

EXTENSIVE ORGANIC MOLECULAR EVOLUTION IN DIFFERENT TAGISH LAKE METEORITE FRAGMENTS. Y. Kebukawa¹, G. D. Cody¹, C. M. O'D Alexander², L. R. Nittler², C. D. K. Herd³, A. L. D. Kilcoyne⁴, ¹Geophysical Laboratory, Carnegie Institution of Washington, ²Department of Terrestrial Magnetism, Carnegie Institution of Washington, ³Department of Earth and Atmospheric Sciences, University of Alberta, ⁴Advanced Light Source, Lawrence Berkeley National Laboratory.

Introduction: The molecular structure of insoluble organic matter (IOM) extracted from meteorites has been shown to reflect the extent of parent body alteration, particularly in the case of IOM from type 3 chondrites (e.g. [1]). The molecular structure of IOM from the more primitive type 1 and 2 has been shown to vary considerable across groups (e.g. CR, CI, CM); where such variation was interpreted to reflect variation in the oxidation state of the parent body fluids during low temperature oxidation [2]. The principal inference has been that the molecular structure of IOM changes (and reflects) as a result of environmental conditions in the parent body. The recently initiated studies of individual pieces (stones) [3] of the Tagish Lake meteorite provides insight into the wide range of compositional and textural complexity that exists locally, i.e., in a single meteorite.

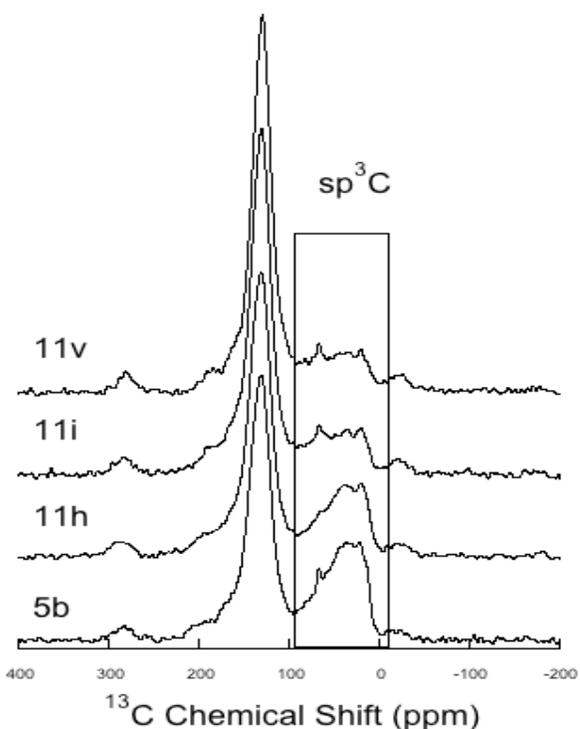


Figure 1: ¹³C solid state NMR spectra (VACPMS) of IOM isolated from different Tagish Lake stones (designated 5b, 11h, 11i, and 11v).

Here we report on the enormous variation in molecular structure of IOM across four individual stones. By applying ¹³C (VACPMS) NMR, ¹H MAS NMR, C-, N-, and O-XANES, and FTIR, we have obtained a highly constrained and self-consistent picture of the variation in molecular structure spanning the Tagish Lake Stones 5b, 11h, 11i, and 11v [3]. The ¹³C NMR spectra of IOM from different stones is presented in

Fig. 1, where it is revealed that there exists a very wide range in aromatic carbon content; from 54.5 % in 5b up to 73 % in 11v. The increase in aromatic carbon is balanced with a significant reduction in sp³ carbon (CH_x and CH_xO, x = 1-3); from 37.2 % in 5b down to 20.1% in 11v. Note the carbonyl content (from 160 to 230 ppm) remains nearly constant.

