

WATER-ORGANIC D-H ISOTOPE EXCHANGE DURING PLANETESIMAL ALTERATION: A SIMPLER EXPLANATION FOR THE VARIATION IN DEUTERIUM ABUNDANCE IN EXTRATERRESTRIAL MATERIALS G. D. Cody¹, ¹Geophysical Laboratory, CIW, Washington DC 20015, Y. Kebukawa², ²Yokohama National University, Japan, Y. Wang³, ³Georgia Tech, Atlanta Georgia, C. M. O'D. Alexander⁴, Department of Magnetism, CIW, Washington DC *E-mail: gcody@ciw.edu

Introduction: One of the more peculiar aspects of carbonaceous chondrites is the apparent complete lack of any systematic relationship between deuterium content and elemental composition of organic solids [1]. Equally perplexing is the variation in deuterium abundance in cometary water [2] and more recently water bound in hydrous phases in different carbonaceous chondrites [3]. This confusing situation has stood until the recent analyses of the Tagish Lake Clasts [4,5]. The recognition that the molecular structure of Insoluble Organic Matter (IOM) varies systematically with D/H content across various clasts (fragments) from the Tagish Lake meteorite is a potentially extremely important result [4,5]. In particular it raises the question as to why such systematic change in D/H with variation of aromatic carbon content or H/C [4,5] in Tagish Lake is not observed across other primitive carbonaceous chondrites.

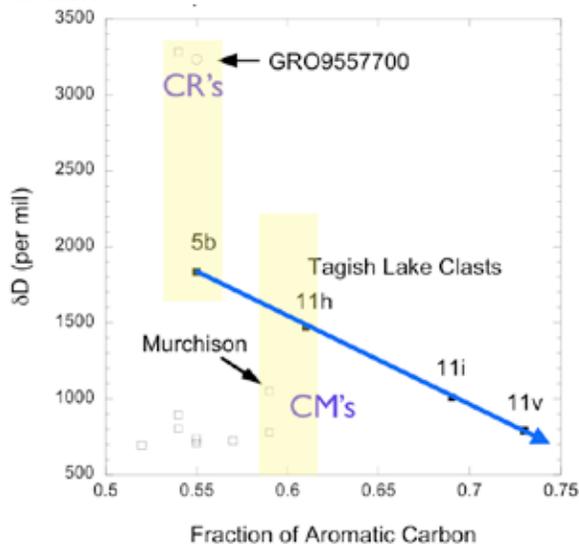


Fig. 1. Across IOM from different chondrite groups and within the CM group there exist no correlation between deuterium content and fraction aromatic carbon. Within the Tagish lake clasts, derived from a single solar system object, one observes a very strong negative correlation, where as aromatic content increases, deuterium content decreases.

Aromatic content is a robust indicator of the degree of alteration amongst the most primitive chondritic organic solids [6]. In figure 1 we plot the deuterium

content [1] vs % aromatic carbon for IOM from a number of CMs (including Murchison), IOM from an ultraprimitive CR [GRO955770], and IOM isolated from four different Tagish Lagish Lake clasts [4,5].

The data in Fig 1 strongly suggest that within Tagish Lake clasts there exists a clear correlation between deuterium abundance and molecular evolution as evidenced by systematic reduction of D content with increase in aromatic content (and reduction of H/C [4,5]). Whereas the reduction in H/C could be related to exclusively H-loss, the increase in aromatic carbon content requires a loss of aliphatic carbon. In fig 2 the ¹³C NMR spectra show that whereas the aliphatic content of TL clast 5b is larger than that of Murchison IOM, the reduction in deuterium content much less than that moving from the CR to TL clast 11h and greatest moving from the CR to Murchison.

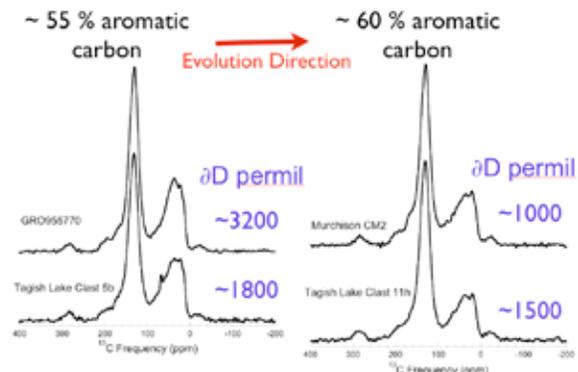


Fig. 2. Left: A comparison of ¹³C solid state NMR spectra ultra primitive IOM from the CR GRO955770 and TL Clast 5b, both with an aromatic content on the order of 55 %, but where the D/H vary considerably. Right: A comparison of the nearly identical molecular structures slightly more altered Murchison IOM with that of TL Clast 11h. Note the lower aliphatic carbon content evident at ~ 30 ppm.

