

HYDROGEN ISOTOPIC EVOLUTION OF WATER AND ORGANIC COMPOUNDS ON CHONDRITIC ASTEROIDS. L. Piani^{1*}, L. Remusat², F. Robert² and H. Yurimoto¹. ¹Department of Natural History Sciences, Faculty of Science, Hokkaido University, Japan (*corresponding author: laurette@ep.sci.hokudai.ac.jp). ²IMPMC, UMR CNRS 7590 - Sorbonne Universités - UPMC - IRD - MNHN, France.

Introduction: Organic matter and hydrated minerals found in primitive meteorites (chondrites) are the remnants of organic and water components occurring in the protoplanetary disk 4.6 billion years ago. These phases show systematic but variable enrichments in the heavy isotopes of hydrogen comparing to the Sun. Although at least a part of these enrichments argues for low temperature ion-molecule reactions in the protoplanetary disk or in the molecular cloud, it is unclear how these isotopic signatures might have been modified by chemical reactions (kinetic fractionation or isotope exchanges) occurring on the asteroidal parent body.

Bulk chondrite measurements have recently revealed correlations between the D/H and C/H ratios measured in different chondrites selected from for two different groups of carbonaceous chondrites (CCs) (CM and CR types, [1]). These correlations show that the bulk hydrogen isotopic compositions of these CCs result from mixing between hydrated silicates and organic matter and that the hydrogen isotope intercepts correspond to the isotopic compositions of the initial water in each group [1]. This measurement put considerable constraints on the nature of the water sampled by carbonaceous chondrites in the inner protoplanetary disk, which turned out to be less D-rich than previously thought. Though, this bulk measurement does not allow chemical exchange(s) between water and organics on the asteroid to be decrypted. The isotopic composition of remaining water is still difficult to evaluate due to the low-scale mixing between hydrated minerals and organics [e.g. 2]. Moreover, the initial isotopic composition of organics remains poorly constrained.

In situ variations of hydrogen isotope compositions at the (sub)micrometer-scale in a large pool of chondrites can help to trace the chemical processes on asteroids. By constraining the extent of these processes and the differences between chondrite classes and groups, the composition of the initial water and organic components in the early solar system might also be more thoroughly constrained.

Methods: Using secondary mass spectrometers (NanoSIMS at MNHN-Paris and SIMS IMS-1280HR at Hokkaido University), we are probing the *in situ* variations of the hydrogen isotopes in the matrix of chondrites as well as on isolated organic components (IOMs). Different analytical methods by SIMS are used to estimate the D/H ratios of the different phases

(matrices and IOMs) and meteorites (ordinary chondrites and CCs) [3-7]. Isotopic measurements are also associated with other analytical and observational techniques, such as transmission electron microscopy or Raman and XANES spectroscopy. Here, we present and discuss our recent results together with recent bulk and *in situ* isotopic studies by others [8-13].

Results and discussion: *Carbonaceous chondrites.* In carbonaceous chondrites, the D-richest component corresponds to organic matter, while hydrated silicates have a comparatively D-poor composition. The IOM was shown to be isotopically heterogeneous with the occurrence of D-rich micron-sized hot spots and, to a lesser extend, D-poor cold spots [3, 9-10]. Hot and cold spots correspond to minute amount comparing to the total amount of IOM and are lost when the IOM is flash-heated at 600°C [3].

In situ isotopic measurements in the matrix of CI, CM and CR chondrites did not reveal any significant self-diffusion of deuterium between the D-rich organic matter and the depleted hydrated minerals that are surrounding them [4]. Nevertheless, in CR chondrites, *in situ* measurements have shown the presence of D-rich hydrated minerals [12-13] and high isotopic heterogeneities in the coarse-grained silicates at a micrometer scale [13]. CC water and organic compounds may have evolved through parent body processes and/or preserved some of the isotopic heterogeneities of their ice precursors.

We are now measuring the D/H and C/H ratios of matrices in different carbonaceous chondrites (CCs) at the scale of some micrometers by using SIMS IMS-1280 at Hokkaido University. Depending on the position of the primary beam in the matrix, the D/H and C/H ratios vary as a function of the relative amount of organic matter to hydrated minerals. The presence of a correlation between the two ratios (e.g. Fig. 1, data from [6]) shows that each phase bears its own isotopic composition.

It also allows the current water isotopic composition to be estimated for each chondrite as it corresponds to the intercept for C/H = 0. We recently found positive correlations for the measured D/H and C/H ratios in the CI chondrite Orgueil and in a set of CM chondrites including Murchison, Mighei, Murray and Cold Bokkeveld. The D/H ratio of water in these chondrites appears to be higher than the initial isotopic

value of water reported by [1] indicating an isotopic evolution of water in the asteroidal parent body.

