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Carbon and nitrogen isotope ratios in meteoritic organic matter: indicators of alteration processes on the parent asteroid

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Abstract: Macromolecular organic materials in chondrites display significant variations in carbon and nitrogen stable isotopes. In recent years, these variations have been interpreted as a record of aqueous and thermal processing on asteroids shortly after the birth of the Solar System. In this paper we review and summarize the key data and main interpretative approaches related to this study area. Armed with these methods we attempt to reinterpret the whole rock chondrite data set in the literature.

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Introduction

Our Solar System was built from materials originally residing in an interstellar cloud. Following contraction in the cloud and the formation of the young Sun a rotating disk of dust and gas, termed a solar nebula, contained the matter from which the planets were to form. Collisions between dust particles created increasingly larger objects ultimately leading to the planets. Geological processes on the planets recycled the materials inherited from the interstellar cloud removing most indicators of their provenance. Asteroids, small bodies of rock mostly located between Mars and Jupiter, were not incorporated into the planets and remain relatively unaltered since shortly after the birth of the Solar System. Impact ejected fragments of asteroids fall to the Earth surface as meteorites, and pieces of the most primitive asteroids represent a class of meteorite known as the carbonaceous chondrites. These ancient objects contain a rich and varied record of processes that in some cases predate the formation of the Solar System, and in others document the formation events themselves, as well as subsequent low-temperature parent body effects.

An important part of the record in carbonaceous chondrites is preserved within carbon- and nitrogen-bearing components that vary widely in structure and provenance (Table 1). Materials like silicon carbide and some of the graphite, with their highly unusual isotopic compositions, record primary nucleosynthetic processes, reflecting their birth as stellar condensates from the stars that existed before the Sun (e.g. Anders & Zinner 1993). Diamonds too are likely to have a pre-solar origin, either in supernovae explosions (Clayton et al. 1995) or circumstellar environments (Kerckhoven et al. 2002). Carbonate minerals were formed on asteroids during a period of aqueous processing after the main Solar System formation events had taken place (e.g. Grady et al. 1988). Yet all these components are quantitatively subordinate to the main carbon- and nitrogen-bearing material in carbonaceous chondrites – organic matter (Sephton 2002).

It should be noted that the degree of aqueous and thermal processing on the parent asteroids allows the carbonaceous chondrites to be subdivided into several types: the lowest of which (Type 1) has experienced extensive aqueous alteration while the highest (Type 6) has been subjected to significant amounts of thermal metamorphism. Carbonaceous chondrites are given an additional two letter designation reflecting their chemical composition, which is made up of the letter ‘C’, representing carbonaceous, followed by the first letter of the type specimen for the subdivision (e.g. the Mighei meteorite is the type specimen of the CMs). The two classification systems are often combined so that Mighei, for instance, is a ‘CM2’. A detailed explanation of the meteorite classification system can be found in Sears & Dodd (1988).

Stable isotopes are valuable tools when attempting to decipher the record present in carbon- and nitrogen-bearing components in meteorites. Because isotopic information can be used as an indicator of both source and alteration history, and as bulk carbon and nitrogen stable isotope ratios differ between meteorites, there is much potential for translating chemical information into plausible reconstructions.
of early Solar System environments (e.g. Alexander et al. 1998).

The first comprehensive survey of carbon, nitrogen and hydrogen isotopic compositions of carbonaceous chondrites was performed in the 1980s and sought to detect systematic patterns of secondary processing based on whole rock data (Kerridge 1985). The carbonaceous chondrite data set for carbon and nitrogen displayed significant intra- and inter-meteorite heterogeneity, but did not reveal any clear patterns that could be related to parent body alteration.

The most abundant carbon- and nitrogen-bearing component in carbonaceous chondrites is organic matter which can account for up to 5 wt% of the meteorite (Sephton 2002). Organic matter in carbonaceous chondrites is dominated by a complex macromolecular material, which is insoluble in organic solvents and non-oxidizing acids such as HF and HCl. It follows, therefore, that the state of the macromolecular material must exert a strong control on whole rock carbon- and nitrogen-based signatures.

