

MOLECULAR AND COMPOUND-SPECIFIC HYDROGEN ISOTOPE ANALYSIS OF INSOLUBLE ORGANIC MATTER FROM DIFFERENT CARBONACEOUS CHONDRITE GROUPS. Y. Wang¹, Y. Huang¹, C. M. O'D. Alexander², M. Fogel³ and G. Cody³, ¹Department of Geological Sciences, Brown University, Providence, RI 02912-1846 (Yi.Wang@brown.edu, Yongsong.Huang@brown.edu), ²Department of Terrestrial Magnetism and ³Geophysical Laboratory, Carnegie Institute of Washington, Washington, DC 20015.

The carbonaceous chondrites are primitive meteorites that contain up to several weight-percent of carbon, most of that is present as organic matter. Studies of the molecular distributions and isotopic composition [1] of this organic matter indicate that it retains a record of its origin and secondary thermal and aqueous alteration histories. 75% or so of organic matter in carbonaceous chondrites exist in the form of insoluble organic matter (IOM) [2]. IOM has high molecular weight and relative immobility precluding the possibility of terrestrial contamination, a concern that is most often associated with extractable organic compounds in carbonaceous meteorites [3].

Applications of new analytical techniques to the meteorite IOM have great potential to provide new information on the compositions and origin of organic matter in carbonaceous chondrites. The δD values of individual organic compounds may provide the most sensitive isotopic tracer for studying the prebiotic evolution, and for differentiating sources of organic compounds in carbonaceous chondrites. However, despite many studies on the bulk hydrogen isotope ratios of meteorite organics [e.g. 4], there has been no study on the D/H ratios of individual compounds derived from IOM pyrolysates.

We have conducted the first systematic analyses of molecular distribution and δD values of individual compounds in pyrolysates of IOM from different carbonaceous chondrite groups, using flash pyrolysis coupled to gas chromatography-mass spectrometry and compound-specific D/H analysis. IOM samples from six meteorites of different classifications, EET92042 (CR2), Orgueil (CI1), ALH83100 (CM1/2), Murchison (CM2), ALH85013 (CM2), and the unique Tagish Lake (C2) were isolated and studied. Our goal is to combine the molecular and hydrogen isotopic characteristics of the pyrolysis products to identify the similarities and differences in these samples and to understand how post-synthesis processes (e.g., aqueous and/or thermal alteration) affect the organic matter compositions. Because IOM is the dominant fraction of the organic matter in carbonaceous meteorites, our data could yield new insights into the origins and formation pathways of meteorite organic compounds.

Except for the Tagish Lake IOM sample, pyrolysates of all five meteorite IOM samples were dominated by an extensive series of aromatic (C₁ to C₇ alkyl-

substituted benzenes, C₀ to C₂ alkyl-substituted naphthalenes), and aliphatic (straight chain and branched C₉ to C₁₅ alkanes) hydrocarbons, with several S- and O-containing compounds (C₁ to C₂ alkylthiophenes, benzothiophene, benzaldehyde) being also present (Figure 1). The strong similarity in the pyrolysates of different carbonaceous chondrites suggests a common origin and conservative nature of the IOM during the subsequent chemical evolution (e.g. aqueous and/or thermal alteration occurred during parent body processing) in the space environments. The Tagish Lake IOM sample is unique in that its pyrolysate contains much smaller amount of substituted aromatic hydrocarbons than the pyrolysates from the other samples studied, suggesting distinctively different formation processes.

The bulk δD values of four IOMs studied follow the order below: EET92042 (+3004 ‰) > Orgueil (+972 ‰) > Murchison (+777 ‰) > Tagish Lake (+596 ‰). All the data so far indicate CR type samples contain the IOMs with the highest δD values, often about 2000 ‰ higher than other carbonaceous meteorite types.

Significant variability in the δD values of individual IOM pyrolysates indicates considerable heterogeneity in the origins and modification of the organic matter in these samples (Figure 2). Previous studies have shown significant variability in soluble organic compositions as well as isotopic ratios of soluble fractions when different sub-samples from the same parent meteorite (e.g., Murchison) were analyzed [e.g. 5]. Our data indicate that such heterogeneity also exists in the D/H ratios of different structure sub-units in the organic macromolecules. It is possible that these structure sub-units with large differences in D/H ratios formed at different times and/or under different conditions (e.g., temperature), or more likely have undergone different degrees of oxidation/aqueous alteration.

The chain length distributions of δD values for both alkylbenzenes and *n*-alkanes show an increase in δD values at shorter carbon number range (*n*-alkanes from C₉ to C₁₃, alkylbenzenes from C₁ substituted to C₄ substituted), whereas the trend reverses at the higher carbon numbers (Figure 2). We argue that our observed isotopic trend results from a combined effect of two opposing isotopic fractionations associated with compound formation and with the pyrolysis degradation process. Shorter chain *n*-alkanes and alkylben-

zenes are derived from their higher carbon number homologues during pyrolysis. Because H-containing fragments will be produced in a higher rate than D-containing fragments, the pyrolysis reaction products (lower n -alkanes or alkylbenzenes) are depleted in D relative to higher homologues. The reversal of isotopic trend at higher carbon number range (i.e., from C_{13} to C_{15} for n -alkanes, and C_4 to C_7 substitution for alkylbenzenes) can be considered as being dominated by kinetic isotope effects during organic matter synthesis reactions.