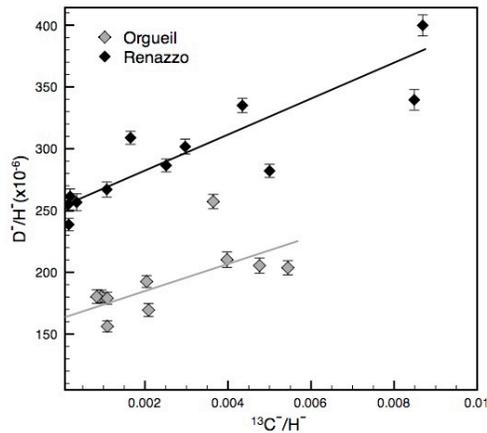


Fig. 1. Measured D/H ratio versus $^{13}C/H$ ratio for Renazzo and Orgueil matrices forming a positive linear correlation (black and grey lines). Adapted from [6].

Ordinary chondrites. We have developed a method by NanoSIMS to uncover the D-richer component in the fine-grained matrix of chondrites containing a mixture of organics and hydrated silicates [5]. We found hydrated silicates with extremely variable D/H ratios in the ordinary chondrite Semarkona with δD_{SMOW} from -40 to as high as +10,000‰ [6]. Organic matter in this chondrite is comparatively less D-rich ($\delta D_{SMOW} \approx 2300$ ‰). Our results argue for a limited isotopic exchange between organic matter and water. They also indicate that a D-rich reservoir of water has existed in the protoplanetary disk and could also explain the D-rich water found in comets [6].

In the IOM isolated from ordinary chondrites (Semarkona LL3.0, Bishunpur LL3.15 and Grosvenor Mountains 95502 L3.2 (GRO 95502)), very few micron-scale D-rich anomalies were found in comparison with CC IOMs [7] consistent with earlier measurements done in Krymka (LL3.2) IOM [11]. However, the most pristine chondrite (Semarkona and Bishunpur) IOMs seem to be constituted of at least two isotopically distinct components at a scale of several microns. A flash heating experiment was conducted on the IOM of GRO 95502 at 600°C: its D/H ratio drastically increases while the opposite trend was observed for the CC IOM (Fig. 2) [3, 7]. It thus seems that at least a part of the IOM accreted by the ordinary and carbonaceous chondrite parent bodies was different: the D-rich component of the ordinary chondrite IOM is thermally recalcitrant and remains after heating, resulting in a global increase of the D/H ratio. It does not seem necessary to involve exchange between a D-rich

water and IOM to explain the enrichment in D of ordinary chondrite IOM with metamorphism [11].

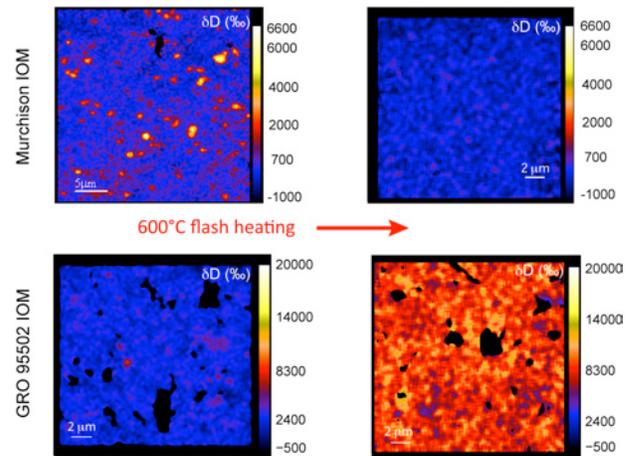


Fig. 2. Comparative evolution of δD NanoSIMS images for the carbonaceous chondrite Murchison and the ordinary chondrite GRO 95502 IOM upon 600°C flash heating, from [7] with data for Murchison from [3]. While the IOM of the CC Murchison has lost its D-rich hotspots after flash heating, the IOM of the ordinary chondrite GRO 95502 becomes D-richer.

A preliminary comparison of carbonaceous and ordinary chondrite hydrated mineral and organic matter characteristics seems to indicate a difference of precursors for at least a part of their water- and organic-bearing components. In carbonaceous chondrites, the parent body alteration seems to have efficiently enhanced and homogenized the isotopic composition of the water. The effect on organic matter remains unclear. In ordinary chondrites, the thermally recalcitrant organic component and the huge isotopic heterogeneities of hydrated minerals suggest that these chondrites have, for a part, accreted singular materials, that were not sampled by the carbonaceous chondrites.

References: [1] Alexander et al. 2012, *Science*, 337, 721–3 [2] Le Guillou et al. 2014, *GCA*, 131, 368–392 [3] Remusat et al. 2009, *Astrophys. J.* 608, 2087–2092 [4] Remusat et al. 2010, *Astrophys. J.* 713, 1048–1058 [5] Piani et al. 2012, *Anal. Chem.* 84, 10199–206 [6] Piani et al. 2015, *EPSL* 415, 154–164 [7] Remusat et al. 2016, *EPSL* 96, 319–335 [8] Alexander et al. *GCA*, 2007, 71, 4380–4403 [9] Nakamura-Messenger et al. 2006, *Science* 314, 1439–42 [10] Busemann et al. 2006, *Science* 312, 727–730 [11] Alexander et al. 2010, *GCA* 74, 4417–4437 [12] Deloule and Robert 1995, *GCA* 59, 4695–4706 [13] Bonal et al. 2013, *GCA* 106, 111–133.