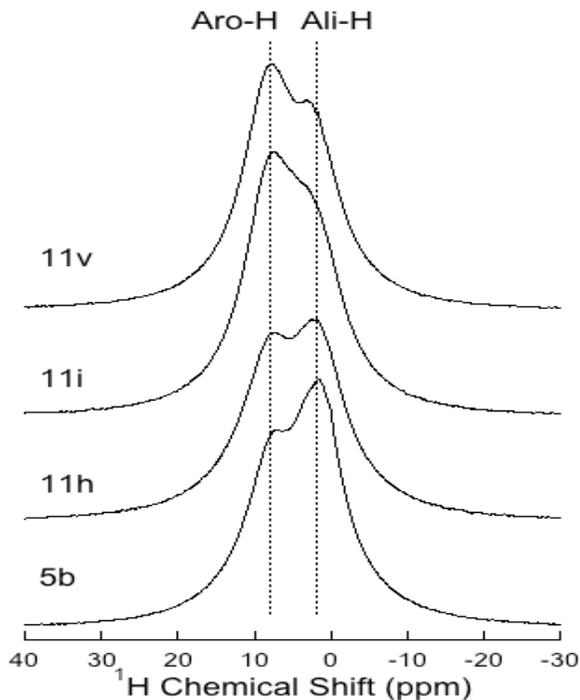


Figure 2: ¹H NMR spectra of Tagish Lake specimens 5b, 11h, 11i, and 11v revealing systematic changes in the relative abundance of aromatic and aliphatic hydrogen.

Solid state ¹H NMR provides complementary information (Fig 2) revealing a systematic shift from a predominance of aliphatic H (5b) to a predominance of aromatic H (11v). Thus, in both the ¹³C and ¹H NMR we observe the full range of molecular evolution in IOM moving from CR, CI, CM to the earlier sample of Tagish Lake [2]. These trends are also documented in the C-XANES and FTIR data (not shown here).

Given the constraint of elemental chemistry (H/C) and these NMR data one can make the following observations. First as the aromatic content increases from 5b up to 11v, the extent of aromatic substitution increases significantly. In the case of 5b, the average degree of aromatic substitution is 45 %, 11h this rises to 51 %, 11i this rises to 56 %, and for 11v this rises to 63 %. C-XANES spectra (not shown) clearly reveal that as the TL IOM becomes more aromatic, the aromatics become more condensed, evident by the growth of higher energy 1s-π* transitions indicating a larger

manifold of π^* states that arises from more polycondensed aromatic systems (e.g. benzene has 3 π^* states, phenanthrene has 7 π^* states, ...etc.).

Similarly, one finds that the average H/C ratio of aliphatic carbon decreases with increased aromatic carbon content, starting at 1.13 for 5b, dropping to 1.01 in 11h, dropping to 0.99 in 11i, and down to 0.83 in 11v. This is independently verified by inspection of aliphatic region in Fig. 1. Note that in order to have an aliphatic H/C below 1.0 requires that there exists non-protonated sp^3 carbon.

These data reveal that there exists a continuous evolution in molecular structure of IOM in different TL stones from the same meteorite. Previously, similar molecular evolutionary trends across CR, CI, CM, and TL were interpreted to be the result of selective loss of aliphatic carbon through low temperature oxidation, where the oxidant was possibly HOOH. In the present case, how one interprets the spectroscopic data is subject to adopting a specific reference frame with respect to carbon. For example, if one adopts the perspective that carbon is largely conserved, then loss of sp^3 -C occurs predominantly through the formation of aromatic carbon (Fig. 3); interestingly the carbonyl content increases then decreases with aromatization. As a further consequence of adopting this perspective, one finds that the aromatic hydrogen content does not increase, rather it stays nearly constant until dropping moving from 11i to 11v. Thus essentially all hydrogen loss moving from 5b to 11i is from aliphatic carbon.

