

MOLECULAR IDENTIFICATION OF THE CARRIER OF THE D-ANOMALY IN INSOLUBLE ORGANIC MATTER OF ORGUEIL METEORITE: REVISING THE ORIGIN OF THE IOM?

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Introduction: Insoluble organic matter (IOM) in primitive carbonaceous meteorites has preserved its composition and its isotopic heterogeneity since the Solar System formed ca. 4.567 billion years ago. IOM is known to be enriched in deuterium, with D/H ratios $> 300 \times 10^{-6}$ [1]. It is also characterized by a high degree of isotopic heterogeneity, as demonstrated by the molecular distribution of the D [2] and by the observation of D-rich “hot spots” in NanoSIMS ion microprobe images [3]. Understanding the origin of this heterogeneity represents a fundamental challenge with implications for the origin and distribution of organics in the interstellar medium and in the protoplanetary disk from which our planetary system formed. Moreover, it can have implication on the origin of life in the solar system, as IOM was delivered to the early Earth and may have provided the molecular precursors to life.

Molecular characterisation of IOM reveals that it is constituted by rather small aromatic units, highly substituted [4, 5] and linked to each other by short and branched aliphatic linkages [6]. Pyrolysis and ruthenium tetroxide oxidation release the building blocks of IOM which can be isotopically (D/H) analysed by gas chromatography-isotope ratio mass spectrometry. This has led to the identification of distinct D-compositions at the molecular level [2]. Three different types of H were distinguished based on their C-H bond energy, which is related to their position within the macromolecule. These are aromatic, aliphatic and benzylic H (fig.1). This study reveals that, surprisingly, the weakest C-H bond is the most enriched in D.

Recently, NanoSIMS imaging of IOM has revealed the occurrence of D-rich hot spots [3]. Regions of some hundreds of nm to 1 μ m appear to have D/H isotopic ratios ranging from 460 to 720 $\times 10^{-6}$ (fig. 2A). This is 2 to 3 times the bulk D/H. These areas do not exhibit special chemical characteristics (e.g. C/H or N/C ratios) compared to the bulk, indicating that they do not consist of organic matter significantly different from the bulk IOM itself.

Electron paramagnetic resonance (EPR) spectroscopy allows the identification and the quantification of organic radicals in the IOM [7]. This technique reveals that organic radicals exhibit a specific behavior in chondritic IOM. In contrast to terrestrial organic matter, radicals in IOM are heterogeneously distributed. They appear to be concentrated in small areas with higher local concentration than the bulk concentration. This pattern

leads to the assumption that organic radicals are implied in the formation of the D-rich hot spots. Furthermore, pulsed EPR has shown that hydrogen in the benzylic bond of organic radicals has a deuterium to hydrogen (D/H) ratio of $1.5 \pm 0.5 \times 10^{-2}$ in Orgueil IOM, which is the highest solar system D/H ratio ever reported [8].

Experimental: H, D along with ¹²C, ²⁶CN and ¹⁸O images of Orgueil IOM were acquired at the same time and the same location with the NanoSIMS 50 installed at the Museum National d’Histoire Naturelle. The images were analysed thanks to l’image software, developed by L. Nittler, allowing the determination of ratio images (fig. 2). The instrumental fractionation, determined from a standard charcoal, was corrected for.

An upper threshold was applied to the image to erase the hot spots and to determine the isotopic ratio of the organic matter that does not exhibit the isotopic anomaly of the D-rich hot spots (fig. 2B).

Results: By combining pulsed EPR data with quantitative image analysis recorded at a high spatial resolution with the NanoSIMS, we are able to prove that the organic radicals can account for the deuterium excess in the IOM D-rich “hot spots”. First, by considering the local radical concentration in radical rich regions and the D/H isotopic ratio of these radicals, it is easy to determine that the D/H of these regions is higher than 500×10^{-6} . The only areas where so high D/H values occur are the D-rich hot spots. Second, the surface covered by the D-rich hot spots (15-38%) is broadly consistent with the volume estimation of the radical-rich areas (20%). It must be noted that thermally altered IOM do not exhibit D-rich hot spots, consistent with the thermal instability of the organic radicals.

D/H isotopic ratio in IOM can be considered as a mixing between organic radicals and radical free organic matter. Then a simple mass balance equation can be defined : $(D/H)_{\text{bulk}} = (D/H)_{\text{radicals}} \times (H_{\text{radicals}}/H_{\text{total}}) + (D/H)_{\text{radical-free}} \times (1 - H_{\text{radicals}}/H_{\text{total}})$. $(D/H)_{\text{radicals}}$ is given by pulsed EPR, all the other isotopic ratios are determined from NanoSIMS data. Then, this equation offer the determination of $H_{\text{radicals}}/H_{\text{total}}$, which can also be determined independantly by EPR. Our estimate from NanoSIMS images lies between 1.65 and 2.9 $\times 10^{-3}$ in agreement with the EPR estimation ($3.2 \pm 1.2 \times 10^{-3}$, [7]). This results implies that D-rich hot spots can be attributed entirely to organic radicals.

