	3906	−2.8	79,615	−7.8	664	−15.1
520	1146	−33.7	787	−16.3	2027	−20.0			9882	−1.9			1244	−13.9
525							4661	−22.0			114,510	−8.0		
540	1208	−35.2	663	−16.3	1019	−19.7			13,036	−2.0			2371	−12.8
550							2413	−10.6			112,190	−8.7		
560	1222	−33.5	766	−21.7	974	−25.6			14,086	−1.3			5684	−7.8
575							1256	−10.8			83,343	−8.9		
580													10,582	−6.1
600	1272	−29.6	1280	−29.8	1582	−36.0	813	−11.0	11,251	−1.6	43,900	−9.2	12,684	−5.5
620													11,399	−6.5
625											24,472	−9.3		
640													11,585	−6.1
650	510	−35.9	1518	−29.5	1506	−33.0	751	−10.4	8395	−2.3	11,298	−10.1		
660													13,296	−4.8
700	540	−46.4	248	−6.4	516	−41.2	488	−13.4	10,664	−2.3	4862	−7.6	23,500	−3.5
750							205	−17.7	16,152	−2.0	2067	−7.7	47,811	−2.2
800	449	−50.0	172	−32.0	501	−47.6	125	−18.9	23,406	−1.7	1360	56.5	72,320	−1.4
850							79	−19.1			470	164.1		
900	431	−51.2	98	−36.4	375	−47.3	84	−15.0	636	−11.8	58	92.9	43,614	−0.8
950											93	17.7		
1000	425	−51.2	98	−39.0	380	−47.1	86	16.4	312	12.1	28	−9.8	2023	−49.3
1050											66	−21.0		
1100	486	−51.7	441	−46.1	476	−49.1	116	49.3	298	1.0	445	−18.0	2300	−51.2
1200	408	−51.1	441	−43.5	1802	−50.0	96	16.7	599	−20.1	818	−22.7	2324	−50.6
1300	533	−51.3	2874	−43.4	1286	−48.3	141	4.1	528	−25.4	1058	−27.5	2106	−50.7
1400	662	−50.4									1044	−28.8		
Total	114,780	−19.2	98,134	−21.6	101,840	−23.4	125,060	−18.5	177,330	−7.0	577,250	−10.6	277,300	−5.6

Appendix 2. Nitrogen, Carbon, and Helium Yields and Nitrogen Isotopic Compositions for HF/HCL Residues Analysed by Stepped Combustion.

T (°C)	Murchison HF/HCl N (ppm)	$\delta^{15}N$ (‰)	C (ppm)	N/C	$^4He \times 10^{-5}$ (c/g)	Murchison HyPy 320°C N (ppm)	$\delta^{15}N$ (‰)	C (ppm)	N/C	$^4He \times 10^{-5}$ (c/g)	Murchison HyPy 330°C N (ppm)	$\delta^{15}N$ (‰)	C (ppm)	N/C	$^4He \times 10^{-5}$ (c/g)	Orgueil HF/HCl N (ppm)	$\delta^{15}N$ (‰)	C (ppm)	N/C	$^4He \times 10^{-5}$ (c/g)
200	1.2	43.0	507	0.002	1.13											15.4	0.0	779	0.020	0.50
250	12.8	65.9	3001	0.004	1.90											27.8	53.5	3074	0.009	1.10
300	81.5	86.0	7276	0.011	1.65	112.9	71.3	3290	0.034		21.5	32.2	2086	0.010		112.5	45.9	7219	0.016	1.21
325	90.7	73.5	6405	0.014	1.64											41.1	81.9	7114	0.006	2.26
350	149.3	53.9	8438	0.018	1.58	47.6	4.5	6502	0.007	0.20	34.7	1.5	2588	0.013	0.08	133.8	59.2	7848	0.017	2.35
375	411.8	29.3	13,489	0.031	1.46											213.0	32.2	8657	0.025	0.96
400	1146.0	7.9	15,481	0.074	1.47	216.0	−26.1	17,219	0.013	0.56	77.0	−25.7	6025	0.013	0.30	191.8	4.0	9818	0.020	0.86
420	709.5	2.4	10,378	0.068	1.58	425.2	−18.7	20,691	0.021	0.36	170.1	−35.4	8995	0.019	0.23	184.4	−3.6	9169	0.020	0.82
440	428.7	15.5	5728	0.075	1.34	1385.5	−16.3	25,930	0.053	0.37	310.7	−36.1	13,685	0.023	0.30	197.8	−5.8	8575	0.023	0.98
450						182.1	5.3	7058	0.026	0.36										
460	153.7	30.8	3196	0.048	1.28	15.9	−16.4	1098	0.014	0.07	523.2	−29.2	17,493	0.030	0.42	150.5	−3.4	7474	0.020	1.77
480	16.5	−29.2	421	0.039	1.24	11.0	−53.0	741	0.015	0.47	613.7	−18.9	14,665	0.042	0.67	114.8	−2.9	6256	0.018	3.37
500	16.3	−59.6	522	0.031	1.90	7.3	−82.1	528	0.014	0.74	410.3	−19.0	10,030	0.041	0.95	83.6	4.7	4890	0.017	5.01
520	19.6	−68.2	624	0.031	2.32	6.9	−104.7	577	0.012	1.07	146.9	−24.9	4489	0.033	1.29	66.6	22.9	3097	0.021	2.42
540	18.6	−49.9	579	0.032	2.64	7.3	−126.2	730	0.010	1.88	17.5	−63.9	1063	0.016	1.82	42.6	40.4	1990	0.021	1.22
560						7.5	−117.4	752	0.010	3.22	13.5	−85.2	732	0.018	2.20	28.8	46.3	1367	0.021	0.14
600	27.1	−26.4	413	0.066	2.72	9.2	−61.1	786	0.012	5.01	24.4	−61.9	1342	0.018	4.99	28.3	26.6	1296	0.022	0.36
650	7.4	−16.1	164	0.045	0.46	10.9	−23.4	270	0.040	1.38	14.2	−23.8	484	0.029	1.24	31.9	54.0	808	0.040	0.50
700	5.9	−13.0	146	0.040	0.24	6.7	−23.9	139	0.049	0.28	7.2	−15.2	81	0.088	0.03	38.7	59.0	409	0.095	
800	4.5	−3.6	117	0.038	0.06	20.7	−11.8	307	0.068	0.95	5.7	−7.4	44	0.132	0.06	68.2	61.6	465	0.147	0.07
900	3.3	9.6	55	0.060		5.5	0.0	111	0.049	0.01	5.5	−4.7	24	0.224	0.07	8.5	55.9	120	0.070	
1000	3.2	4.1	63	0.051		6.3	1.4	399	0.016	0.04	5.9	−6.4	29	0.204	0.05	7.4	46.2	100	0.074	
1100	3.4	10.4	14	0.246		6.9	18.6	6842	0.001	0.10	6.5	−5.8	23	0.281	0.11	5.9	−13.3	85	0.070	
1200	3.8	8.9	3031	0.001		6.0	7.5	365	0.016	0.18	6.3	−12.3	16	0.407	0.18	5.6	−0.2	83	0.067	
1300	5.4	11.5	1251	0.004	0.08	7.7	5.9	201	0.038							7.0	−11.2	121	0.058	0.18
1400	6.2	11.4	1283	0.005	0.11	8.6	5.7	17	0.499							14	2.6	210	0.066	0.53
Total	3327	15.8	82,584	0.040	26.78	2514	−12.7	94,553	0.027	17.10	2415	−25.4	83,894	0.029	15.01	1820	20.6	91,022	0.020	26.60

