EXTREME DEUTERIUM ENRICHMENT IN ORGANIC MATTER FROM COMETARY ANTARCTIC MICROMETEORITES.

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Introduction: Hydrogen isotopes in extraterrestrial materials provide unique insights on the origin of organic matter (OM) in the solar system. Large deuterium (D) enrichments have been reported in micrometer-sized regions ("hotspots") of interplanetary dust particles [1, 2], and insoluble organic matter (IOM) extracted from primitive meteorites (carbonaceous and ordinary chondrites) [3]. Although an heritage from cold interstellar chemistry has often been favoured to explain these isotopic anomalies, both the origin of the organic matter (OM) and the location of its deuteration remain largely undetermined [4, 5].

Samples and methods: Since the pioneering work of M. Maurette in Adélie Land [6], large collections of micrometeorites (MMs, interplanetary dust particles with sizes ranging from ~ 20 to 1000 µm) have been collected in Antarctic ice and snow [7, 8]. Since 2000, we have collected unaltered micrometeorites from central Antarctic surface snow in the vicinity of the permanent French-Italian CONCORDIA station located at Dome C [9]. MMs studied here were extracted from ultra-clean snow in a trench at depths ranging from 3.3 m to 4.3 m, corresponding to fall on Earth between 1955 and 1970. Among the recovered fine-grained micrometeorites, we selected particles exhibiting a fluffy fine-grained texture with no evidence of heating during atmospheric entry (i.e. vesicles and/or magnetite rim) [10]. A scanning electron microscope survey of this subgroup revealed 6 particles with sizes between 40 x 80 µm and 110 x 275 µm that are exceptionally rich in carbon, hereafter referred as UltraCarbonaceous Antarctic MicroMeteorites (UCAMMs) [11, 12]. We characterrized the structure and mineralogy of two UCAMMs, DC06-09-19 and DC06-09-119 (hereafter quoted #19 and #119) by field emission gun - scanning electron microscopy and Transmission Electron Microscopy (TEM). Using the NanoSIMS-50 National Facility at LEME-MNHN (Paris), we performed isotopic imaging of their C, H and O isotopic compositions.

Results: UCAMMs # 19 and # 119 consist of fine scale assemblages of OM and submicron to micron mineral phases including Mg-rich olivines and pyroxenes, Fe-sulphides and Mg-rich carbonates [13]. Carbon is dominantly present in the form of OM and represents from 60% up to 80% of the particle's volume. The presence of both Fe-sulphides and carbonates in UCAMMs indicate that they experienced little to no modification upon atmospheric entry and during their terrestrial residence at low temperature ($-75°C < T < -25°C$) in the surface snow of Dome C [11, 14].

Carbon and oxygen maps exhibit homogeneous isotopic distributions close to solar values mostly consistent with those previously reported in bulk meteoritic IOM [4]. By contrast, both UCAMMs exhibit extreme deuterium excesses (Fig. 1) which are associated with carbon rich areas. Contrary to previous analyses of meteoritic IOMs where high D/H ratios are confined to sub-micron hotspots having a negligible contribution to the bulk IOM D/H value [3, 15], the bulk D/H ratios of UCAMMs is controlled by the D-rich regions. The regions in UCAMMs with $D/H > 10^{-3}$ ($\delta D > 6400$ ‰) extend over 139 µm² and 208 µm² in #19 and #119, respectively, accounting for 27% and 83% of the analyzed surface. It is, to our knowledge, the first time that such deuterium enrichments are observed over such large areas.

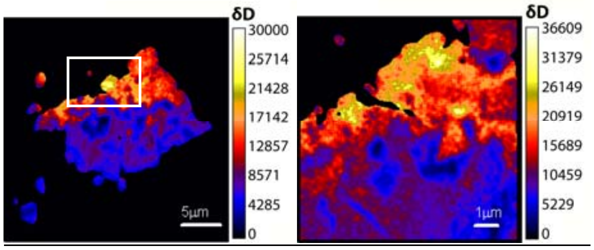

Figure 1 : (left) hydrogen isotopic mapping of an ultracarbonaceous micrometeorite fragment crushed on gold foils (DC06-09-119) ($\delta D = [(D/H)_{sample}/(D/H)_{SMOW}-1]*1000$); (right) detail of the D-rich zone (box in left figure).