Carbon and nitrogen isotopic variability within macromolecular materials was exploited in the late 1990s to gain an insight into the accretion and parent body alteration history of chondritic organic matter (Alexander et al. 1998). A relatively constant ratio of interstellar diamonds (sometimes called nanodiamonds on account of their nanometre dimensions) to organic macromolecular material was observed. This relationship suggested that the relative abundance of these components was determined prior to the accretion of the meteorite parent bodies and that all carbonaceous chondrites accreted a common organic progenitor. It is a necessary consequence of this theory that much organic matter would also predate the formation of the Solar System. It was proposed that the organic progenitor exhibited an enrichment in the heavy stable isotopes of carbon, nitrogen and hydrogen, and that these were progressively lost during increasing aqueous and thermal processing on the parent asteroid. If this hypothesis is correct, then the level of alteration a carbonaceous chondrite has been subjected to can be assessed by establishing the degree of preservation of its enrichments in the heavy stable isotopes of carbon and nitrogen (Sephton et al. 2003). Detailed analyses of macromolecular materials from carbonaceous chondrites that have been subjected to different levels of natural aqueous alteration on the parent asteroid displayed stable isotopic features analogous to those seen in samples aqueously altered at different temperatures in the laboratory (Sephton et al. 2003). Parent body aqueous alteration, it seems, produces predictable and experimentally-reproducible isotopic characteristics.

Acid-insoluble carbonaceous matter from enstatite chondrites, which have experienced a very different type of alteration on the parent body (graphitization during anhydrous thermal metamorphism), exhibits stable isotopic characteristics that are clearly distinct from those seen after aqueous processing (Sephton et al. 2003). (Hereafter the term macromolecular material refers to this type of organic matter in both its original and metamorphosed forms.)

The combined data set of natural- and laboratory-altered macromolecular material from chondrites suggests, therefore, that carbon and nitrogen stable isotope ratios may be valuable indicators of asteroidal processes in the early Solar System. In this paper we summarize the main concepts pertaining to this method, and attempt to reconstruct events occurring in the early Solar System environment. In the light of recent developments we also re-examine the previously published whole rock chondrite data set for evidence of acid-insoluble carbonaceous matter alteration on the parent asteroid during the early stages of Solar System history.

## Materials and methods

### Laboratory aqueous alteration

Acid-insoluble organic materials in carbonaceous chondrites are isolated by digesting the inorganic matrix with cycles of HF and HCl acids (Amari et al. 1994). Free organic matter is removed with organic solvents, most commonly dichloromethane and methanol mixtures (93:7). Isolated macromolecular materials are aqueously altered using hydrous pyrolysis (320 or 330 °C; 72 hours) during which heated samples are in contact with liquid water for the duration of the experiment (Lewan et al. 1979). Initially used as a tool for simulating oil-generation from organic-rich terrestrial samples, hydrous pyrolysis has become widely accepted in
recent years as a means for liberating fragments of macromolecular material from meteorites (Sephton et al. 1999).

**Stable isotope analysis**

The stable isotopic composition of extraterrestrial materials is a reflection of nucleosynthesis, nuclear processing and chemical fractionation processes (Penzias 1980). Meteorites, and the organic matter within them, are the end result of large-scale mixing and processing of various pre-solar materials. By establishing the isotopic composition of meteoritic organic matter, the significance of each extraterrestrial source region in its production and modification may be constrained.

Early analyses performed on meteoritic macromolecular materials involved its investigation as a bulk residue following various chemical treatments (Krouse & Modzeleski 1970; Smith & Kaplan 1970; Robert & Epstein 1982; Yang & Epstein 1983). However, such results were at best weighted averages of the isotopic compositions of what may be a wide variety of organic structures. More incisive stepped heating experiments, which distinguish between carbon phases by their susceptibility to combustion or pyrolysis, have identified a number of isotopically-distinct components within the acid insoluble carbonaceous matter in meteorites. Stepped heating experiments have been central to efforts successfully applied to understanding the carbon and nitrogen record of parent body processing (Alexander et al. 1998; Sephton et al. 2003).