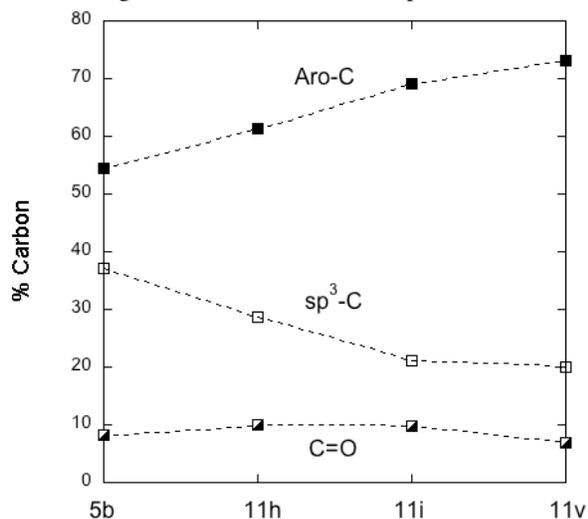


Figure 3: Variation in major carbon functional groups in IOM across Tagish Lake stones, as observed and if total organic carbon is conserved.

Alternatively, one can adopt the perspective that aromatic carbon remains essentially constant (Fig 4). In this reference frame, the increased aromatic content is balanced by a loss of aliphatic carbon to the environment (up to 25 %), either as soluble organics and/or CO_2 and H_2 . With this perspective the carbonyl content (C=O) remains ~ constant from 5b to 11h and then progressively drops from 11h to 11v (Fig. 4). Furthermore, adopting this perspective, one finds that both

aromatic and aliphatic H content drop moving from 5b to 11v.

The cross-group variation in IOM from CR, CI, CM, and TL adopted the conservation of aromatic carbon content [2]. From NMR data alone, however, it is not possible to pick between the two perspectives. It is interesting to note that the amount of carbon in various stones is very similar [3], suggesting that the constant carbon content perspective may be correct.

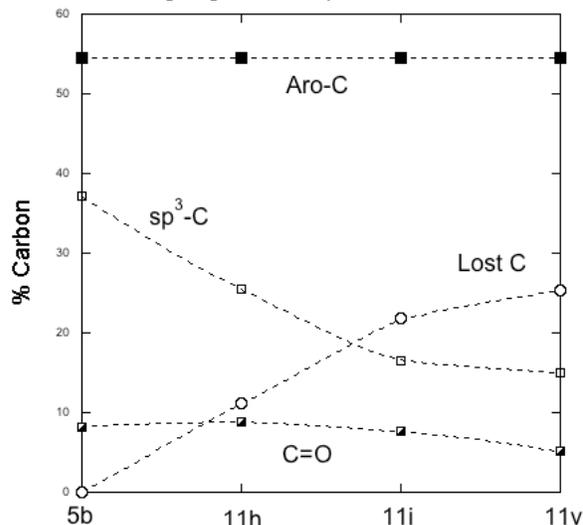


Figure 4: Variation in major carbon functional groups in IOM across Tagish Lake stones, assuming that aromatic carbon is conserved, and aliphatic carbon is preferentially lost.

The most likely scenario to explain these changes is hydrothermal alteration, although why some stones are effected and others not is interesting. It is worth noting that the changes in C-XANES spectra from 5b to 11v are very similar (albeit less extensive) to those observed when comparing the residue of flash heated IOM (600 °C at 500 °C/s) to unheated IOM [1]. Thus the changes in TL IOM from different stones may reflect differing degrees of flash heating due to impact processes. It is noted that even flash heating to 400 °C for 1 second liberates a substantial amount of low molecular weight compounds. In the case of Murchison, flash pyrolysis at 615 °C, yields ~ 30 % pyrolysate and 70 % solid residue. Such a scenario would support the evolution model presented in Fig. 4.

It is clear that as much molecular variation observed across petrologic type 1 and 2 chondrite groups [2] is observed in a single type 2 (ungrouped) meteorite. The combined NMR, XANES, and FTIR analysis provides an unique perspective into Tagish Lake parent body history.

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References: [1] Cody, G. D. et al. (2008) *EPSL*, 272, 446-455. [2] Cody, G. D. and Alexander C. M. O'D (2005) *GCA*, [3] Herd C. and Alexander C. M. O'D (2009) *MAPS, sci. suppl.* 5302.