HRTEM AND EFTEM OBSERVATIONS OF MATRIX IN THE OXIDIZED CV3 CHONDRITE ALH 84028: IMPLICATIONS FOR THE ORIGINS OF MATRIX OLIVINES Neyda M. Abreu and Adrian J. Brearley, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA (e-mail: abreu@unm.edu, brearley@unm.edu).

Introduction: The determination of the nature, distribution, and origin of organic material in carbonaceous chondrites is fundamental to understanding early solar nebular conditions and the origin of life. Using a variety of extraction techniques, followed by detailed chemical analysis, an extensive suite of organic compounds has been identified in carbonaceous chondrites [i.e., 1, 2]. These data have provided key information on the diversity and isotopic composition of the organic component in chondrites. However, one disadvantage of extraction techniques is that all information regarding the spatial distribution of the organics on a fine scale is lost. This is especially important for the insoluble macromolecular carbon, which constitutes ~70% of the carbon in carbonaceous chondrites such as Murchison. The distribution and mineralogical associations may provide important constraints on the possible origins of the carbonaceous material. Our previous studies of the CV3 chondrites Allende and Vigarano [3,4] have demonstrated that energy filtered transmission electron microscopy (EFTEM), combined with high resolution TEM (HRTEM) are powerful tools for the *in situ* characterization of insoluble organic matter in carbonaceous chondrites. In this study, we have used SEM and TEM techniques to characterize the matrix mineralogy of the CV3 chondrite ALH 84028 and examine the distribution and mineralogical associations of carbon. We are especially interested in establishing whether the occurrence of poorly graphitized carbon (PGC), observed in Allende matrix olivines [3], is common to all oxidized CV3 chondrites or is a unique feature of Allende.

Methods: Regions of the matrix were characterized in detail by SEM. Selected representative regions of the matrix were then removed from the thin sections and were ion-milled and studied by TEM using a JEOL 2010 HRTEM and a JEOL 2010F FEG TEM/STEM fitted with a GATAN image filtering (GIF) system.

Results: ALH 84028 is an Antarctic find and belongs to the Allende-like subgroup of the oxidized CV3 chondrites [4,5]. According to [4,5], ALH 84028 has petrographic characteristics that are very similar to Allende and our SEM observations are consistent with these prior descriptions. ALH 84028 shows no obvious evidence of brecciation and we did not observe any dark inclusions in either of the thin sections studied. The edges of chondrules show evidence of secondary fayalitic olivine replacing Mg-rich olivine and Fe-sulfides and metal show evidence of extensive alteration, typical of oxidized CV chondrites. The matrix appears to be relatively homogeneous in texture and there are no major textural or mineralogical differences between the matrix and the rims in BSE images. BSE images also show that the matrix consists largely of abundant lath-shaped, elongate, iron-rich olivine, 2-20 μm in length. The olivine grains are similar in morphology to those described in Allende and appear to have a similar range of grain sizes. Sulfides are also commonly disseminated throughout the matrix and Ca-rich pyroxene is also present as subhedral grains, 30-40 μm in diameter.

TEM observations are generally consistent with the SEM data, but show that there is considerable diversity in the microstructures and morphologies of the matrix olivine grains at the micron to sub-micron levels. Analytical electron microscopy shows that olivines have compositions in the range Fa_{42-58} with a mean composition of $Fa_{52.6}$. This range is comparable to the range of olivine compositions found in the Allende matrix (Fa_{45-55}). The morphology of the grains ranges from elongate, subhedral crystals to sub-rounded grains. TEM observations show that the acicular olivines that can be easily observed by SEM have grain sizes that extend to 1 μm in length and < 0.2 μm in width.The subhedral to subrounded grains range from ~ 1 μm to < 0.1 μm in size. The majority of the matrix olivines are characterized by high densities of dislocations and commonly have a highly strained appearance. Nevertheless, grains with very low dislocations densities are also relatively common. These grains often appear to be overgrowths that have formed by recrystallization of highly strained olivine crystals. In addition to the presence of dislocations, the most common feature of many matrix olivines and pyroxenes is the presence of inclusion phases. Isolated hercynitic spinel crystals in the matrix of comparable size to matrix olivines also contain inclusions.

In many olivine grains the abundance of inclusions is extremely high, but the distribution of inclusions, both within grains and between grains is variable. Some grains are virtually inclusion-free: these grains are commonly those with low dislocation densities. We have identified several types of inclusions present within olivine and pyroxene grains: (1) Fe,Ni sulfide inclusions, (2) spinel inclusions, (3) carbon-bearing inclusions. We have also identified olivines containing two distinct types of voids.

Sulfide and oxide phases are the most common type of inclusion in matrix olivines. Sulfides and spinels appear to be equally abundant and typically occur within the same crystal. The sulfides sometimes occur in clusters of grains that are distinct from spinel inclusions: the two phases are rarely spatially associated. Sulfides occur as randomly oriented, euhedral crystals that are often well-facetted and have grain sizes of ~10-40 nm. EDS analyses of these inclusions show that they are Ni-rich, Fe-sulfides. Electron diffraction data for these grains are consistent with pentlandite.

