

H- AND N-ISOTOPE DISTRIBUTIONS IN THE INSOLUBLE ORGANIC MATTER OF RYUGU SAMPLES. L. Remusat¹, M. Verdier-Paoletti¹, S. Mostefaoui¹, H. Yabuta², C. Engrand³, the Hayabusa2-initial-analysis IOM team, H. Yurimoto⁴, T. Nakamura⁵, T. Noguchi⁶, R. Okazaki⁷, H. Naraoka⁷, K. Sakamoto⁸, S. Watanabe⁹, Y. Tsuda⁸ and S. Tachibana¹⁰

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Introduction: Regolith samples of the carbonaceous asteroid 162173 Ryugu were returned by the Hayabusa2 spacecraft in December 2020. More than 5 g of samples were collected from two sampling sites. Preliminary investigation of selected grains from each sampling site has revealed the occurrence of an abundant macromolecular insoluble material, similar to that of carbonaceous chondrites [1]. Understanding the origin of organic matter on carbonaceous asteroids and its subsequent evolution due to secondary processes as well as space weathering is one of the prime goals of the Hayabusa2 sample-return mission [2].

Isotope composition of organic material found in extraterrestrial samples is a powerful proxy for tracking its origin and evolution during the solar system events [3,4]. The heterogeneity and diversity of organic grains in chondrites, micrometeorites and IDPs can be assessed by employing isotope and elemental imaging with the NanoSIMS [5,6].

To document the H- and N-isotope signatures of IOM contained in the Ryugu samples, we have used the NanoSIMS installed at the National Muséum of Natural History in Paris. We present here data acquired on the IOM isolated from grains of both chamber A and chamber C, which enclosed sample at the first and second touchdown sites, respectively. The comparison with the IOM of carbonaceous chondrites allows for evaluating the influence of space weathering and aqueous alteration on the IOM in carbonaceous asteroids.

Methods: Solvent extraction and HF/HCl leaching were employed to isolate the insoluble organic matter (IOM) from the intact aggregates A0106 and C0107 [1]. IOM samples were pressed on clean indium foil and gold coated (20 nm thick). δD and $\delta^{15}N$ images were recorded using a 16 keV primary Cs^+ beam. Secondary ions of $^{16}O^-$, $^{12}C_2^-$, $^{26}CN^-$, $^{27}CN^-$ and $^{32}S^-$ were analyzed to determine N/C, O/C and S/C ratios in addition to $\delta^{15}N$ images in a first session. Then H⁺ and D⁺ were recorded to obtain δD images in a second session. The primary beam was set to around 1 pA for N isotope and 12 pA for H isotope measurements, leading to a spatial resolution of about 150 nm and 300 nm, respectively. We collected 256×256 pixel images

covering 20×20 μm^2 with a raster speed of 1 ms/pix. Prior to each analysis, we applied a 25×25 μm^2 presputtering step using a 300 pA primary current during 15 minutes. During the session, the vacuum did not exceed 5×10^{-10} torr.

All the NanoSIMS data were processed with L'image software developed by Larry Nittler (CIW). Data were corrected using reference samples: terrestrial type 3 kerogens from Virginia, USA, and the Miocene Monterey formation, a charcoal, polystyrene samples of variable D/H ratios as well as the IOM of the Orgueil meteorite.

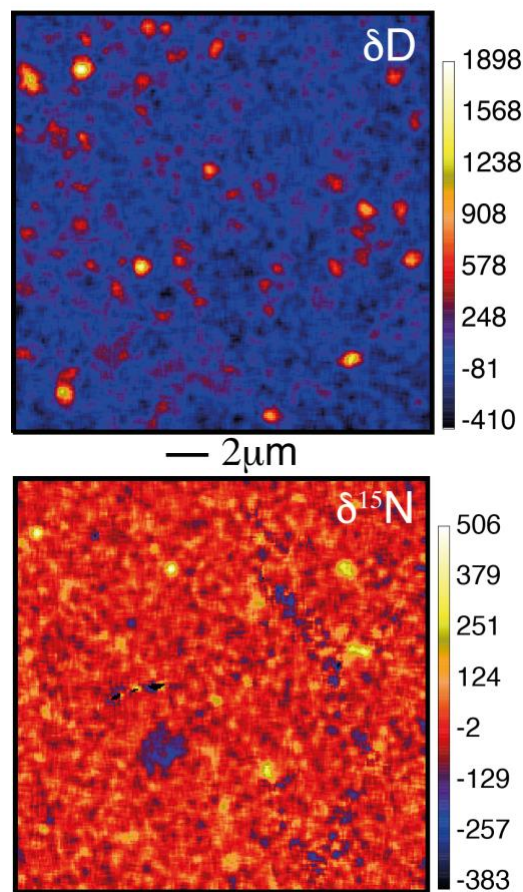


Fig. 1: H and N-isotope images of the IOM of the C0107 aggregate. We notice abundant D and ^{15}N -rich hotspots comparable to those observed in the IOM of CI, CM and CR carbonaceous chondrites.

