Evolution of the isotope signature of the Insoluble Organic Matter of the Orgueil meteorite under reducing conditions: comparison with the IOM of Ryugu samples.

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Despite similarities with the Insoluble Organic Matter (IOM) of the Orgueil meteorite, the IOM isolated from the Ryugu samples shows differences in its stable isotope distributions [1]. On one hand, the D/H ratio appears lower in Ryugu IOM compared to Orgueil IOM, isolated from samples of both chamber A and C: δD = 460 +/- 50‰ and 970 +/- 10‰ in Ryugu and Orgueil, respectively. On the other hand, N-isotope distribution is consistent in Orgueil and Ryugu IOMs. The difference in H isotopes is unexpected as it has often been proposed that aqueous alteration or terrestrial weathering would lower the IOM δD by exchange with D-depleted water on the parent body or with moisture during the contact with the terrestrial atmosphere [2, 3]. The IOM of the less altered (and freshly recovered) Ryugu samples is D-depleted compared to the heavily altered Orgueil meteorite. One possible hypothesis to face off this descrepancy is that the IOM isolated from the Ryugu samples has interacted with a D-depleted gaseous source on the asteroid [4]. As Ryugu grains returned by the Hayabusa 2 spacecraft were sampled at the surface of the asteroid, exposed to the molecular hydrogen of the solar nebula or the hydrogen contained in the solar wind that could modify local redox conditions, we have tested the hypothesis that the difference in isotope composition of the IOM in Orgueil and Ryugu was related to reduction processes, known to produce D-depleted hydrogen.

A sample of the Orgueil CI chondrite was experimentally set to evolve in reducing conditions during 50 hours at 300 and 500°C, and 500 hours only at 300°C. We allotted ~50 mg of powder sample for each temperature condition, and heated the sample under vacuum conditions (~10^{-6} torr) in the presence of iron powder placed beside the samples into the furnace to control the oxygen fugacity. Mineralogical characterization of the heated products revealed that phyllosilicates did not decompose in the samples heated at 300 °C even for 500 hours, but partially decomposed by heating at 500 °C [5]. Fe L-edge XANES analysis indicates that some reduction of Fe in the phyllosilicate-rich matrix occurred by heating at 300 °C for 50 h, confirming that reduction processes occurred during the experiment.

After the experiment, the experimental products were dissolved using the classical protocol for IOM isolation using HF/HCl. The IOM of the samples exposed at 300°C-50 h, 300°C-500 h, 500°C-50 h conditions were recovered and analyzed by NanoSIMS to investigate H and N-isotope distributions using a 16 keV primary Cs^+ beam. IOM grains were pressed on cleaned indium foil and gold coated (20 nm thick). During a first session, secondary ions of H^- and D^- were recorded to obtain δD images. The primary beam was set at 12 pA. We collected 256×256 pixel images covering 20×20 μm² with a raster speed of 1 ms/pix. Prior to each analysis, we applied a 25×25 μm² presputtering step using a 800 pA primary current during 10 minutes. The vacuum in the analysis chamber did not exceed 5×10^{-10} torr. In a second session, a 1 pA Cs^+ primary beam was used to record secondary ions of $^{12}CH^-$, $^{16}O^-$, $^{12}C_2^-$, $^{26}CN^-$ and $^{27}CN^-$ in multicollection mode to monitor $\delta^{15}N$ as well as N/C, O/C and H/C ratios. All other acquisition parameters were identical. We paid attention to match the same areas for H and N-isotope analyses. We mapped between 2000 and 2800 μm² of each experimental sample. Instrumental bias was checked using the unheated Orgueil IOM, a type 3 kerogen and a set of PS films having D/H ratios up to 8 times the natural terrestrial abundance. Data was processed using the L'image software developed by Larry Nittler (CIW).

