REDISTRIBUTION AND EVOLUTION OF ORGANICS DURING AQUEOUS ALTERATION: NANOSIMS-SXTM-TEM ANALYSES OF FIB SECTIONS FROM RENAZZO, MURCHISON AND ORGUEIL. C. Le Guillou[1], L. Remusat[2], S. Bernard[2] and A. J. Brearley[1]. [1]Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87106, USA (corentin.san@gmail.com).[2]Laboratoire de minéralogie et de cosmochimie du Muséum, CNRS/MNHN, Paris, France.

Introduction: The physical nature of the Organic Matter (OM) at the time of accretion in chondrites, as well as its subsequent modification during asteroïdal aqueous alteration, can provide clues to the origins of this material and its isotopic evolution. [1] suggested that OM in CR carbonaceous chondrites was accreted together with water ice and was then redistributed in the immediate surroundings by liquid water. These interactions could have affected the carbon speciation of the OM [2, 3]. To investigate this hypothesis further, we have studied 3 meteorites covering a range of degrees of aqueous alteration from type 2 to type 1: Renazzo (CR2.0), Murchison (CM2) and Orgueil (CI).

Insoluble OM in CR chondrites contains the highest deuterium and ^{15}N anomalies, as well as the highest aliphatic to aromatic ratio known [2, 4]. [5] showed that they also contain a metastable amorphous silicate in their matrices, an indicator of very limited aqueous alteration and thermal metamorphism. For these reasons, CRs are the optimum meteorites for studying the best preserved OM. Murchison and Orgueil have been more altered, probably under different temperature conditions and/or water:rock ratios. We want to investigate how OM and secondary alteration phases are distributed and how carbon speciation has evolved along aqueous alteration. We are also investigating the relationship between OM particles with various D/H signatures and their immediate mineralogical environment, to test the hypothesis that chondrites initially sampled a mixture of OM particles with heterogeneous isotopic characteristics [6].

Experimental: Fragments of matrix, pressed in indium, were analyzed by NanoSIMS to locate the OM grains and measure their D/H compositions *in situ* [6]. Two grains from each sample are then extracted by the focused ion beam (FIB) technique. FIB sections are first measured by scanning transmission X-ray microscopy (STXM) at the carbon K-edge prior to transmission electron microscopy (TEM) study, to avoid any possible electron irradiation damage. We also used energy filtered TEM images at the carbon edge to locate the OM at the nanoscale in the FIB sections after STXM measurements.

Results: In Renazzo, the matrix was studied for the first time at the TEM scale. Surprisingly, it strongly resembles the material described previously in CR3.0 chondrites [1, 5]. Indeed, we found a mixture of Fe-rich amorphous silicates, phyllosilicates, sulphides and OM grains. This indicates that despite the higher alteration degree, the amorphous silicate can be preserved. As described by [1] in MET00426 (CR3.0), the OM is mainly present as particles clearly separated from the silicates. In addition, some of the grain boundaries between the silicate and the sulphides are filled with OM. Finer-grain material (<10 nm) can also be found more intimately mixed with the phyllosilicates. The identified deuterium-rich grains have a rounded morphology. The first one has a resemblance to a nanoglobule but don't show void in the middle. The second one is larger (2-3 µm) and extends into a crack.

The XANES characterization of these individual particles is similar to spectra published elsewhere for other meteorites (Orgueil, Murchison, Ivuna) [7, 8], and show an aromatic peak (284.7 eV), a C=O peak (286.3 eV) and a –COOH peak (288.5). Spectra are mostly homogeneous throughout the section.

In Murchison and Orgueil, the situation is clearly different and our results are quite consistent with the work of [3] done by TEM-EELS on CI. Deuterium-rich grains are also rounded individual particles but OM is found at a much smaller scale throughout the sections compared with Renazzo OM, finely intermixed with nano-phyllosilicates (<10 nm).

As expected, the mineralogy in the Murchison FIB sections consists mostly of coarse (several hundreds of nanometres) Fe-cronstedtite grains and nanometer-sized grains of Mg-rich serpentine (Fig. 1). In Orgueil, in addition to Fe-oxides, most of the material is made of fine grained (<50 nm) phyllosilicate fibers.

In Murchison, heterogeneous XANES spectra are found among individual particles but also between different fine grain "phyllosilicates+OM" regions (Fig. 1). In addition to the 3 peaks described in Renazzo spectra, fine-grained regions show peaks at 287.4, 289.3 (possibly ketone, alcohol or ether functional groups) and 290.3 eV (carbonates), all with variable relative intensities. Interestingly, as in [3], TEM images in those regions showed that the typical grain size is smaller than ~50 nm, indicating that we may have found carbonates at a very early stage of development.

In Orgueil, in addition to the fine-grained OM, 2 individual OM grains, located 1 µm apart from each other and identified as having different D/H anomalies (δD=3983±816‰ and 6260±889‰, respectively), show significant spectral differences, especially in the aromatic peak contribution to the spectra. The more deuterium-rich grain has the lowest aliphatic contribution. No obvious differences in their immediate mineralogical environment could be found.