The abundances of stable isotopes are commonly expressed using the $\delta$ notation. These indicate the difference, in per mil ($\\permil$), between the relevant ratio in the sample and the same ratio in an international standard as follows:

$$\delta(x) = [(R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}] \times 1000,$$

where $R = ^{13}\text{C}/^{12}\text{C}$ for carbon and $^{15}\text{N}/^{14}\text{N}$ for nitrogen; the standard for carbon (PDB) has $^{13}\text{C}/^{12}\text{C}=0.112372$ and that for nitrogen (air) has $^{15}\text{N}/^{14}\text{N}=0.003765$.

**Organic matter types**

Stable isotopic analyses of extracts and residues from procedures aimed at isolating and aqueously altering extraterrestrial macromolecular materials from the organic-rich Murchison meteorite have led to the identification of three main types of organic matter (Sephton et al. 1998). The organic fractions are defined by their physical and chemical responses to laboratory procedures and, by analogy, to parent body processes. The divisions rely on simple operational characteristics and although each organic fraction may respond to processing in a similar way, they may be composed of molecules from a number of extraterrestrial sources. For example, free organic matter is comprised of various compounds classes (such as amino acids, carboxylic acids, aromatic hydrocarbons, etc.) but all can be extracted by common organic solvents. Macromolecular materials are structurally complex and more intractable but some can be broken down using heating techniques. In contrast, the most refractory macromolecular materials must be reacted with oxygen at high temperatures before degradation takes place.

The first step in isolating macromolecular material in meteorites involves the removal of inorganic minerals with cycles of HF and HCl acids followed by solvent extraction to remove any free organic matter. Fig. 1(a) shows that for Murchison these procedures leave a HF/HCl residue with $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values that are lower than those of the whole rock. The data are consistent with a loss of carbonate minerals ($^{13}\text{C}$-enriched) and free organic matter ($^{13}\text{C}$- and $^{15}\text{N}$-enriched). In an experiment where a Murchison HF/HCl-resistant residue was treated artificially to aqueous alteration in the laboratory at 320 and 330 °C the macromolecular material became increasingly depleted in $^{13}\text{C}$ and $^{15}\text{N}$ (Fig. 1(a)), consistent with the removal of isotopically heavy ‘labile’ organic entities (i.e. partial destruction of the macromolecule itself). However, even at the most elevated laboratory alteration levels the residues retain significant amounts...
of carbon and nitrogen, suggesting that a ‘refractory’ macromolecular component must be present. In contrast to the free and labile organic fractions, the refractory phase is characterized by a relative depletion in $\delta^{13}C$ and $\delta^{15}N$.

Carbon and nitrogen isotope data, therefore, reflect the presence of three distinct types of organic matter in carbonaceous chondrites. Definitions and typical $\delta^{13}C$ and $\delta^{15}N$ values for these fractions in the Murchison meteorite are given as follows (Sephton et al. 2003).

- Free organic matter is present within the whole rock meteorite, is easily removed with organic solvents and is enriched in both $\delta^{13}C$ and $\delta^{15}N$ ($\delta^{13}C \sim +7\%_0$; $\delta^{15}N \sim +88\%_0$).
- Labile organic matter has a macromolecular structure, is not removed by solvent extraction or HF/HCl treatment but is released by laboratory aqueous alteration. Labile organic matter is enriched in both $\delta^{13}C$ and $\delta^{15}N$ ($\delta^{13}C \sim -5\%_0$; $\delta^{15}N \sim +85\%_0$).
- Refractory organic matter is not removed by solvents, HF/HCl treatment or laboratory aqueous alteration, and is depleted in both $\delta^{13}C$ and $\delta^{15}N$ ($\delta^{13}C \leq -20\%_0$; $\delta^{15}N \leq -25\%_0$).

Next we will consider how these three types of organic matter may react to processing on the parent asteroid to produce intermeteorite variations in stable isotopic compositions. It must be recognized that each type of alteration (aqueous, oxidative and thermal) is unlikely to have occurred alone. For simplicity, however, the following discussion is subdivided into first-order processes.

**Aqueous alteration**

Fig. 1(b) displays the carbon and nitrogen stable isotopic composition of the three types of organic matter in Murchison. The organic matter on the left of the figure is more readily removed by laboratory processing than that on the right. Hence, it is easy to visualize how increased aqueous processing progressively exposes the isotopically-light refractory organic matter. It is this effect that leads to variations in $\delta^{13}C$ and $\delta^{15}N$ values for the residues plotted in Fig. 1(a).