The key issue in in Fig. 2 is that if the process that results in a change in the TL IOM molecular structure from an aromatic content of 55 to 60 % is ultimately responsible for the observed deuterium reduction, than it should affect any IOM (isotopically) in a similar way. By way of example, if one were to back transform Murchison IOM to a molecular structure identical to the CR, the anticipated deuterium content

would be 1300 ‰, not 1800 ‰ (TL 5b) nor 3200 ‰ (GRO955770). Organic transformation accompanying planetesimal metamorphism cannot, therefore, explain the variation in IOM deuterium abundance.

Recently, it has been proposed that organic solids in chondrites are derived from polymerization reactions that occurred (post accretion), within the interiors of planetesimals [7,8], where the primordial source of the carbon that becomes IOM is interstellar formaldehyde associated with the accretionary ices that supplied the water to these primitive solar system objects.

If this IOM origin scenario is correct, then it appears unlikely that variation in deuterium content could be ascribed to primordial variations in deuterium content of the IOM precursor (formaldehyde), prior to accretion. Given the likely turbulent nature of the early dust disk, extensive mixing of ice coated interstellar dust grains was likely prior to accretion of planetesimals. Such homogenization of grains would seem to average out any isotopic heterogeneity in the IOM precursor.

It has been recently proposed that the deuterium content of water may have been different radially with respect to the Sun prior to accretion of planetesimals [9]; assuming that the water in the earliest solar system was initially isotopically heavy and reacted with solar deuterium abundance H_2 . This potential scenario is supported, in part, by a study of meteorites from different meteorite groups that unambiguously reveal that the deuterium content of matrix water is different, e.g. CR's matrix water (associated with clays) is heavier (above terrestrial) than that of CM's (below terrestrial)[3]. It is, therefore, clear that matrix water in different chondrites also varies isotopically as does IOM. In this regard, chondritic water may be as isotopically varied as cometary water [2].

Alexander et al. [3] adopted the point of view that initially there existed a primitive organic solid end member (represented by the most isotopically primitive chondritic organic matter analyzed so far [1], IOM from CR chondrites with a high deuterium abundance of 3500 ‰). Using this composition as a critical end point, projection through bulk D/H vs C/H data points towards the y-axis intercept providing a means of determining the D/H of matrix water. Employing this perspective [3] leads to the conclusion that whereas primordial organic matter is a solar system constant, the D/H constant of solar system water is variable, a point supported by [7], thus the deuterium content of chondritic water potentially becomes a marker of radial distance at the point of accretion.

This point of perspective may well be correct, but here we adopt an alternative view that provides an equally valid (albeit at the quantitative level) explanation for the variation in deuterium abundance in both ET water and organic solids, but does not require variations in deuterium content in either solar system water or chondritic organic solids. Rather we consider the simple case where there exists a single primordial organic precursor for IOM that is the deuterium carrier and we further assume that solar system water exists at deuterium abundances that are at solar levels.

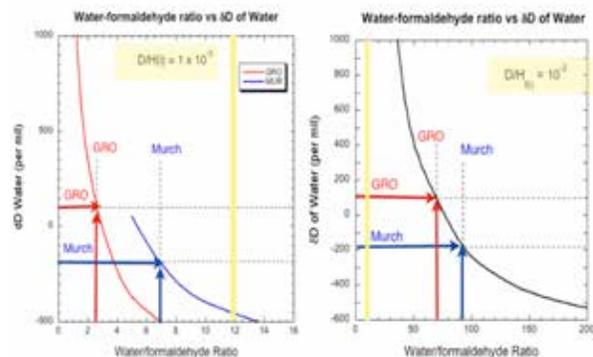


Fig3. Left, D-H exchange curves between IOM precursor ($D/H=10^{-3}$) and water ($D/H=-800$ ‰), Right D-H exchange between IOM precursor ($D/H=10^{-2}$). Points where D-H of IOM meets D-H of matrix water are indicated for GRO95577 and Murchison. Yellow line indicates the ratio of matrix water to IOM.

The point at which the D content of IOM equals that observed [1] then the D content of matrix water [3] is a function of the D-content of IOM precursor and water/IOM ratio. Starting with a D/H of 10^{-3} requires less water than currently exists in the matrix; with a D/H of 10^{-2} requires a water/IOM ratio of 70-90. Interestingly, a recent analysis of IOM formation suggests that CC's have lost most of their initial water [10], with initial Water/IOM ratios estimated to be ~ 70 . If this scenario is correct, it implies that a small amount of highly deuterated formaldehyde was the predominant carrier of D into the Solar System.

References: [1] Alexander et al. GCA, 71, 4380 (2007), [2] Hartogh et al. Nature, 478, 218 (2011), [3] Alexander et al. Science, 337, 721 (2012), [4] Herd et al. Science, 332, 1304 (2011), [5] Alexander et al. MAPS, 49, 503 (2014), [6] Cody and Alexander, GCA, 69, 1085 (2005), [7] Cody et al. PNAS, 108, 19171, (2011), [8] Kebukawa et al. ApJ 2013, [9] Yang et al. Icarus, 226, 256 (2014), [10] Kebukawa & Cody Icarus 248, 412 (2015).