Discussion: In a D/H vs C/H representation mixing between two components appears as linear correlations [e.g 2]. The data for sub-micron units of the UCAMMs given in Fig. 2 reveal a high density of data points on a broad linear trend hereafter referred to as the *OM-baseline* (see Fig 2). All data above the *OM-baseline* are included in a triangular shaped area with an apex located above $D/H = 5 \times 10^{-3}$.

The high density of data points defining the *OM-baseline* can be explained by the mixing of an OM component similar to bulk carbonaceous chondrite IOM [4] ($C/H \sim 1$ to 2 and $D/H \sim 3 \times 10^{-4}$) with a carbon-rich endmember with C/H ~ 10 and D/H ~ 1.5 x 10^{-3}. High resolution TEM and Micro-Raman analysis of UCAMM complementary fragments indicate that their constituent OM is highly disordered [13]. We observed graphitic nanodomains with sizes of thousand nm² but their low abundance (< 250 ppm) cannot account for the carbon-rich component (C/H ~10) that is more likely to be highly disordered carbon. Using data from [4], we observe that bulk IOM from both CI and CM chondrites and unaltered ordinary chondrites are plotting along the *OM-baseline* defined here, indicating that the mixing defined above occurs at all scales.

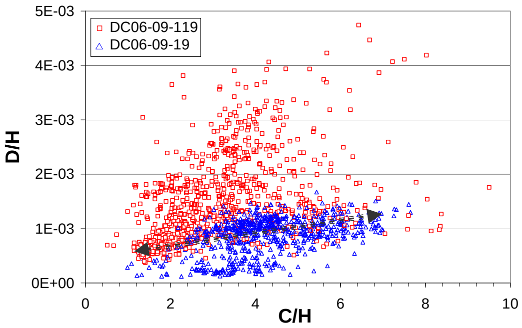

Figure 2 : D/H vs C/H of submicron zones on particle # 19 (in blue) and # 119 (in red). The dotted arrowed line materializes the *OM-Baseline* (see text).

The data above the *OM-baseline* can be explained by the interaction of a precursor located on the *OM-baseline* with an extreme D-rich endmember with D/H well above 5 x 10^{-3}. The origin of such large deuterium enrichments has long been attributed solely to interstellar chemistry where even higher D/H ratios are observed in the gas phase of cold molecular clouds [16]. In that picture, the isotopic anomalies carried by interstellar OM, like presolar grains, survived until their incorporation in interplanetary dust. If the D-rich OM analysed here is of interstellar origin, UCAMMs contain one of the least altered interstellar heritage ever reported. However, we note that the mineral phases intimately associated with OM in both #19 and #119 do not exhibit any oxygen isotopic anomaly suggestive of the presence of any presolar grains. Recently, the analysis of IOM from Orgueil and Murchison revealed distinct D enrichments at the molecular level, suggesting an isotopic exchange between an isotopicaly solar (or-near-solar) OM and a D-rich local reservoir within the nascent solar system [5]. Moreover, organic radicals with D/H = (1.5 ± 0.5) x 10^{-2} have been reported in Orgueil carbonaceous chondrite [17]. It is now well established that young stellar objects exhibit singly and multiply deuterated molecules with abundances of 10 to 50% relative to their hydrogenated counterparts [18]. In such objects, the deuteration is triggered by the fast ion-neutral reaction between H_3^+ ions and the HD reservoir to form H_2D^+, HD_2^+ and D_3^+ [19] and large deuterium enrichments are obtained in the cold mid-plane regions where heavy-element bearing molecules (mainly CO that quickly reacts with H_2D^+) are highly depleted in the gas phase [20]. If the UCAMM OM deuteration indeed occurred within the solar system itself, these pristine objects provide a unique tool to probe the early history of the colder regions of the protoplanetary disk.

The high carbon contents of UCAMMs have no counterparts in meteorites and are similar to that of CHON particles from comet Halley [21]. Assuming an isotopic exchange with a reservoir having D/H ~ 10^{-2} and taking the reaction exothermicity values reported in [22], we obtain a maximum exchange temperature of T~ 50 K, that is compatible with a formation and preservation of the UCAMM in the cold regions where comets formed.

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