To determine the extent to which these effects are evident in naturally processed organic matter, a HF/HCl residue (essentially mixtures of isolated labile and refractory macromolecular materials) from a different carbonaceous chondrite has been analysed. Orgueil, a Type 1 (CI1) carbonaceous chondrite, has been subjected to much more aqueous alteration on the meteorite parent body than Murchison, a Type 2 (CM2). For a recent study, different HF/HCl residue preparation steps for Orgueil and Murchison (the latter had been subjected to density separation to remove silicon carbide) made information from bulk residue $\delta^{13}C$ values incomparable (Sephton et al. 2003). However, macromolecular material from Orgueil exhibits low $\delta^{13}C$ and $\delta^{15}N$ values characteristic of refractory organic matter at lower temperatures during stepped heating indicating that, if both meteorites inherited a common organic progenitor (Alexander et al. 1998), significant amounts of labile organic matter ($^{13}C$- and $^{15}N$-enriched) might have been removed already by aqueous processing on the parent asteroid (Sephton et al. 2003). The data indicates that natural aqueous alteration performs the same function as laboratory aqueous alteration, i.e. labile organic matter is removed to leave a residue which contains an increasing proportion of refractory organic matter and, therefore, becomes progressively isotopically lighter.

However, one complicating factor is that greater amounts of organic carbon and nitrogen are present in the more altered Orgueil than in the less altered Murchison. The most straightforward interpretation is that the two types of meteorites contained different proportions of organic starting materials relative to inorganic components. Alternatively, if carbonaceous chondrites did accrete similar amounts of a common organic progenitor then a mechanism must be invoked in which partially-altered organic residues or degradation products are transported within the parent body.

**Oxidation**

A process that may be equally as effective as aqueous alteration for removing labile organic components enriched in $^{13}C$ and $^{15}N$ is oxidative metamorphism, i.e. the reaction of organic matter with oxidized gases, liquids or minerals at raised temperatures. Type 3 (e.g. CV3 and CO3) carbonaceous chondrites have been heated from 400 to 500 °C on their parent bodies (Zolensky & McSween 1988), much higher than the less than 150 °C temperatures experienced by the Type 1 and 2 meteorites (e.g. CI1 and CM2) (Clayton & Mayeda 1984). In the presence of excess oxygen these temperatures lead to the complete combustion of organic matter. Only small amounts of oxidizing agents would be required to cause the partial loss of organic matter at the relatively high temperatures experienced on the Type 3 parent bodies. Presumably, as in the aqueous processing experiments, the more reactive $^{13}C$- and $^{15}N$-enriched labile organic matter would be lost first, leaving a residue containing more $^{13}C$- and $^{15}N$-depleted refractory organic matter. 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, b; Halbout et al. 1986).

**Thermal metamorphism**

Macromolecular materials in enstatite chondrites (EH and EL) have been subjected to anhydrous thermal metamorphism (i.e. the transformation of organic matter at raised temperatures in the absence of oxidizing agents) on their parent asteroid (Mason 1966). If it is assumed to be true 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), then these samples provide an opportunity to examine how anhydrous heating affects the labile organic $^{13}C$- and $^{15}N$-enrichments in macromolecular materials.

Stepped heating data for enstatite chondrite macromolecular materials reflecting varying levels of parent body metamorphism reveal little compelling evidence of a
progressive loss of $^{13}$C with increasing parent body temperature (Sephton et al. 2003). Such data indicates that relatively small amounts of $^{13}$C-enriched labile organic matter are lost during anhydrous thermal metamorphism. Much of the $^{13}$C-enriched labile organic matter (and presumably some incorporated free organic matter) carbon has been ‘locked up’ and preserved during graphitization.