We also computed the weighted average δD values of individual pyrolysates (δD_{WA}) using the peak intensities on the IRMS, in order to compare with bulk δD values of IOMs. The δD_{WA} values display the same order for the meteorite samples, i.e., EET92042 (+3309 ‰) > Orgueil (+1207 ‰) > ALH83100 (+1040 ‰) > Murchison (+932 ‰) > ALH 85013 (+568 ‰) > Tagish Lake (+416 ‰). The δD_{WA} values of individual pyrolysates well correlate with the bulk δD values. The data suggest that the compounds released by pyrolysis are isotopically representative of the bulk IOMs. The data also indicate that the pyrolysate records thermally derived molecules that sampled the same H and D reservoir as the bulk IOMs. The high temperature and rapidity of the pyrolysis experiment make it likely that little D/H fractionation occurs during the process.

Recent analyses using solid state combined 1H and ^{13}C NMR [6] provide important structural information on EET92042, Orgueil, Murchison, and Tagish Lake IOMs. Our pyrolysis data and D/H analyses offer additional insights into the origin of the different meteorite IOMs. As the low temperature oxidation reaction progresses, the D/H ratios of the IOMs decrease. During low temperature oxidation reactions, exchange between the aqueous media and organic matter would have occurred. Therefore, as the oxidation reaction progress, the D/H ratios of the remaining IOM would decrease. The larger the isotopic difference between the organic phase and aqueous phase is, the greater decrease in D/H ratio of the remaining organic matter will be.

References: [1] Cronin J. R. and Chang S. (1993) In *Chemistry of Life's origin*, Kluwer, 209–258. [2] Bandurski E. L. and Nagy B. (1976) *GCA*, 40, 1397-1406. [3] Robert F. and Epstein S. (1982) *GCA*, 46, 81-95. [4] Kerridge J. F., Chang S., and Shipp R. (1987) *GCA*, 51, 2527-2540. [5] Cronin J. R. and Pizzarello S. (1983) *Adv. Space Res.* 3, 5-18. [6] Cody G. D., Alexander C., and Tera F. (2004) *GCA*, in press.

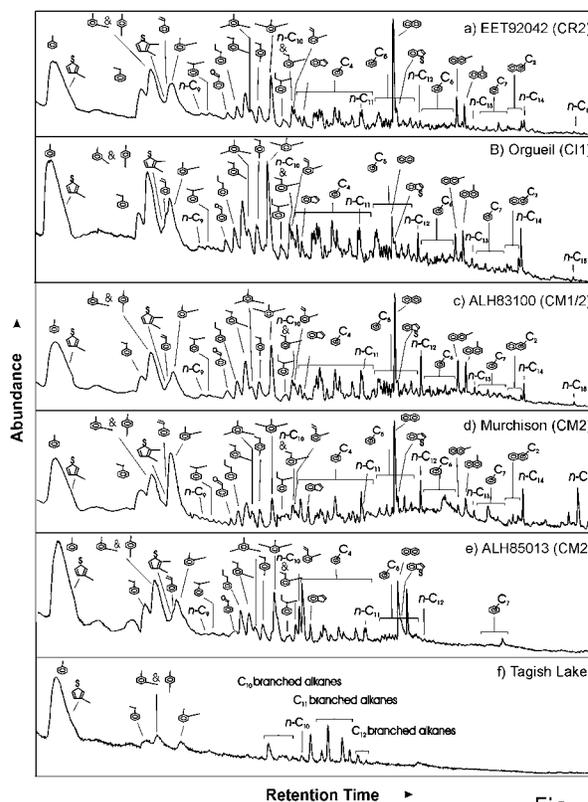


Fig. 1

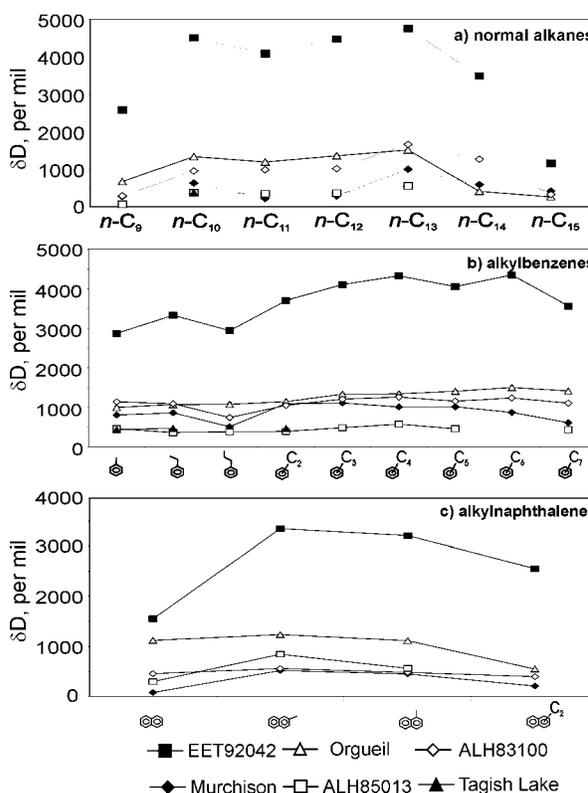


Fig. 2