ESRF	**Experiment title:** Textural and mineralogical transformations during asteroidal aqueous alteration	**Experiment number**: ES-296
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Report:

Carbonaceous chondrites are primitive meteorites presenting evidence for early water-rock interactions that occurred on their asteroidal parent bodies. Deciphering the conditions of these aqueous alteration events is essential for understanding the formation of small solar system bodies that might have significantly contributed to the terrestrial water budget[1]. It relies on the determination of the reactions of hydration, which are difficult to evaluate because different chondrites with different degrees of alteration do not necessarily come from the same parent bodies, and because the alteration phases are nanophases that are difficult to identify, and which distribution at mesoscale, which has to be determined in order to understand their processes of formation, cannot be easily obtained by composition maps. Here we have performed coupled 3-dimensional x-ray diffraction (3D-XRD, 100µm box beam), x-ray absorption computed tomography (CT), and x-ray diffraction CT (XRD-CT, $\approx 10*10 \mu m^2$ focused beam) experiments on variously altered fragments of the same meteorite, the Paris chondrite, where primary components are exceptionnally preserved, and where various degrees of alteration are observed at the 100µm to mm scale[2,3]. A collaboration with J. Wright has been initiated during the experiment. The analysis procedure was performed using modules already implemented in FABLE[4] as well as new ones developed by J. Wright. The analysis is still in progress and we will apply for beamtime for performing complementary experiments with a higher spatial resolution.
The first important result is that XRD-CT allows to isolate areas enriched in hydrated alteration phases, allowing for their identification, often hindered in bulk XRPD by the large amount of phases. Moreover, it should make the structure refinement of these nanometer sized phases possible, which is important since such data are scarce and generally obtained through electron diffraction, which can induce beam damage. In the example of Fig. 1, bassanite, an hydrated calcium sulfate, could be identified as a major alteration product in a metal rich fragment (sample_1) of the Paris chondrite. It is an important observation since bassanite (recently discovered at the surface of Mars) has only been seldomly observed, and only in highly altered, nearly metal-less, meteorites[5]. This suggests oxidising conditions at early stages of alteration, despite the lack of oxygen in the environment of the asteroid.

Second, the comparison of XRD-CT and CT images of variously altered fragments allows to evaluate the enrichment and distribution of secondary phases. CT images allow for the recognition of chondrules, the more abundant primary objects, which are coarse grained aggregates of ferromagnesian minerals and Fe,Ni alloys, characterized by a strong absorption of the incoming beam. Focusing on the most abundant alteration phases, the Fe-rich serpentines, we observe that they are seldom observed in sample_1 whereas they are much more abundant and replace parts or whole altered chondrules in the more altered sample_2 (Fig. 2). In the reconstructed XRPD of Fe-rich serpentines in sample_1 and in sample_2, we observed a shift in the (001) basal reflection, from a distance d=7.10 Å close to that of the mixed-valent Fe end-member cronstedtite (d=7.09 Å) to higher and variable distances (from 7.17 to 7.20 A), closer to the Mg end-member of serpentine, in sample_2. This is consistent with our previous indirect observations at mesoscale[6] (magnetic properties on 100µm-mm size samples of different meteorites) and observations at nanoscale[7] suggesting an early precipitation of cronstedtite followed by fluid assisted transformations towards Mg-richer serpentines as alteration proceeds. Our results therefore bridge the gap between the nano and meso-scales and provide new information about the processes, as we observe an evolution of the basal reflection in sample_2 according to the environment of formation. Another consequence is that the precipitation of the Fe^{3+}-rich mineral cronstedtite at early stages of alteration again points towards an early oxidising environment in the asteroidal parent body of the meteorite. With a higher resolution, down to the sub-micrometer scale, XRD-CT would allow us to identify the sub-micrometric primary phases associated with dense patches of cronstedtite observed in sample_1 and therefore to check for the hypothesis of a mineral catalysis of the process of oxidation by water of aqueous Fe^{2+} leached by the alteration of metallic alloys. The hypothesis of a catalytic role of spinel was indeed suggested from our nanoscale study[7]. The importance of such mechanism stems from the fact that it generates H_2, which may have played a role in prebiotic organosynthesis via the reduction of inorganic carbon.