The same mass balance, applied to D-rich hotspots, leads to a concentration $(H_{\text{radicals}}/H_{\text{total}})$ in average 6.5

times higher, in good agreement with the EPR observation that local radical concentration is 6 times higher than the bulk radical concentration in Orgueil IOM [7].

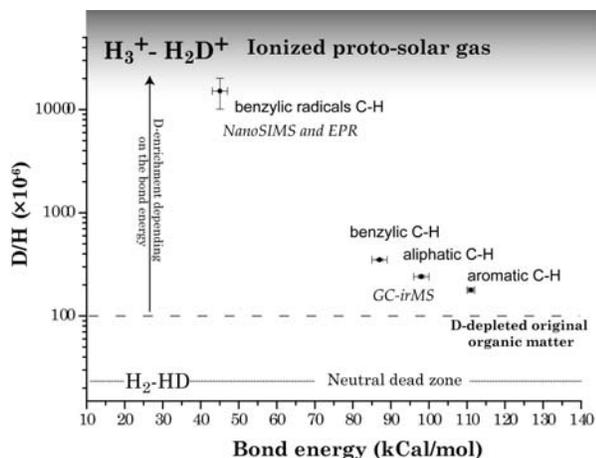


Figure 1: D/H isotopic ratio versus the C-H bond energy for different types of H depending on their location at the molecular scale. The observed trend can only be explained by the D-enrichment of an organic macromolecule initially depleted in D. This process is a kinetic exchange as the weak C-H bond is supposed to exchange faster than the strong ones [10].

Discussion: We have determined that the organic radicals are the carrier of the isotopically anomalous hydrogen in IOM isolated from the carbonaceous chondrite Orgueil. Furthermore, as shown by figure 1, the radicals fall on a well-defined trend between D/H ratio and C-H bond energy [2], consistent with a new interpretation of the hydrogen isotopic variations in solar system organics according to which pre-existing organics exchange their D with highly deuterated gaseous molecules, such as H_2D^+ or HD_2^+ in the early stages of the solar system. The distributions of these deuterated species is now being mapped in protostellar disks [9]. Moreover, experiments under UV irradiations tend to reproduce the trend evidenced in fig. 1 [10].

This conclusion runs contrary to previous interpretations, according to which the IOM is an interstellar product reprocessed in the protosolar gas and that D-rich hotspot are relics of pristine interstellar organic matter, which escaped solar nebula or parent body processes. The D-isotopic signature could instead be a consequence of early irradiation of the solar nebula gas by the young sun.

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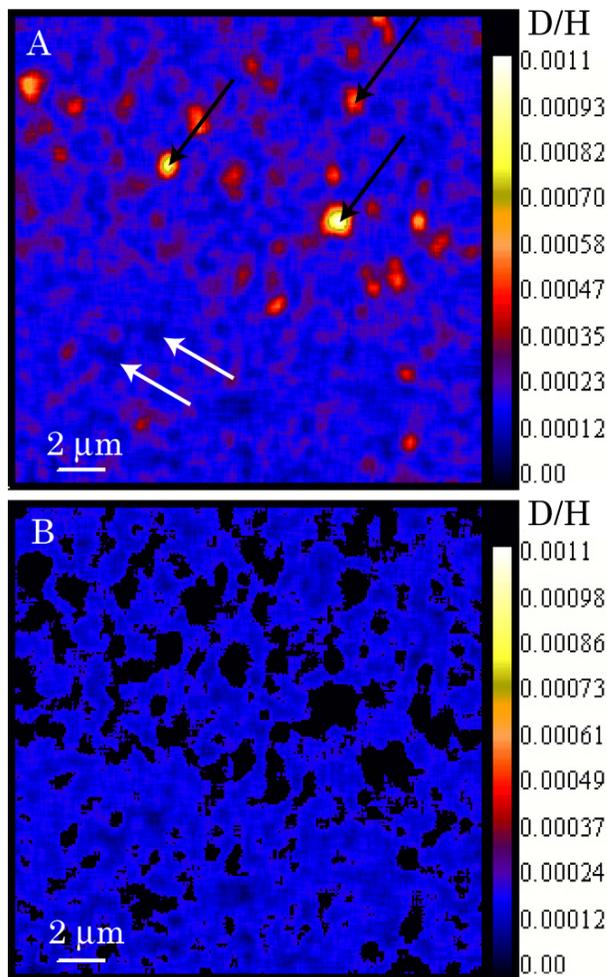


Figure 2: NanoSIMS images of the ratio D/H in Orgueil IOM. Each image is a square of $20 \times 20 \mu m^2$. A: Orgueil IOM exhibits D-rich hotspots (dark arrows) and also small regions depleted in D, so called cold spots (white arrows). These cold spot could be related to the original D-depleted organic matter. B: if an upper threshold is applied, the D-rich hotspots can be removed leading to an image of the “radical free” organic matter.