EARLIEST STAGES OF METAMORPHISM AND AQUEOUS ALTERATION OBSERVED IN THE FINE-GRAINED MATERIALS OF TWO UNEQUILIBRATED ORDINARY CHONDRITES.

E. Dobrică[1] and A. J. Brearley[1], [1]Department of Earth and Planetary Sciences, MSC03-2040, 1University of New Mexico, Albuquerque, NM 87131-0001, USA. (edobrica@unm.edu).

Introduction: The textural and mineralogical characteristics of fine-grained materials, i.e. interchondrule matrix and fine-grained rims, in the most unequilibrated ordinary chondrites (UOCs) can be used to constrain the physico-chemical conditions of dust formation in the solar nebula. In addition, these nanometer-sized materials are also sensitive to post-accretionary processes on the parent body such as thermal metamorphism, aqueous alteration, brecciation or shock [1-3]. To reconstruct the environment in which such natural nanomaterials formed and evolved, it is necessary to characterize their textures, mineralogy and elemental distributions at the micro to nanoscales.

In order to understand the effects of the earliest stages of metamorphism and aqueous alteration on the matrices of UOCs, we investigated two UOCs, MET 00526 (H) and QUE 97008 (L), both classified as petrologic type 3.05 [3]. These observations were performed by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). In particular, we focus on the implications of the relationships between crystalline minerals and amorphous phases and the possible redistribution of elements due to mobilization by a fluid during aqueous alteration processes on the chondrite parent body.

Methods: Two polished thin sections of MET 00526 and QUE 97008 were initially studied on a FEGSEM operating at 30 kV using backscattered electron (BSE) imaging. Elemental distribution maps were acquired by energy dispersive spectroscopy (EDS) for initial identification of different mineral phases. After SEM characterization, two TEM sections were prepared from representative areas of matrix, using the focused ion beam (FIB) technique using a FEI Quanta 3D FEGSEM/FIB instrument. Bright field TEM images and qualitative EDS X-ray analyses were carried out at 200 kV on a JEOL 2010 high resolution TEM (HRTEM) and JEOL 2010F FEG TEM/Scanning TEM (STEM).

Results: TEM investigations of the matrices of two UOCs show that they share a number of similarities. The major notable difference is that QUE 97008 has a higher porosity and a higher abundance of fine-grained minerals than MET 00526. However, matrices in both meteorites contain nanometer-sized minerals embedded in an amorphous silicate material that commonly shows evidence of the development of an assemblage of nanocrystalline phyllosilicate. Several larger crystals (1-3 µm) are observed. These grains were identified as Mg-rich pyroxenes (En_{98-99} - MET 00526), one Fe-rich olivine (Fa_{68}) and two plagioclase grains (QUE 97008). These feldspars occur either as individual grains or as a micrometer-sized aggregate (3 µm). Their compositions are essentially homogeneous ranging from $An_{84}Ab_{16}Or_2$ to $An_{92}Ab_8Or_6$.

The fine-grained silicates in both UOCs are dominated by olivines and pyroxenes (MET 00526 – Fo_{37-93}, En_{95-100}, QUE 97008 – Fo_{40-84}, En_{99}). In MET 00526, generally, the iron rich, fine-grained anhedral olivines were observed in veins which crosscut the amorphous and phyllosilicate-rich regions (Fig. 1-a), producing a mosaic texture, with islands of amorphous/phyllosilicate-rich material surrounded by veins of FeO-rich olivine. In the matrix of MET 00526, we have often identified isolated Mg-rich olivines (up to 500 nm in diameter) with more Fe-rich rims.

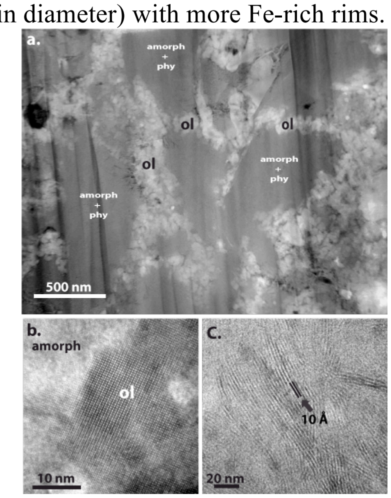

Figure 1. a) Dark field STEM image of fine-grained, iron-rich olivine (ol - light grey phases) veins in MET 00526 which crosscut regions of amorphous silicate material and phyllosilicate (phy) minerals. HRTEM micrographs showing olivine (b) and smectite (c) with basal spacing of ~10 Å.

In both UOCs nanocrystalline phyllosilicate phases are present with basal spacing lattice fringes of ~1 nm, consistent with smectite (Figs. 1-c; 2-b). These phases are associated with regions of amorphous silicate material enriched in Mg, Al and Fe (< 6 at%) (Figs. 1, a-b and 2).

Taenite and tetrataenite (FeNi) grains (less than 50 nm) were identified in both meteorites (MET 00526 – $Fe_{57-52}Ni_{43-48}$; QUE 97008 - $Fe_{50-67}Ni_{33-50}$). This mineral is abundant compared to the Fe,Ni metal alloy (kamacite) which was identified so far only in QUE 97008.

Nanometer-sized sulfides are heterogeneously distributed in the analyzed samples. Generally, Ni-poor sulfides are more abundant. Both Ni-rich and Ni-poor sulfides appear to be concentrated in groups of grains, associated with phyllosilicates and amorphous material. In MET 00526, several nanosulfides are commonly observed in contact with the tetratenite grains (Fig. 3). In QUE 97008, the sulfides are present both as isolated crystals and as aggregates embedded within regions of phyllosilicates (Fig. 3,a).