To improve the mineralogical budget of alteration, we rely on the identification and structure refinement of primary phases using 3DXRD. We are also able to index µm-10µm sized single crystal phases from the XRD-CT data and structure refinements are planned. We identified two kinds of olivine, a predominant pure forsterite, the Mg end-member, and a less abundant Fe-rich one (≈70 mol% Fe[8]). We are working on the quantification of these phases across variously altered areas, and their association to cronstedtite to understand their reaction of formation, by replacement of Fe-rich olivine or via precipitation from solution, possibly triggered by the oxidation of aqueous Fe^{2+} by water. Coupling with XANES at the Fe $L_{2,3}$-edges on FIB sections will provide complementary information on Fe valence state.

As a conclusion, this first spatially resolved X-ray diffraction study of complex water-rock interactions in chondrites has proven the feasibility of the approach. The results shed light on the processes of hydration of primary, nebular component, and highlighted the relatively oxidising conditions on the parent body of the meteorite. These methods have the unique ability to bridge the gap between the µm to mm scale, relevant to the circulation of the fluids and the processes of alteration, and the nanometer scale. Our objective is now to perform XRD-CT at the sub-micrometer scale on relevant assemblages, i.e. heavily altered primary objects, where not only alteration minerals are nanophases, but also the scarce remnants of primary phases. Such an approach will open new perspectives for understanding hydration processes in the early solar system in a non destructive way, which is essential for rare and unvaluable objects such as meteorite falls.

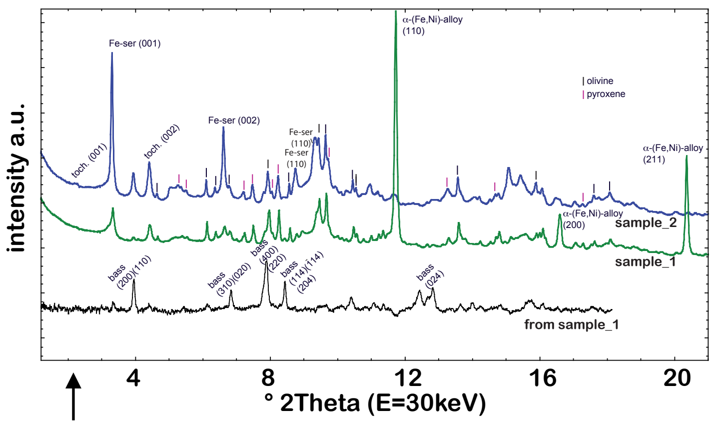

Fig. 1: xrpd patterns from average XRD-CT sinograms of 10µm thick slices of metal rich (sample_1, green) and metal-poor (sample_2, blue) extracts of the Paris meteorite and reconstructed xrpd pattern of a bassanite rich area from sample_1 (corresponding to the white box in Fig. 2).

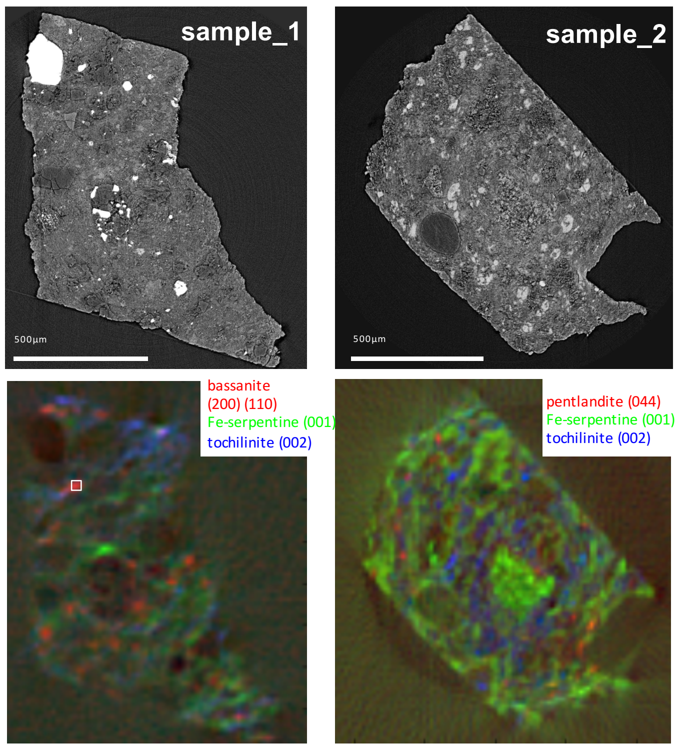

Fig 2.: Examples of absorption CT (upper row, inverted LUT) and x-ray diffraction CT (lower row) reconstructions (same slices as in Fig. 1). The large grains aggregates containing metal in sample_1 are chondrules (primary objects).

References

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