A DUAL ORIGIN FOR WATER IN THE CM CARBONACEOUS CHONDRITES. L. Piani1*, H. Yurimoto1 and L. Remusat2. 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: Hydrated minerals and organic matter (OM) found in chondrites are the remnants of primordial reservoirs of volatile elements present in the protoplanetary disk 4.6 billion years ago.

Among primitive chondrites, CM-type carbonaceous chondrites constitute a well-identified chemical group that presents a wide range of hydrothermal alteration degrees on their asteroidal parent body and may be one of the dominant sources of meteoritic material fallen on Earth [1]. They contain significant quantity of hydrated minerals and OM intertwined at a sub-micrometer scale in their fine-grained matrix [2-3]. CM chondrites are thus valuable samples to study both the origin and the preservation of the primordial reservoirs in the protoplanetary disk and in asteroids.

Hydrogen isotopes can be used to trace the chemical processes involving water and/or OM on parent bodies, and to discuss the origin of accreted materials on asteroids and planets [4 and references therein].

In this study, we analyzed the D/H and C/H ratios in the fine-grained matrices of different CM chondrites at the scale of some micrometers by secondary ion mass spectrometry (SIMS). Depending on the position of the primary beam on the matrix, the D/H and C/H ratios vary as a function of the relative amount of hydrated minerals to OM. Since the D/H ratio is higher for organics than water in CM chondrites [2], correlations between the D/H and C/H ratios, due to the local variations of proportions between hydrated minerals and organics, can be used to estimate the D/H ratio of water in each chondrite [5-6]. Differences in the D/H ratio of water between CM chondrites having different alteration degrees are used to examine the extent of water-organic isotope exchanges, to discuss the conditions and/or the duration of the alteration process and to assess the initial D/H ratio of primordial volatile reservoirs.

Materials and methods: Sub-millimeter pieces of 6 CM chondrites (from the most altered to the least altered: Sayama CM2, Cold Bokkeveld CM2.2, Murray CM2.4, Mighei CM>2.4, Murchison CM2.5, Paris CM2.7-2.9) were pressed in indium foils. As the Paris chondrite contains local differences in its alteration degree [7], both fresh and more altered areas were collected and mounted separately. Fine-grained matrix areas were then selected under optical and electron microscopes. The SIMS IMS1280-HR at Hokkaido University was used to measure their D/H and C/H ratios on areas of 10 x 10 µm². The samples were sputtered by a 10 keV Cs⁺ primary beam and H⁻, D⁻, 13C⁻ and 29Si⁻ ions were collected using electron multipliers in two different sessions of analyses (in Dec. 2015 and Oct. 2016). A 2σ reproducibility of ≤ 90‰ for the D/H ratio was obtained on the terrestrial serpentine and kerogen standards.

Results and discussion: Positive correlations between the measured D/H and C/H ratios were obtained in all CM chondrite matrices (Fig. 1 A and B). The Paris chondrite shows the highest scattering around the D/H vs. C/H trend.

Figure 1. Measured D/H and C/H ratios in the matrices of the different CM chondrites studied: (A) measurements per
formed in Dec. 2015, (B) measurements performed in Oct. 2016. All CM chondrites present a positive correlation between the two ratios.

For all CMs but Paris, the positive correlations indicate that their hydrogen isotopic compositions can be explained by a two-endmember mixture between a D-poor water and a D-rich OM. Surprisingly, the mixing trends have similar slopes and intercepts within errors in all of these CM chondrites, in spite of their different alteration degrees (Fig. 1.A and Fig. 1.B for Sayama). Using the zero intercept of the correlations, we have estimated the D-poor water isotopic composition to be of $\delta D = -350 \%$ in each chondrite.

In Paris, the least altered lithologies show a clear and systematic D-enrichment comparing to other CMs and some C-rich points, while the more altered lithologies tend to have an hydrogen isotopic distribution and a C/H ratio closer to the other CMs (Fig. 1.B).

The D-richer trend obtained in the least altered lithologies of Paris compared to the more altered lithologies and to the other - more extensively altered - CMs ruled out the possibility that significant isotope exchanges have occurred between OM and water during the parent body alteration. Indeed it should have enhanced preferentially the D/H ratio of water by interaction with the D-rich OM in the more altered lithologies.

**Origin of the D-enrichment in Paris:** In order to understand the D-enrichment (and to a lesser extend C-enrichment) in the least altered lithologies of the Paris matrix, several hypotheses are envisaged.

Considering that the CM parent body was homogeneously accreted, parent body processes should be evoked to explain the H isotopic peculiarities of Paris. A difference in the oxidation degree between Paris and the other chondrites could be the reason of a higher degree of $H_2$ loss leading to substantial D-enrichments by Rayleigh-type process comparing to the other CMs. Escape of $^{13}C$-depleted methane during aqueous alteration has already been proposed to explain the carbon isotope patterns in carbonates [8]. However such an higher oxidation state is not obvious in the Paris chondrite (e.g. presence of tochilinite or unaltered metal in the least altered parts). Models involving rapid fluid ($H_2$ gas and liquid water) transport to the external part of the parent body, such as recently proposed by [9], could also lead to an heterogeneous redistribution of water and, potentially, of hydrogen isotope fractionation. However, the high alteration temperatures recently estimated for alteration fluids from the oxygen isotopic composition of carbonates in CM chondrites [10] and the low permeability of CM materials [11] may limit the hydrogen isotope fractionation and fluid transport.

The D-rich (and C-rich) matrix of Paris could also be explained by the presence of a tiny amount of a third mixing component: a D-rich water accreted as ice, independently on the D-poor water and OM. A third component in the mixing would also explain the scattering around the D/H vs. C/H trend in Paris. This D-rich water endmember is not significantly represented in other CM chondrites, possibly because the amount of the D-poor water is higher and hides the third, less abundant component. The presence of two sources of water in the Paris chondrite is consistent with recent carbonate oxygen isotope measurements [12]. Indeed, an 8% contribution of an interstellar-like water ($^{16}O$-poor and probably D-rich) is proposed to explain the oxygen isotope composition of several $^{16}O$-poor calcites found in Paris and another CM chondrite LON 94101 [12].

Our results show that the least altered lithologies of Paris have preserved the signature of a D-rich water component, in addition to the D-poor water and OM components seen in more altered lithologies of Paris and in other CMs. These three components could be pre-accretional and come from independent reservoirs of the disk.