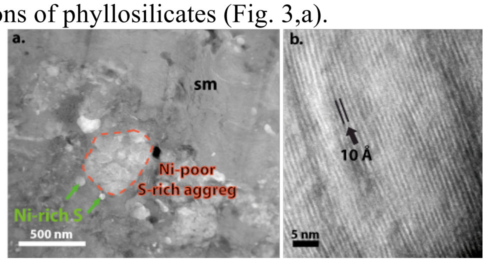

Figure 2. a) Dark field STEM image of a region of fine-grained matrix in QUE 97008 showing phyllosilicates (smectite - sm), Ni-rich sulfides and an aggregate rich in Ni-poor sulfides (orange dashed line). b) HRTEM image showing the presence of smectite with basal spacing of ~1.0 nm.

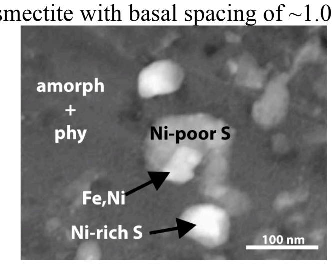

Figure 3. Dark field STEM image of an aggregate of Ni-rich sulfides (S) and tetrataenite (Fe,Ni) embedded in amorphous silicate (amorph.) material and phyllosilicates (phy) in the matrix of MET 00526.

Ca phosphates (apatite) were identified in both UOCs. In MET 00526, they are present in a large aggregate (1.1 x 2 µm). In QUE 97008, only one phosphate was identified in a nanometric association with Ni-poor sulfides.

Discussion: Our preliminary observations of the matrices of these two very low petrologic type chondrites provide new data on the response of matrix materials to aqueous alteration and weak thermal metamorphism. We have clearly identified mineral phases, notably phyllosilicates, Ca-phosphates and Ni-rich sulfides, which demonstrate that aqueous alteration played an important role in the evolution of their chondrite parent body. However, in comparison with the Semarkona (LL3.0), the lowest petrologic type OC, the effects of aqueous alteration are only minimal as indicated by the fact the phyllosilicate phases are much finer grained and poorly-crystalline and are heterogeneously developed. In addition, unaltered primary Mg silicates and Ni-poor sulfides are also present suggesting that a significant component of the pre-accretionary mineral assemblage remains in these meteorites.

Our observations place important constraints on the origin of the Fe-rich olivines that are the common constituents of matrices in UOCs of petrologic subtype >3.2. The absence of abundant, subrounded to euhedral FeO-rich olivines in the matrices of these two chondrites further demonstrates that such olivines are not a primary component of pristine chondrite matrices. Instead, the occurrence of Fe-rich olivines in distinct submicron veins that crosscut the amorphous and phyllosilicate-bearing regions suggests that the formation of Fe-bearing olivine may have involved an aqueous fluid. The formation of ferroan olivine by hydrothermal growth has been suggested as an important mechanism for the origin of matrix olivines in carbonaceous chondrites [4-6]. In comparison, our new observations reveal the very earliest stages of this process that represents the initial response of fine-grained matrix materials to metamorphic heating in the presence of an aqueous fluid. Larger, micron to submicron Mg-rich olivines that were present in the precursor matrix dust have responded to metamorphism by partial diffusive exchange resulting in the development of normal zoning.

The close association of Ni-rich sulfides and tetrataenite observed in MET 00526 could suggest sulfurization processes of the tetrataenite during the aqueous alteration and low-grade metamorphism. The presence of tetrataenite which forms by ordering the Fe and Ni atoms in taenite crystals suggest that this meteorite was heated at low temperatures and cooled slowly [7].

Conclusion: The matrices of two very unequilibrated ordinary chondrites (type 3.05, H and L chondrites) provide new insights into the earliest stages of aqueous alteration and thermal metamorphism. Both meteorites provide evidence that the matrix precursor materials consisted of an unequilibrated mixture of amorphous silicate material and unequilibrated crystalline phases. The amorphous silicate material has undergone at least partial hydration to form nanocrystalline phyllosilicates, but the main metamorphic effect is the formation of submicron veins of ferroan olivine. Further TEM studies will constrain the mechanisms of formation of the matrix olivine, the processes of phyllosilicate formation and the redistribution of mobile elements such as Ca and S at the micron to submicron scale.

Acknowledgements: This work was funded by NASA Cosmochemistry grant NNG06GG37G to A. J. Brearley (PI).

References: [1] Alexander C.M.O.d., *et al.* (1989) *Geochim. Cosmochim. Acta* **53**, 3045-3057. [2] Ashworth J.R. (1977) *Earth Planet. Sci. Lett.* **35**, 25-34. [3] Grossman J.N. and Brearley A.J. (2005) *Meteorit. Planet. Sci.* **40**, 87. [4] Krot A.N., *et al.* (2004) *Antarctic Met. Res.* **17**, 153. [5] Brearley A.J., in *Lunar Planet. Sci.* 2009. p. 1791. [6] Krot A.N., *et al.* (2000) *Meteorit. Planet. Sci.* **35**, 1365-1386. [7] Clarke R.S. and Scott E.R.D. (1980) *Am. Mineral.* **65**(7-8), 624-630.