Appendix 3. Nitrogen and Carbon Yields and Nitrogen Isotopic Compositions for HF/HCl Residues Analysed by Stepped Combustion

T (°C)	LEW87223 N (ppm)	δ¹⁵N (‰)	C (ppm)	N/C	Indarch N (ppm)	δ¹⁵N (‰)	C (ppm)	N/C	Yilmia N (ppm)	δ¹⁵N (‰)	C (ppm)	N/C
200	1.9	−19.7	637	0.003	3.2	15.7	614	0.005	0.8	13.1	126	0.007
250	6.1	−12.2	4602	0.001	4.6	25.8	2529	0.002	0.9	−7.1	460	0.002
300	15.6	−4.7	9123	0.002	16.4	6.6	4921	0.003	2.6	9.0	931	0.003
325	19.8	2.7	6963	0.003	20.9	−2.4	4325	0.005	3.4	3.1	715	0.005
350	35.4	9.4	7639	0.005	30.2	−4.8	3363	0.009	6.0	2.1	567	0.011
375	59.1	11.5	7779	0.008	42.4	−2.7	2682	0.016	17.0	2.9	523	0.032
400	99.9	13.7	7565	0.013	59.9	1.7	3210	0.019	5.3	4.9	214	0.025
420	116.1	15.8	6587	0.018	73.6	5.4	3734	0.020	6.2	3.6	179	0.034
440	123.5	16.0	6627	0.019	71.1	1.4	4370	0.016	10.6	10.7	271	0.039
460	112.3	16.0	7136	0.016	74.8	−15.1	8011	0.009	17.1	10.5	353	0.048
480	87.2	13.5	7855	0.011	76.7	−28.7	13,799	0.006	20.4	9.7	465	0.044
500	39.9	8.4	7122	0.006	68.5	−27.8	18,876	0.004	31.7	13.1	1339	0.024
520	18.0	4.0	6791	0.003	153.2	−6.6	22,386	0.007	14.4	9.6	1323	0.011
540	11.2	2.2	7661	0.001	128.5	−1.4	23,994	0.005	15.3	8.0	2145	0.007
560	9.2	4.3	7186	0.001	47.7	−2.6	24,135	0.002	20.4	5.9	3508	0.006
600	8.3	−1.2	6380	0.001	38.1	−4.3	29,231	0.001	27.9	6.5	4458	0.006
650	8.2	−4.0	7703	0.001	45.6	0.5	34,660	0.001	15.3	2.1	7386	0.002
700	10.9	−9.0	13,415	0.001	56.0	−0.7	36,218	0.002	10.6	−11.5	14,152	0.001
800	17.4	−9.6	41,430	0.000	119.9	−16.9	34,610	0.003	47.8	−28.3	28,639	0.002
900	21.5	−12.3	7556	0.003	102.5	−11.0	32,322	0.003	442.8	−36.9	32,989	0.013
1000	41.1	−13.9	171	0.240					122	−35.5	37,662	0.003
1100	27.8	−13.5	223	0.125					107	−29.4	30,302	0.004
1200	8.7	−32.0	214	0.040					32	−33.1	10,174	0.003
1300	27.8	−32.5	430	0.065					31	−34.6	122	0.253
1400									73	−40.0	165	0.443
Total	927	7.3	178,790	0.005	1234	−7.5	307,990	0.004	1081	−26.5	179,170	0.006