Results: We have imaged between 2800 and 3200 μm^2 of the IOM of each chamber, for N- and then H-isotope investigations. Figure 1 reports δD and $\delta^{15}\text{N}$ images of the IOM from aggregate C0107.

N-isotope distributions: the bulk $\delta^{15}\text{N}$ is $+17.4\text{‰}$ and $+30\text{‰}$ for the IOM of chamber A and chamber C, respectively. These IOMs contain both ^{15}N -enriched and depleted carbonaceous grains, with $180\text{‰} < \delta^{15}\text{N} < 800\text{‰}$ for hotspots and $-380\text{‰} < \delta^{15}\text{N} < -180\text{‰}$ for coldspots. Hotspots define a Poisson distribution with a mode value of $+241\text{‰}$ and $+348\text{‰}$ for chamber A and chamber C, respectively.

Elemental ratios: Bulk N/C, O/C and S/C of Ryugu IOM are 0.035, 0.12, 0.032 and 0.027, 0.04, 0.025 for chamber A and chamber C, respectively. The N/C ratio of individual ^{15}N -rich and depleted grains are comprised between 0.01 and 0.07 (Fig. 2), with those in the IOM of A0106 being slightly more N rich. Similarly, O/C and S/C ratios are also slightly higher in A0106.

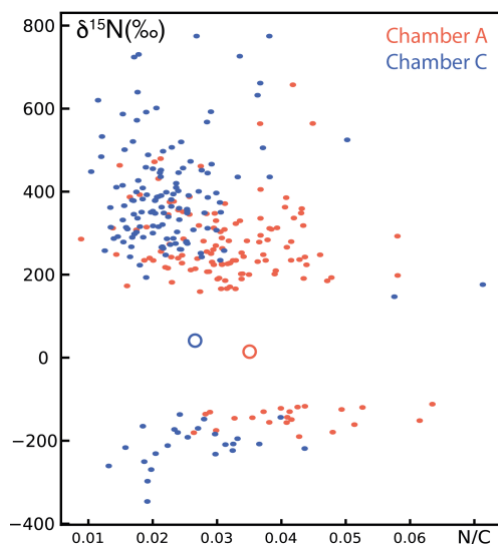


Fig. 2: N/C elemental ratio vs $\delta^{15}\text{N}$ of individual hotspots and coldspots in Ryugu IOM. Data for A0106 are reported in red and in blue for C0107. Uncertainties on $\delta^{15}\text{N}$ are smaller than 50‰. Open circles are bulk values for each IOM.

H-isotope heterogeneities: Ryugu IOM exhibits bulk enrichments in D with $\delta\text{D} = +306\text{‰}$ and $+440\text{‰}$ for chamber A and chamber C, respectively. Numerous D-rich hotspots, are observed, with $+600\text{‰} < \delta\text{D} < +6000\text{‰}$. They define a Poisson distribution, with a mode value of $+1030\text{‰}$ and $+1374\text{‰}$ for chamber A and chamber C, respectively. Of note, a few D-depleted organic grains are also observed ($0\text{‰} > \delta\text{D} > -200\text{‰}$).

Discussion: Subtle differences are observed between the IOM of chamber A and chamber C: the IOM is less enriched in heavy isotopes in chamber A, and more enriched in N, O and S. This may reflect some heterogeneity at the scale of the asteroid, or the influence of sampling depth, hence the influence of space weathering.

The bulk $\delta^{15}\text{N}$ in Ryugu IOM is commensurable to levels reported in CI chondrites, despite the occurrence of hotspots being more ^{15}N -rich in Ryugu [7]. The range of $\delta^{15}\text{N}$ covered by these hotspots is, however, consistent with the IOM of CM chondrites and Tagish Lake, but remains in the lower end of the hotspots in CR chondrites. N/C, O/C and S/C ratios are consistent with the IOM in hydrated carbonaceous chondrites, *i.e.* CI, CM and CR chondrites and Tagish Lake [8]. Although bulk values are significantly lower, the distribution of δD in Ryugu IOM is consistent with the IOMs in CI and CM chondrites. We did not observe enrichments as large as those reported in CR chondrites and in Tagish Lake [5,9]. The abundance of D- and ^{15}N -rich hotspots appears similar in Ryugu and carbonaceous chondrites.

Conclusion: Overall, the elemental and isotope compositions of the IOM in Ryugu are similar to those of hydrated carbonaceous chondrites, as expected if carbonaceous asteroids are a source of hydrated carbonaceous chondrites. The most notable difference is the bulk δD which is lower than in the IOM of hydrated carbonaceous chondrites. If we assume common organic precursors, this may indicate that the samples collected at the surface of Ryugu may have suffered from space weathering, inducing a decrease of D/H in organic compounds by H implantation. Presumably, this would not significantly affect ^{15}N -enrichments and elemental ratios. We cannot, however, rule out the influence of another process related to aqueous alteration.

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