However, with increasing enstatite chondrite petrographic type (from Type 3 to Type 6) and, therefore, parent body temperature, the macromolecular materials show some evidence of a progressive loss of $^{15}$N. Furthermore, the $\delta^{15}$N values for the highly metamorphosed enstatite chondrite macromolecular materials are significantly lower than those in carbonaceous chondrites. If the carbonaceous chondrite organic matter is analogous to the progenitor of the enstatite insoluble carbon then significant amounts of $^{15}$N-enriched labile organic matter (and initially incorporated free organic matter) have been lost during extreme parent body metamorphism. The expulsion of nitrogen during the graphitization of organic matter is a predictable consequence of parent body metamorphism.

Although displaying comparable $\delta^{13}$C values, the thermally metamorphosed enstatites contain much smaller amounts of organic carbon and nitrogen than the Type 1 and 2 carbonaceous chondrites. Again, the simplest explanation is that the two types of meteorites contained different proportions of organic starting materials relative to inorganic components. Arguments involving material transfer are less plausible for the water-poor enstatite parent body.

**Towards an organic progenitor**

Our discussions above have a bearing on attempts to identify which type of carbonaceous chondrite contains the most pristine organic material. Bulk geochemical studies suggest that the Type 1 meteorites have elemental abundances closest to the Sun and represent, therefore, an overall chemistry least changed since the formation of the Solar System (Anders & Grevesse 1989). In contrast, petrographic studies suggest that the Type 3 carbonaceous chondrites contain the least altered minerals (McSween 1979). Now, the stable isotopic data indicates that, for the organic matter at least, it is the Type 2 carbonaceous chondrites that contain the most primitive material based on their relative enrichments in $^{13}$C and $^{15}$N. The primitive nature of the organic matter in Type 2 chondrites has been noted previously (Alexander et al. 1998).

**Record of alteration in whole rock chondrites**

The original surveys of carbon and nitrogen isotopes in chondrites were performed over a quarter of a century ago. Since then our understanding of how the major carbon- and
nitrogen-bearing components in meteorites responded to accretion and subsequent processing in the early Solar System (Fig. 2) has increased markedly. We know that chondritic macromolecular materials change in the following ways:

- aqueous alteration evident in Type 1 and Type 2 chondrites (CIIs and CMs) reduces $^{13}$C- and $^{15}$N-enrichments to leave a $^{13}$C- and $^{15}$N-depleted residue;
- oxidation apparent in Type 3 chondrites (COs and CVs) most likely reduces $^{13}$C- and $^{15}$N-enrichments to leave a $^{13}$C- and $^{15}$N-depleted residue;
- and hydrous metamorphism perceptible in EH and EL chondrites retains $^{13}$C-enrichments but is less able to maintain $^{15}$N-enrichments.

Hence it is appropriate to re-examine published data sets to see if trends established by recent work on macromolecular materials are manifest in the whole rock samples. Fig. 3 displays published whole rock data (Kerridge 1985; Grady et al. 1986) as box and whisker plots. This type of plot is useful for intrinsically heterogeneous meteorite data as trends are relatively unaffected by outliers. It appears that each of the responses outlined above are evident in the whole rock data sets.

**Conclusions**

Carbonaceous chondrites contain organic matter, which can be subdivided operationally into three types. Free organic matter is relatively enriched in $^{13}$C and $^{15}$N and is soluble in organic solvents. Labile organic matter is also enriched in $^{13}$C and $^{15}$N, and has a macromolecular structure making it insoluble in solvents and HF/HCl acids, but can be released by laboratory aqueous alteration. Refractory organic matter is unaffected by solvents, HF/HCl treatment and laboratory aqueous alteration, and is relatively depleted in $^{13}$C and $^{15}$N. Laboratory simulations indicate that the varying susceptibilities of these organic matter types to aqueous and thermal processing allow carbon and nitrogen stable isotope ratios to be used as proxies for alteration on the asteroidal meteorite parent body.

In whole rock meteorites, the macromolecular entities (labile and refractory organic matter) are by far the most abundant organic components present and, as a result, have a major influence on the overall isotopic composition. The relative abundance of labile to refractory organic matter is a reflection of the degree of secondary processing by water and heat on the meteorite parent body, and the effects are evident in bulk stable isotope measurements of whole rock samples. Carbon and nitrogen isotope ratios, it seems, represent a valuable record of aqueous and thermal processing on asteroids shortly after the birth of the Solar System.

**References**


