HYDRATION AND OXIDATION OF POROUS MICROCHONDRULES IN SEMARKONA. E. Dobrică, C. Le Guillou, and A. J. Brearley.

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Introduction: Previous studies have shown that FeO-rich porous microchondrules (µch.) are relatively common in the matrices of unequilibrated ordinary chondrites (UOC) [1]. These porous µch. are compositionally distinct from non-porous µch. that occur in the same meteorites [1]. However, texturally and compositionally, porous µch. resemble the vesicular, amorphous groundmass that occurs in the matrices of UOCs. Given the significant amount of evidence of parent body oxidation of amorphous matrix materials in UOCs [2], we have investigated the iron oxidation state of one porous µch. and the surrounding fine-grained matrix in Semarkona (LL3.00), to understand if porous µch. have been modified by aqueous fluids. Iron L-edge X-ray Absorption Near Edge Structure (XANES) spectroscopy was performed on a porous µch. and the surrounding matrix on one focused ion beam (FIB) section using synchrotron-based scanning transmission X-ray microscopy (STXM). The obtained Fe$^{3+}$/∑Fe ratios of these materials were then coordinated with transmission electron microscope (TEM) observations [3].

Methods: Fe L-edge XANES spectroscopy was performed on one porous µch. (~11 µm in diameter) identified in the fine-grained matrix of Semarkona (Fig. 1). The µch. was characterized by Scanning Electron Microscopy (SEM) on a FEI Quanta 3D FEGSEM/FIB operating at 30 kV, using backscattered electron (BSE) imaging. After detailed SEM characterization, an electron transparent section of this porous µch. was prepared using the FIB technique with a FEI Quanta 3D Dualbeam® FIB instrument. STXM-XANES measurements were conducted at the Canadian Light Source (CLS), following the analytical conditions and calibration from [3]. After the STXM-XANES measurements, bright and dark-field TEM images and quantitative energy dispersive X-ray spectroscopy (EDS) analyses and maps were obtained at 200 kV on a JEOL 2010F FEG TEM/Scanning TEM (STEM).

Results and discussion: The TEM observations show that pores are heterogeneously distributed within the µch. and have variable diameters (0.1-1 µm in size). One texturally and compositionally distinct, highly porous, subrounded region was identified inside the µch. (Fig. 1-2). Additionally, the chemical composition of the most porous regions in the µch. contain a higher amount of carbon (~16.6 at.% C) compared to the ones with lower porosity (~9.8 at.% C). The matrix around this µch. consists of a groundmass composed of amorphous silicates, fine-grained phyllosilicates, sulfides and several coarse-grained silicates (En$_{97}$, Fig. 1). STEM-EDS elemental composition maps were obtained from the same area where the STXM measurements were performed (Figs. 2-3). Bulk chemical compositions of the porous µch. and the matrix (amorphous silicates and the fine-grained phyllosilicates) are then compared with the average composition of the porous µch. reported elsewhere [1] (Table 1).

Figure 1. Backscattered electron and dark-field images made by SEM and STEM showing the porous µch. identified in the fine-grained matrix of Semarkona and studied by STXM. Phases identified in the FIB section: Carb = carbide, tta = tetrataenite, S = sulfide and En = low-Ca pyroxene.

The major element composition of the µch. is consistent with the average bulk composition of µch. reported by [1]. The µch. is Fe-rich with ~7.5 at.% Fe. The XANES data show, however, that the Fe in the µch. is highly oxidized, with elevated, but variable Fe$^{3+}$/∑Fe contents. The Fe$^{3+}$/∑Fe ratio varies between 54% and 71%. As discussed by [3], such elevated ferric iron contents are very unlikely to be the result of nebular processes, but rather result from an oxidation event within a parent body environment. Following the arguments of [3], we infer that the high ferric iron content of the µch. is the result of parent body oxidation due to interaction with an aqueous fluid that has also affected the adjacent, highly oxidized matrix material.
(Fe$^{3+}/\sum$Fe ratio of 63). Based on the absence of crystalline phases within the µch., we assume that the µch. was originally glassy; however, it now consists of a hydrated, amorphous gel-like phase that probably shares some structural similarities with the amorphous Fe-rich silicate that is present in the matrix.

Figure 2. SEM BSE image (a) and STEM EDS maps (b-e) showing the distribution of Fe, S, Na and C within the area outlined by the solid line rectangle, in the porous µch. and in the surrounding fine-grained matrix of Semarkona.

The oxidation of the µch. appears to have occurred heterogeneously with an almost 20 mol% variation in the Fe$^{3+}/\sum$Fe ratio between the three distinct regions that are apparent in the STXM spectral map (Fig. 3). The reasons for this variability are not easy to assess, but it could be, at least partially, related to primary textural and compositional heterogeneity in the µch. For example, the subrounded, highly porous region within the µch. (red region, Fig. 3) is clearly compositionally distinct from the rest of the µch., with significantly higher volatile (C, Na and S) contents than the two other distinct regions. This region has an intermediate oxidation state. It is possible that primary composition and perhaps the higher organic content of this region impeded oxidation. However, the reason for the differences between the least and most highly oxidized regions of the µch. are less clear. There are no major compositional or textural differences between the two regions that might have controlled the degree of oxidation. The variability in this case may simply be a reflection of heterogeneous diffusion of water into the glass phase, perhaps along preexisting cracks or due to a local, higher initial porosity. Ultimately oxidation did not go to completion, perhaps because the fluid was completely consumed.

With the exception of the least oxidized area being associated with high concentrations of volatile elements, there is no evidence of any other correlation between the degree of oxidation and the chemical composition of the different regions of the µch. This observation suggests that despite secondary alteration and oxidation the composition of the µch. was not modified significantly within the parent body. This observation supports the conclusion of [1] that the primary compositions of porous µchs. are distinct from those of non-porous µchs.

Figure 3. a and c) correlation image built from the XANES spectra; b and d) XANES spectra of the amorphous material in the porous µch. and the adjacent matrix from which the left images were obtained. The Fe$^{3+}/\sum$Fe ratio values for the different regions are shown in Figs. 3b and d.

Table 1. Concentrations of major and minor elements (in at.% element) determined by EDS (TEM) measurements in porous µch., matrix and the different (diff.) regions where STXM measurements were performed (the colors correspond to those shown in Fig. 3). N = number of measurements.

Acknowledgements: This work was funded by NASA Cosmochemistry grants NNX12AH59G and NNX15AD28G to A. J. Brearley (PI).