ENRICHMENT OF DEUTERIUM IN INSOLUBLE ORGANIC MATTER FROM PRIMITIVE METEORITES: A SOLAR SYSTEM ORIGIN? L. Remusat[1,2], F. Palhol[3], F. Robert[2] and S. Derenne[1], [1] LCBOP-BioEMCo, CNRS-ENSCParis, France (sylvie-derenne@enscp.fr); [2]LEME, MNHN, CNRS, Paris, France ; [3]Lab. des Isotopes Stables, CRPG, CNRS, Vandoeuvre les Nancy, France.

Introduction: The origin of water and organic molecules in the early solar system has been under intense scrutiny since it was realized that these compounds were systematically enriched in deuterium relative to molecular hydrogen in the protosolar nebula (PSN). (D/H)PSN = 25 x10^{-6} i.e. δD = -840‰. For example, in the Orgueil meteorite [1], water has a D/H ratio of 160x10^{-6} or δD= +40‰ and some components of insoluble organic matter (IOM) are characterized by D/H ratio of 350 x10^{-6} or δD= +1250‰. An interstellar origin was considered for IOM based on its systematic enrichment in deuterium. However, the D/H ratio in IOM remains much lower than those measured in the organic molecules commonly observed in the dense interstellar medium (ISM; D/H≈ 10^{-2}). It has therefore been proposed that the IOM is indeed an interstellar product but that the IOM formed at temperatures much higher (120 K) than canonical ISM temperatures (10-20K) [2]. A lack of homogeneity in the isotope composition in the IOM. has also been invoked. This has been especially shown using step combustion experiments but did not allow determining if this non-homogeneity occurs at the molecular level. To address this question, it is necessary to assess compound specific isotope composition by combining gas chromatography and isotope ratio mass spectrometry (GC-irMS).

The IOM consists of small aromatic units highly substituted and cross-linked by short aliphatic linkages, which can link more than two aromatic units. In the present study, we have determined the D/H ratio of aliphatic and aromatic moieties in Orgueil IOM. Although aromatic moieties in chondritic IOM are known to be easily released by pyrolysis and have been widely studied [3], molecular information on the aliphatic linkages was only recently provided with the development of the ruthenium tetroxide oxidation technique [4]. This chemical degradation results in oxidation of the aromatic units and release of the aliphatic chains, mainly as dicarboxylic acids. Compound specific D/H isotope measurements can then be performed on both the pyrolysis products and on the acids after derivatisation into their trimethylsilyl (TMS) esters.

Results: Analytical procedures are described in [5]. Among the aliphatic compounds, the most abundant oxidation products namely butanedioic, methylbutanedioic, ethylbutanedioic, pentanedioic, 2- and 3-methylpentanedioic acids were analysed. The δD values of the aliphatic acids range from +801‰ (± 77‰) to +1270‰ (± 112‰), i.e. D/H ratios range from 280x10^{-6} to 350x$10^{-6.}$ Aromatic moieties, C_2- to C_4-benzene, C_0- to C_2-naphthalene, phenanthrene /anthracene, fluoranthene and pyrene, show slightly lower values than aliphatic moieties, with a range from +602‰ (± 24‰) to 1111‰ (± 46‰) (i.e. D/H ratios ranging from 250x10^{-6} to 330x10^{-6}).

Although δ^{13}C values of *soluble* compounds in Murchison meteorite and of pyrolysis products in IOM from Orgueil, Murray and Murchison meteorites have been shown to correlate with the carbon number, no correlation was observed between δD and either H/C ratio or the number of substitutions. As a result, no mechanism of hydrogen addition during synthesis can be proposed to account for these data. Nevertheless, the δD values of the products recovered by pyrolysis and chemical degradation can be supposed to reflect internal molecular isotopic heterogeneity.

Three types of organic groups (Fig. 1) hold most of the H in IOM. **Type 1** is benzylic H, i.e. H bound to the C atom α to an aromatic ring. **Type 2** is non benzylic aliphatic H. **Type 3** is aromatic H. In order to understand the δD distribution among the different products recovered during pyrolysis and chemical degradation, these 3 types of H were assumed to exhibit 3 different isotope compositions. For each analysed compound, the proportion of hydrogens of type 1, 2 and 3 was calculated, considering that the recovered products bear the isotope labeling of the starting macromolecule *before* any treatment.

The C-H bond dissociation energy differs for the above three types: Type 1 (benzylic) being characterized by a lower C-H bond dissociation energy than for the other aliphatic C-H bonds – Type 2- , the C-H aromatic bond (Type 3) dissociation energy being even higher. The higher this energy, the stronger the bond. Any exchange between hydrogen in IOM and an external reservoir is affected by the binding energy and C-H bond-breaking is a prerequisite to D-incorporation. So Type 1 H is supposed to be more exchangeable than Type 2, and Type 2 more exchangeable than Type 3.

