NANOPHASE, LOW-NI METAL GRAINS IN FINE-GRAINED RIMS IN THE MURCHISON CM2 CHONDRITE: INSIGHTS INTO THE SURVIVAL OF METAL GRAINS DURING AQUEOUS ALTERATION

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Introduction: Aqueous alteration has played a significant role in the geological evolution of almost all the chondrite groups and attests to the importance of water during the earliest history of the solar system. Among the chondrites that show evidence of aqueous alteration the CM chondrites, in particular, have received considerable attention, because of their primitive composition and the fact that they preserve a record of incomplete hydration. Petrologic studies of this group of meteorites have helped provide important insights into aqueous alteration processes and the nature of the alteration products [1-3]. However, due to the complex history of these chondrites, important details of the alteration remain enigmatic. Among the major problems to be resolved are the location and timing of aqueous alteration as well as the relationship between alteration and brecciation. Although many authors e.g. [1-4] favor aqueous alteration within a parent body environment, there is also evidence that some of the components of CM chondrites may have experienced aqueous alteration prior to accretion [5,6].

One of the key lines of evidence for alteration in a preaccretionary environment is the presence of unaltered metal grains associated with hydrated phases. Low-Ni metal (kamacite) is typically one of the first phases in CM chondrites that alters in the presence of water [7]. However, in some CM chondrites, such as Yamato 791198, micron-sized metal grains are present within the hydrated fine-grained rim material around chondrules [5,8]. In addition, nanometer-sized grains that have been interpreted as being unaltered metal particles have been reported in the relatively heavily altered CM chondrite, ALH 81002 [9]. In most cases, these occurrences have been interpreted as being the result of mixing of anhydrous and hydrous materials prior to accretion. According to this hypothesis, the metal grains remain unaltered because little or no postaccretionary alteration took place. Whilst such a scenario is plausible, no alternative explanations such as the presence of submicron protective layers or a minor element chemistry that might inhibit oxidation have been investigated in detail.

During a study of the distribution of carbonaceous material in fine-grained rims on chondrules in Murchison, previously unidentified, nanometer-sized metal grains were observed. These grains were characterized in detail using high resolution TEM and energy filtered TEM (EFTEM) and provide important insights into how metal grains in CM chondrites may survive aqueous alteration.

Observations: TEM observations were carried out on several well-characterized fine-grained rims in Murchison. The mineralogical characteristics of these rims have been described briefly elsewhere [10], but typically consist of relatively coarse-grained cronstedtite crystals that are set in a very fine-grained, Mg-rich serpentine groundmass. Tochilinite is locally present in aggregates often interlayered with serpentine. Our earlier TEM studies of fine-grained rims found that submicron pentlandite is the dominant opaque phase and is commonly surrounded by a rim of poorly graphitized carbon (PGC) just a few nanometers in thickness [11]. Our new studies show that in some rims, nanophase metallic Fe, Ni particles are relatively abundant.

Fe, Ni metal grains: Fe, Ni metal grains have been observed in two separate rims and occur in several regions of the rims that were studied by TEM. Their presence therefore appears to be a common feature of the precursor rim material. The metal grains occur both as individual, isolated grains and as clusters of up to 4 or 5 grains and are extremely fine-grained (16 to 45 nm). They usually have a rounded morphology, but occasionally elongated, subrounded grains also occur (Fig. 1). These grains were initially studied because of their unusual texture. In all cases, the grains have a zoned microstructure consisting of an inner core, surrounded by a thin layer of lower Z material and an outer layer. The core regions vary in size from ~10-38 nm, but the thickness of the outer layer is identical (6-7 nm) irrespective of the size of the core of the grain. Using high resolution TEM, energy filtered TEM and analytical electron microscopy, it has been possible to characterize these grains in detail. The inner core of the grains is a phase which contains elevated contents of Fe with minor Ni (5 -7 wt% Ni). Electron diffraction patterns of this phase obtained by Fast Fourier Transform (FFT) analysis of HRTEM images are consistent with a BCC structure with lattice spacings matching those of kamacite. The outer layer of the grain consists of a nanocrystalline phase with grain sizes that vary from 5 to 18 nm. EDS analysis shows that this phase consists dominantly of Fe and O. Lattice spacings determined from electron diffraction patterns are consistent with magnetite.