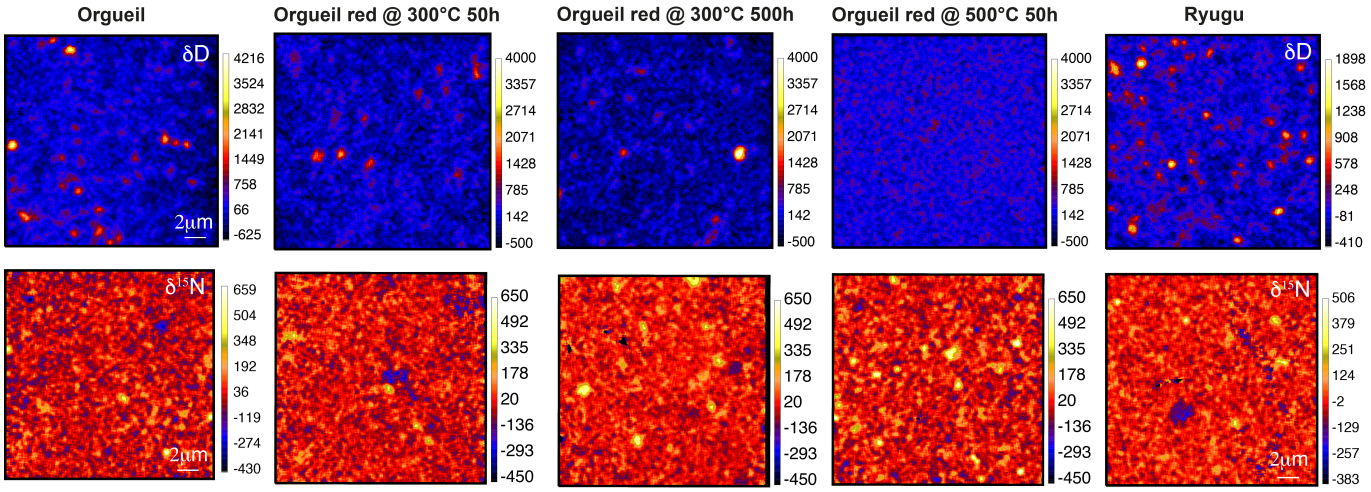

Figure 1. NanoSIMS images of H (top) and N (bottom) isotope distribution in the IOM of Orgueil, Orgueil reduced at 300°C for 50 and 500 hours and Orgueil reduced at 500°C for 50 h. NanoSIMS images of Ryugu IOM (sample from chamber C) are also reported (from [1]).

The bulk $\delta^{15}N$ of Orgueil IOM does not appear to be affected by the experimental conditions (Figure 1). Indeed, we determine bulk $\delta^{15}N$ = 25 +/- 7‰, 31 +/- 7‰ and 28 +/- 6‰ for the IOM of Orgueil300-50, Orgueil300-500 and Orgueil500-50, respectively, to compare with 28 +/- 2‰ for the unheated Orgueil IOM. In the meantime, the range of ^{15}N-enrichment in hotspots is within the same range in the IOM of experimental and unheated samples (211 +/- 23‰< $\delta^{15}N$ <1370 +/- 55‰). A few negative anomalies, called coldspots, also occur, with $\delta^{15}N$ around -200‰, in both unheated and experiment samples. It must be noted that the distribution of $\delta^{15}N$ is slightly shifted toward higher values for the IOM of Orgueil500-50. The elemental N/C ratio shows a continuous decrease from the unheated sample to Orgueil500-50, with N/C going from 0.035 to 0.018. The bulk δD of IOM decreases when Orgueil is subjected to reducing conditions; δD = 180+/- 87‰, 107+/- 45‰ and -22+/- 39‰ for the IOM of Orgueil300-50, Orgueil300-500 and Orgueil500-50, respectively, to compare with 913 +/- 100‰ for the unheated Orgueil IOM. Despite this clear depletion caused by reducing conditions, D-rich hotspots can still be observed in Orgueil300-50 and Orgueil300-500, though their distribution is clearly shifted toward lower values.

Overall, we observe that heating in reducing conditions results in a different isotope evolution compared to heating within anoxic conditions [6]. Indeed, we observe here a drastic D-depletion but the persistence of D-rich hotspots. In the case of heating in Ar, the D-depletion induced by heating up to 500°C was accompanied with the destruction of D-rich hotspots. Considering N and its isotopes, the experiment does not appear to influence the $\delta^{15}N$ (both for the bulk and distribution at the micron scale), as it was also observed after heating under Ar [5], but a clear decrease in N/C is evidenced, while it remains constant in the case of experimental heating under Ar.

This experimental result can support an original interpretation for the striking observation that the IOM of Ryugu samples is depleted in D compared to Orgueil while it seems less altered on the parent body and it is preserved from terrestrial weathering. As in the case of Ryugu IOM, the D-rich hotspots are present in experimentally reduced Orgueil samples. It may then be conceivable that the IOM sampled at the surface of Ryugu, being exposed to hydrogen from the solar nebula and the solar wind, could have been affected by strongly reducing conditions that have modified its H-isotopic composition without affecting much its molecular structure. Hence, the Orgueil IOM may represent the macromolecular reservoir stored in the interior of a Ryugu-like asteroid, preserved from reducing conditions that could have occurred at the surface.

References

[1] Yabuta H. et al. 2023. Science 379, eabn9057. [2] Alexander C. M. O'D. et al. 2017. Geochim. Cosmochim. Acta 71, 4380–4403. [3] Kerridge J. et al. 1987. Geochim. Cosmochim. Acta 51, 2527–2540. [4] Remusat L. et al. 2022. Abstract #1448. 53rd LPSC. [5] Amano et al. 2023. Sci. Adv. 9, eadi3789. [6] Remusat L. et al. 2019. Geochim. Cosmochim. Acta 263, 235–247.