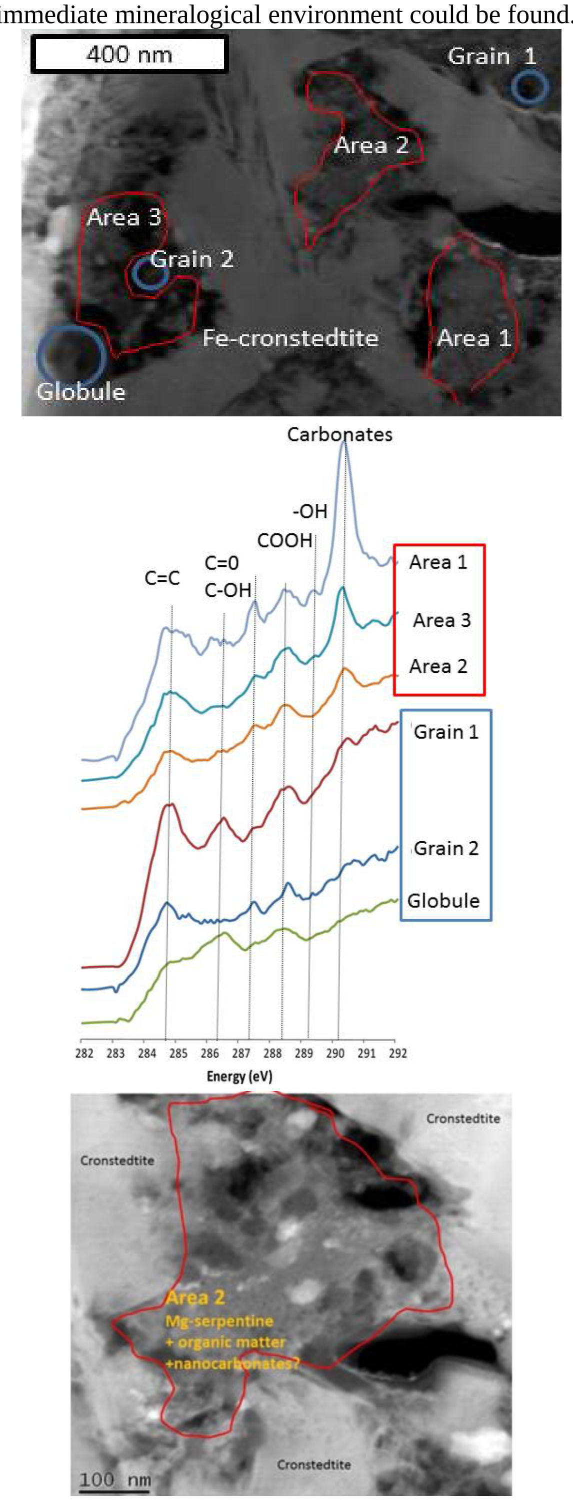

Figure 1: STEM images of a Murchison FIB section showing different areas with large OM grains and smaller distinct particles. XANES spectra at the carbon edge extracted from different areas. STEM image of a fine–grained area showing OM, carbonates and phyllosilicates.

Discussion: The similarity between Renazzo and MET00426 in terms of their "amorphous silicate + phyllosilicates + OM" spatial relationship is a confirmation that Renazzo is also very pristine from the aqueous alteration point of view. The absence of fine-grained OM scattered within the phyllosilicates and the homogeneity of the XANES spectra in Renazzo also confirms that their OM is the most pristine available for study.

Murchison and Orgueil, the more altered samples, display the same three main functional groups (aromatic, ketone, carboxylic), but additional features and more heterogeneities may indicate spatial redistribution and chemical processing during aqueous alteration. A simple model could account for these observations:

1:OM grains, possibly accreted together with water ice are accreted in all three meteorites. Many of them seem to have relatively similar XANES spectra across chondrites groups.

2: Secondary aqueous alteration modified the spatial distribution of the OM. Fluid interacted with the OM grains and transported material away, which was later redistributed with the fine-grained phyllosilicates.

3: The amount of fluid, or perhaps variability in the fluid chemistry at the submicron scale produced variability in the carbon speciation in OM in different fine-grained regions.

4: Carbonate peak in the XANES spectra of Murchison fine-grained regions, coupled with the observation of nanoparticles, is a new observation which indicates that some carbonates nucleate in association with OM and Mg-phyllosilicates. It raises the possibility of a genetic relationship between carbonates and OM.

5: The previous points probably imply that some of the redistributed OM is soluble in aqueous fluids.

6:Chemical and isotopic heterogeneities between individual grains (as in Orgueil) could point towards preservation of initial heterogeneities [6], but may also be interpreted as the result of variable degrees of water-OM interaction, which would have modified the OM to a different extents on a highly localized scale.

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