Taking into account the number of H of each type in both the pyrolysis and oxidation products, the measured δD in each analyzed compound gives a mass balance equation with only three free parameters: the δD of Types 1, 2 and 3 hydrogen. By comparing

iteratively between calculated and measured δD values we determine δD of +1250‰ ±50‰ (i.e. *ca.* D/H=350.10^{-6}), +550‰ ±50‰ (i.e. *ca.* D/H=240.10^{-6}) and +150‰ ±50‰ (i.e. *ca.* D/H=180.10^{-6}) for hydrogen of Type 1, 2 and 3, respectively. Note that the adjustment of the 3 free parameters reproduces the measured δD of the 15 analyzed molecules, and thus that the numerical solution is strongly over-constrained. This does not preclude the presence of other minor types of organic H, having D/H ratio different from those of Types 1, 2 or 3. Note that the average δD of the three main types of H is below the bulk IOM δD value. This points to the presence in the IOM of a minor H component having a much higher D/H ratio than the classical chondritic value.

Discussion : The values we obtain for Types 1-3 hydrogen are surprising if we consider that IOM was an interstellar product, highly enriched in D, which has subsequently exchanged its hydrogen with a solar composition gas; i.e. a gas with relatively low D/H ratio. Indeed, in such a scenario, Type 1 hydrogen would be less enriched in D and Type 3 would be the most enriched in D, because Type 1 hydrogen is more easily exchanged. But exactly the reverse trend is observed in Fig. 2, where the D/H ratios of these 3 types of hydrogen are displayed as a function of the C-H bond dissociation energy along with a value for the water. Any type of isotopic exchange between IOM and a low D/H ratio component would have resulted in an opposite correlation. This correlation demonstrates that the exchange took place after the formation of the IOM with a D-rich reservoir.

We postulate that IOM was a PSN product. In this pristine IOM, the organic sites had D/H ratios with values lying somewhere between the PSN and the D/H ratio of water. After its synthesis, the IOM was transported into regions of the PSN where the physical conditions were comparable to the ISM i.e. a cold ionized medium where ion-molecule reactions could take place and where IOM acquired its D enrichment. In this respect, ionized molecules (such as the most abundant ion H_3^+) rapidly become enriched in D even at low T. Under these conditions, Type 1 hydrogens experienced a higher D exchange rate than Type 2, and Type 2 higher exchange rate than type 3, resulting in the observed relationship (Fig. 2). Because the water D/H ratio also lies on the correlation defined by the three types of organic hydrogen, water might have acquired its D enrichment under similar conditions.

Thus, the present data are consistent with a D enrichment of solar system molecular species at the surface of the turbulent protosolar disk ionized by UV light from the young Sun. If, as we suggest, these organic molecules are contemporaneous with our solar system, one can easily imagine that they are products of protostellar disks in general. Indeed, because the D/H ratio of meteoritic water is consistent with our model, these processes could be the origin of the deuterium enrichment in the inner solar system.

Conclusion : Molecular isotopic composition of hydrogen in IOM oxidation and pyrolysis products demonstrate that D is not homogeneously distributed in the meteorite IOM. The D/H ratios are strongly correlated with the C-H bond energy in their host molecules, the most exchangeable hydrogen atoms having higher D/H isotopic ratio. This excludes that IOM was originally a deuterium-rich interstellar product, later re-equilibrated with the PSN H_2 or in the carbonaceous chondrite parent body with the alteration water. We postulate a D-enrichment by exchange with a D-rich medium and after the IOM formation. This enrichment could have taken place at the surface of the protosolar disk. Chondritic water D/H ratio is explained by the same process. Such a scenario has the potential of explaining the large-scale deuterium enrichment of the inner solar system.

References: [1].F. Robert and S. Epstein (1982) *GCA, 46*, 81-95. [2]. F. Robert. (2002) *Planet. and Space Sc, 50*, 1227-1234. [3]. L. Remusat et al. (2005) *GCA* , *69*, 3919-3932. [4]. L. Remusat et al. (2005) *GCA* , 69, 4377-4386 [5] L. Remusat et al. (in press) *Earth Planet. Sci. Lett.*

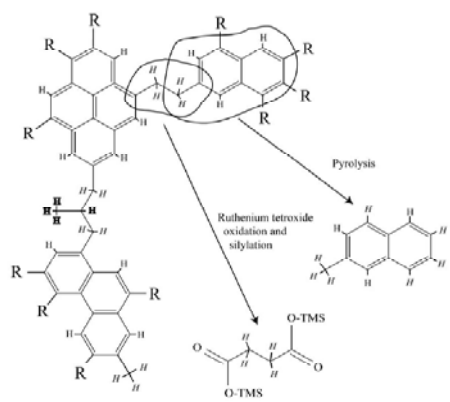

Figure 1: Model structure showing the 3 types of H

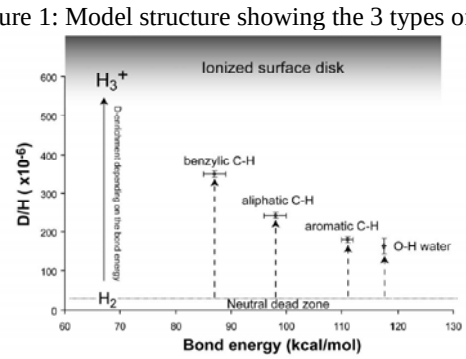

Figure 2: D/H as a function of CH bond dissociation