The Record of Early Solar System
History in the Molecular Structure and
Isotopic Abundances of
Extraterrestrial Organics

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Introduction: The organic matter in carbonaceous chondrites potentially records a succession of chemical histories that started with reactions in the interstellar medium, followed by reactions that accompanied the formation and evolution of the early solar nebula, and, ultimately, ended with reactions driven by hydrothermal and metamorphic alteration in the meteorite parent bodies. One of the challenges in meteorite research is establishing whether one can identify the chemical signatures of these reactions in the organic fractions and whether there exists any relationship between the molecular structure(s) of organic matter within a given meteorite group and the degree of parent body alteration. Recent analysis of a broad suite of organic matter isolates (IOM) from many different chondrite classes, groups, and types reveal clearly defined reaction pathways.

Low Temperature Parent Body Alteration. Solid-state nuclear magnetic resonance (NMR) spectroscopy has been shown to be a highly effective analytical tool for establishing the types and distributions of organic functional groups in IOM (Cody et al. 2002). While lacking the molecular detail of pyr-GCMS, solid-state $^{13}$C NMR can provide a quantitative, albeit averaged, structural picture of organic macromolecules. Through a series of independent NMR experiments Cody and Alexander (2005) proved that the significant differences in the chemistry of IOM across the four meteorite groups (CI, CM, CR, and Tagish Lake and ungrouped C2) reflect primarily differences in the abundance and types of sp³ bonded carbon. The most likely interpretation for this chemical variation is that the differences in type 1 and 2 IOM record a progressive trend in low temperature chemical oxidation that would require the presence of a soluble oxidant in the aqueous phase during parent body alteration. One possibility is hydrogen peroxide, a likely constituent in the icy mantles of dust grains subjected to UV photolysis. In this study of meteoritic IOM, therefore, the CR2 is apparently the least and Tagish Lake is apparently the most chemically degraded. The selective enrichment in aromatic moieties and nano-diamond suggested that these constituents of IOM are relative inert to this oxidation and that their relative abundance may provide a measure of the extent of oxidation. The organic matter contained with the matrices of type 1 and 2 carbonaceous chondrites, therefore, may provide a unique record of the oxidative nature of aqueous fluids that altered each meteorite’s parent body.

Thermal Alteration: In order to study the organic structure of the thermally metamorphosed type 3 chondrites one is faced with the problem that there is generally much less organic matter and we can rarely obtain sufficient amounts of IOM to acquire solid state NMR. To circumvent this difficulty we apply micro Carbon X-ray Absorption Near Edge Structure (C-XANES) spectroscopy. C-XANES provides similar information to that of solid state NMR. While C-XANES lacks the ease of quantization that solid state NMR provides, samples as small as a few microns in diameter can easily be analyzed.
Through the analysis of ~ 25 different IOM samples obtained from type 3 CV, CO, and Ordinary chondrites a clear picture of the effect of thermal metamorphism on IOM has been obtained (Cody et al. in press). Prolonged exposure to elevated temperatures (T > 200 °C) in the chondritic parent body progressively transforms primitive IOM into a highly aromatic material that exhibits semi-conductor like electronic properties. In addition to showing a clear correlation between IOM structure and mineralogic indicators of metamorphic grade, Cody et al. (in press) also showed that laboratory heating of primitive IOM (e.g. from Murchison) leads to the formation of organic structure identical to that in highly heated chondrites. These laboratory derived transformation kinetics can be used as a cosmothermometer revealing that the organic matter spanning the type 3 to type 4 chondrites records a temperature range up to 950 °C.

Finally, a significant result of the study of the type 3 chondrites is the unambiguous demonstration that the constituent primitive organic matter in type 1 and 2 chondrites may be thermally transformed into a structural state that is nearly identical to that observed in thermally metamorphosed type 3 chondrites. As it is generally agreed that type 1 and 2 chondrites never experienced temperatures much in excess of 100 °C; these results require that, in general, meteoritic organic matter was synthesized cold and, at least in the case of the type 1 and 2 chondrite parent bodies, accreted cold.

Deuterium Abundance vs. Metamorphism: The situation becomes a bit more complex when one compares the molecular structure of IOM with its deuterium abundance. The general view is that high deuterium abundance signifies more primitive (less processed) organic matter. Recent data, however, complicates this interpretation. Type 3 IOM exhibits a wide range in structure as a response to thermal alteration during parent body alteration, exhibiting significant loss in hydrogen, nitrogen, and oxygen coupled the growth of large conjugated π systems (Alexander et al. 2007; Cody et al. in press). If variation in deuterium enrichment occurred exclusively during the formation stage of IOM, then subsequent thermal alteration would be expected to exhibit similar isotopic trends. Allende IOM(CV3.6) is more extensively altered than Vigarano (CV3.4) (with T_{max} of 550 °C and 415 °C, respectively, Cody et al. in press). Allende’s IOM carries a δD of 194 per mil, while Vigarano’s IOM has a δD of 894 permil. This might suggest that a reduction in δD results from parent body metamorphism. Among the ordinary Chondrites, however, an opposite trend is observed. For example, the IOM in WSG95300 (H3.4) that was apparently heated to 460°C carries a δD of 11,850 permil, whereas the IOM in MET00452 (LL3.0) that was heated no higher than 200 °C carries a δD of 4,890 permil. These wild shifts in δD across group and accompanying metamorphism are most consistent with extensive isotopic exchange occurring during parent body alteration. These results clearly complicate any interpretation of isotopic enrichment as being a signature of primitive processes.

References: