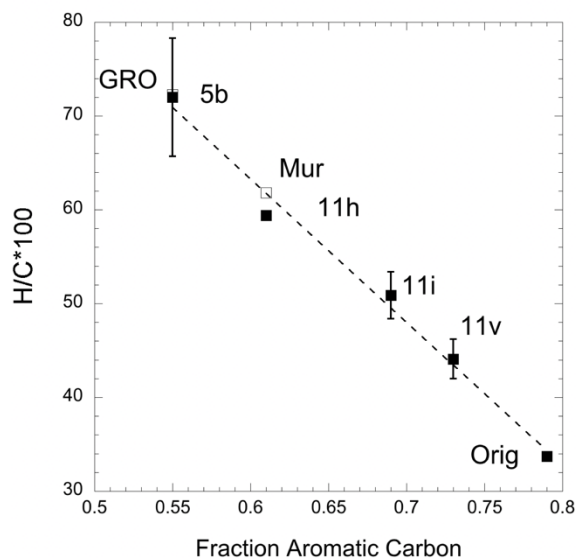


## THE EVOLUTION OF HYDROGEN ISOTOPES IN CHONDRITIC INSOLUBLE ORGANIC MATTER.

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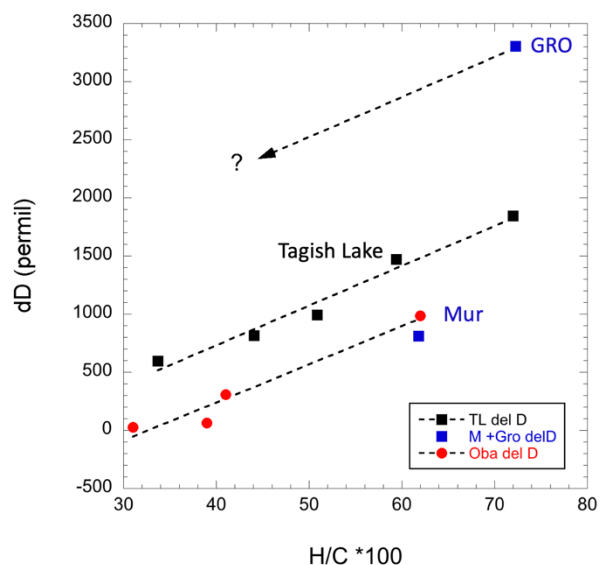
**Introduction:** It has been long established that insoluble organic matter (IOM) is the carrier of the exotic D enrichment characteristic of carbonaceous chondrites (CCs) [1]. Such enrichment firmly establishes some link between IOM and low temperature chemistry capable of fractionating D far above the solar D/H ratio. Over the years, numerous studies have shown that IOM from type 1 and 2 CCs exhibit evidence of surprisingly large degrees of molecular evolution indicated by significant variation in H/C (atm.), from ~ 0.72 down to 0.33, and the fraction of aromatic carbon ( $F_A$ ), from a low of 0.55 up to 0.80 [2-5]. These are remarkable changes in organic molecular structure in meteorites (Fig. 1) where no significant mineralogical indications exist for designation other than type 1 or 2 [6].



**Figure 1:** Variation of H/C x100 vs. Fraction of aromatic carbon ( $F_A$ ) for IOM isolated from GRO 95577 (CR1), Murchison (CM2) (open squares), and the Tagish Lake Clasts (C2, ungrouped) (filled squares).

From studies of the molecular structure of heated CM's [7], there is a very clear directionality in organic molecular evolution, i.e., from high H/C-low  $F_A$  to low H/C-high  $F_A$ .

One of the remarkable discoveries related to the Tagish Lake fall was the identification of discrete clasts [3,6] in which it was shown that there is a very systematic linear relationship between IOM's  $\delta D$  and H/C,  $F_A$  [3], where with increasing degree of molecular evolution,  $\delta D$  drops significantly, suggesting a connection between isotropic depletion and molecular evolution (Fig. 2).



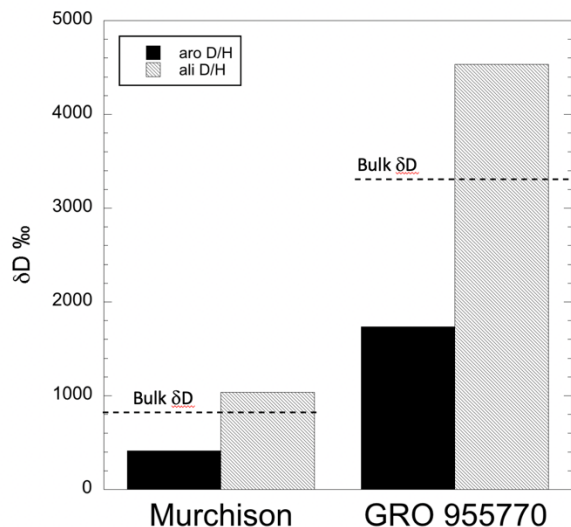
**Figure 2:** Variation in  $\delta D$  (‰) vs H/C x 100 for IOM from the Tagish Lake clasts and variation in the same for Murchison IOM experimentally subjected to hydrothermal alteration [8] along with the bulk  $\delta D$  of Murchison and GRO 95577 IOM.