The spinel inclusions are generally rounded to sub-rounded in shape and range from 10 to 60 nm across. They show no crystallographic orientation relationship with the host olivines. AEM analyses show that these inclusions are compositionally variable, and are solid solutions of chromite, magnetite and hercynite. The Cr/Al ratio is very variable, ranging from

0.27 to 2.22. The trivalent cations, Cr and Al are positively correlated but both elements are anti-correlated with Fe. This suggests that there is a coupled substitution of Cr^{3+} and Al^{3+} for Fe^{3+} i.e., the chromite and hercynite components substituting for magnetite. Both sulfides and pentlandite are often associated with PGC, although this phenomenon appears to be less common for spinel grains. In fact, the bulk of the carbonaceous material in ALH 84028 is found forming rims around these inclusions. The carbonaceous material exhibits a range of degrees of graphitization, but it typically occurs as thin layers, 2-3 unit cells in thickness around the periphery of the inclusion. The degree of graphitization of the carbonaceous material is highest at the surface of the pentlandites and spinels.

In addition to the association of sulfide and spinel with PGC, inclusions consisting solely of carbonaceous material are also present. These inclusions range from subrounded to highly irregular in shape and typically consist of PGC. In addition, PGC is also found along crystallographic defects in olivine crystals.

Two distinct types of voids have been observed in matrix olivines. The first type occurs in olivines that also contain sulfide and spinel inclusions. These voids are usually very abundant and may be irregular or sub-rounded in shape and range from 10-15 nm in size. In some cases, thin layers (<3 nm) of PGC are present rimming the edges of some voids. However, EFTEM imaging for a variety of elements has confirmed that, with the few exceptions in which carbonaceous material is present, the voids are empty. However, olivines may also contain a second type of void structures. The shape of these structures is clearly crystallographically controlled. These void structures generally range from 10 to 50 nm in diameter and occur in densely packed groups. In fact, the void density may be very high in some crystals (up to several tens of voids per grain).

Discussion: The oxidized CV3 chondrites have undergone extensive alteration that overprinted their primary nebular characteristics [4]. However, there is considerable discussion over when and where this alteration took place. It has been argued that Allende may have experienced a complex alteration history involving aqueous alteration followed by thermal metamorphism, although this model is highly controversial [i.e., 3,6,7]. However, our previous observations on Allende matrix appear to be most compatible with parent body alteration, rather than processing in the solar nebula.

Our SEM and TEM observations show that matrix olivines in ALH 84028 share a number of morphological and compositional characteristics with those in Allende, indicating that they share a common origin. Like Allende, ALH 84028 contains matrix olivines with a narrow range of compositions compared with the reduced subgroup and the matrix olivines are typically larger and dominated by acicular, elongate grains. ALH 84028 olivines also have microstructures that are very similar, if not identical, to those in Allende. In both meteorites the olivines are strained and inclusion phases associated with carbonaceous material, pentlandite and chromite, are the same. In addition, the degree of graphitization of the carbonaceous material is very similar in these two meteorites. Voids are also commonly present in matrix olivines in both meteorites. These observations provide strong evidence for a common origin for the matrices in both meteorites. Further, like Allende phyllosilicates appear to be completely absent from ALH 84028 matrix.

It has been suggested that olivines in Allende and some dark inclusions in CV chondrites formed by dehydration of preexisting phyllosilicates during thermal metamorphism [3,6]. The equilibrated olivine compositions and the degree of graphitization of PGC in Allende and ALH 84028 support the view that these meteorites have experienced significant thermal metamorphism. We have also argued that the widespread occurrence of graphitic, sulfide and chromite inclusions in matrix olivines in Allende and now in ALH 84028 is not compatible with nebular origin. Following [3], these inclusions may have formed during dehydration of Ni, Cr and S-bearing phyllosilicates.

Further evidence to support this thermal metamorphism model comes from the presence of some olivines in ALH 84028, that have a very high density of voids. These void structures bear very close similarities to those described in the unique carbonaceous chondrites B-7904 and Y-82162, as well as the CM chondrite Y-86720 [8]. We have not observed grains with these characteristics in either Vigarano or Allende. As in the case of B-7904, Y-86720 and Y-82162, many of these voids seem to be crystallographically controlled. The high density of voids has been attributed to olivine and enstatite formation by dehydration of phyllosilicate minerals formed by a prior aqueous alteration event [8,9]. In B-7904 and Y-82162, the mineralogy is dominated by phyllosilicates. In contrast, phyllosilicates are scarce in Y-86720 [9] and have not been observed in ALH 84028. These data therefore support the contention that ALH 84028 has experience quite extensive thermal metamorphism, sufficient to dehydrate all precursor phyllosilicates.

Conclusions: Most olivines in ALH 84028 are microstructurally similar to Allende, containing inclusions of sulfide, Cr-bearing spinel and PGC. This suggests that olivines in the two meteorites formed by the same mechanism. We suggest that the most likely origin is by thermally-induced dehydration of preexisting phyllosilicates, within a parent body environment as discussed by [3]. This model is supported by the presence of void structures in some olivines in ALH84028 which resemble those in olivines in thermally metamorphosed carbonaceous chondrites.

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