Increases in  $\delta D$  with kerogen molecular evolution are commonly observed [9] and have been demonstrated in step pyrolysis experiments of terrestrial type 3 kerogen [10]. Enrichment in D with thermal metamorphism is thought to be derived from the fact that the C-D bond is stronger than the C-H bond. In this regard the Tagish Lake Trend (TLT, Fig. 2) and the hydrothermal experiments on Murchison IOM [8] are clearly anomalous. Similarly anomalous  $\delta D$  depletion trends with H/C during molecular evolution have been observed in stepped “dry” pyrolysis experiments with Murchison IOM [10].

In order to shed light on the molecular origins of the behavior exhibited in Tagish Lake or C1/2s, we set out to study intramolecular D/H partitioning between aliphatic and aromatic hydrogen reservoirs in IOM employing <sup>1</sup>H and D solid state Nuclear Magnetic Resonance (NMR) spectroscopy. Whereas <sup>1</sup>H NMR is straightforward due to <sup>1</sup>H's high natural abundance and large gyromagnetic ratio ( $\gamma$ ), the terrestrial D/H is extremely low and even in the most D enriched IOM (e.g., GRO 95577  $\delta D = 3300$  ‰) D/H is only 0.04 %, while D's  $\gamma$  is 6 times smaller than <sup>1</sup>H's.

We were able to isolate sufficient IOM from both Murchison (CM2) and GRO 95577 (CR1) to enable acquisition of D NMR from both reservoirs. We find that, relative to the aromatic reservoir, both samples

exhibit considerable enrichment of D in the aliphatic hydrogen reservoir, but GRO 95577 has slightly greater aliphatic D enrichment than Murchison's IOM (Fig. 3). We also performed experiments simulating the formation of IOM from simple sugars in D<sub>2</sub>O and again employing <sup>1</sup>H and D NMR to reveal that the synthetic IOM exhibits a very strong preference to store D in the aliphatic hydrogen reservoir.



**Figure 3:** Intramolecular partitioning of D and H in aliphatic and aromatic hydrogen reservoirs of Murchison and GRO95577 IOM.

While we do not have sufficient IOM from the precious Tagish Lake clasts to obtain D NMR spectra, there is considerable molecular similarity between GRO 95577 and Clast 5b IOM and between Murchison and Clast 11h IOM. The nearly parallel slopes of  $\delta D$  vs H/C (Fig. 2) for the Tagish Lake clasts and hydrothermally altered Murchison IOM [8] suggests that we can use the intramolecular D-H partitioning behavior exhibited in Fig. 3 and impose this onto the molecularly evolved Tagish Lake IOM.

From previous <sup>1</sup>H NMR studies of Tagish Lake IOM from different clasts [3] we have a clear understanding of how the hydrogen reservoirs change during molecular evolution - the ratio of aliphatic-H to aromatic-H decreases linearly with reduction in H/C. Thus, the significant reduction in H/C (Fig. 1) is predominantly driven by a loss of the aliphatic hydrogen reservoir [3]. Similar hydrogen behavior has also been observed for IOM from other CCs [4], suggesting that the molecular structure of IOM from any type 1 and 2 CC will lie somewhere along a highly constrained vector in H/C,  $F_A$ , and  $F_{\text{aro-H}}$  space.

We can, therefore, understand the anomalous trend in  $\delta D$  with H/C exhibited in Fig. 2 as arising from the preferential loss of the D-rich aliphatic hydrogen reservoir with molecular evolution. Applying the D/H partitioning observed in GRO 95577 (Fig. 3) and the

evolution in aliphatic and aromatic hydrogen reservoirs as a function of H/C [3] does predict a reduction in  $\delta D$  with H/C of  $\sim -300$  ‰ over the range of the TLT. This is significantly less, however, than what is observed (Fig. 2) where the reduction is  $\sim 1300$  ‰. Clearly more than just loss of the aliphatic hydrogen reservoir is driving the TLT.

It is well known that the  $\delta D$  of IOM in the CCs is significantly heavier than the  $\delta D$  of water in clay minerals [11], and they are not in isotopic equilibrium. In order to explain the TLT, a model is developed based on the D-H partitioning (Fig. 3) and the molecular evolution of the aliphatic and aromatic hydrogen reservoirs (Fig. 3).

The model predicts that over the span of time during which the TLT emerged, a combination of molecular evolution (diminishment of the aliphatic hydrogen reservoir) and more rapid partial D-H exchange between the aliphatic hydrogen reservoir and the D depleted water can explain the TLT. Interestingly the model predicts that the aromatic hydrogen reservoir will get slightly isotopically heavier ( $\sim 200$  ‰) along the TLT, behavior that is expected and has been shown for terrestrial organic matter molecular evolution, both naturally [9] and experimentally [10].

While this isotopic model does not rely on kinetics directly, it does place some necessary constraints on the time-temperature-transformation domain Tagish Lake's IOM must have been in during the emergence of the TLT. Basically, the molecular evolution and isotopic exchange exhibited across the TLT must have occurred in a thermal regime that enabled molecular evolution to proceed at a faster rate than D-H exchange [12,13]. The kinetics of D-H exchange between IOM and water is surprisingly sluggish [12,13]. Using the experimental results on Murchison [8] (Fig. 2), suggests that the duration of the perturbative hydrothermal event was short term, meaning days, not months or years.

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