It was not possible to determine the composition of the layer of material between the magnetite and the kamacite using EDS. However, high resolution imaging shows that it is amorphous in nature and EFTEM imaging has provided key information on the composition of this phase. Our initial EFTEM imaging focused on examining the distribution of carbon associated with the metal grains. Figure 2 shows an EFTEM C-map of a typical metal grain and its rim of magnetite. The image shows that the magnetite has very low carbon content, but that the layer between the magnetite and kamacite is very C-rich. By heating the sample using a highly focused electron probe, we were able to induce graphitization of this layer, indicating that this layer is composed of graphitizeable, amorphous carbon. In addition, the kamacite also appears to contain enough carbon to be detectable in the EFTEM C-map. O, Fe and Ni EFTEM maps show that the distribution of these elements is consistent with the phase identifications described above. Oxygen is present within the magnetite and not within the core metal grain and Fe is present in elevated concentrations in the metal compared with the magnetite.

Discussion: These data show that fine-grained kamacite grains are relatively common in fine-grained rims in Murchison. To our knowledge this is the first occurrence of nanophase kamacite in Murchison that has been identified unambiguously by electron diffraction and EDS data. These observations are extremely important, because they have significant implications for the preaccretionary vs parent body alteration debate for the CM chondrites.

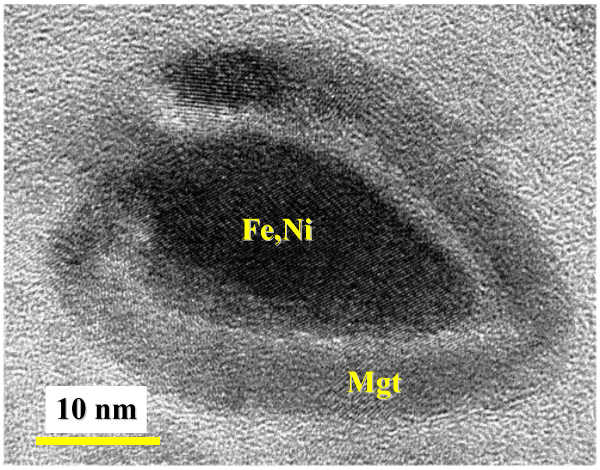

Figure 1. High resolution TEM image of kamacite grain in a fine-grained rim in Murchison surrounded by a continuous rim of nanophase magnetite

The observed textural relations between the kamacite grains and their magnetite rims indicate that the kamacite is not pristine in character, but has undergone oxidation at some stage in its history. However, this reaction clearly did not go to completion. We propose the following model for the preservation of the metal grains. Our EFTEM images show that the surviving kamacite cores contain low, but detectable amounts of carbon. In addition, a layer of amorphous carbon separates the magnetite rim from the metal core. These observations indicate that the observed textures are the result of oxidation of C-bearing metal grains. Magnetite does not incorporate carbon into its crystal structure and therefore as the oxidation reaction proceeds, the carbon will be released from the metal and will build up at the interface between the reactant and the product phases. During the earliest stages in the reaction, this carbon layer will be thin enough or incompletely cover the surface of the metal to allow the oxidant to diffuse through the layer and promote further oxidation of the metal. However, as the carbon builds up, we propose that it forms a protective layer that inhibits oxidation of the metal. This process arrests the oxidation of the metal and protects the remaining metal grain from further reaction, although ultimately it seems probable that complete alteration of the metal will occur. These observations provide a plausible explanation for the survival of low-Ni metal grains during alteration in CM chondrites.

Clearly, the oxidation of the metal grains could have occurred either prior to accretion or within an asteroidal parent body. Our observations provide at least some constraints on the possible alteration environment. The fact that amorphous, rather than graphitic carbon, forms at the kamacite surface shows that this reaction must have occurred at temperatures too low to form graphite during the alteration reaction. This is consistent with low temperature alteration in which water was the oxidizing agent, rather than a higher temperature, nebular oxidation event. Clearly, this could have occurred within a preaccretionary environment or within as asteroidal parent body. However, given the evidence that Murchison has experienced extensive parent body alteration [4], it seems most likely that oxidation of the metal occurred within an asteroidal environment. This conclusion is also supported by the observation that the thickness of the magnetite rims (6-7 nm) is the same on all metal grains, irrespective of their size. This implies that all the grains underwent reaction under the same conditions (P,T, fO_2, etc) for the same period of time. These observations call into question a preaccretionary alteration scenario to explain the presence of low-Ni metal coexisting with hydrous phases such as occurs in the Y791198 and ALH 81002 CM2 chondrites. These occurrences are most likely to simply reflect the partial alteration of C-rich metal grains that have been protected from complete alteration by an impermeable layer of amorphous carbon.

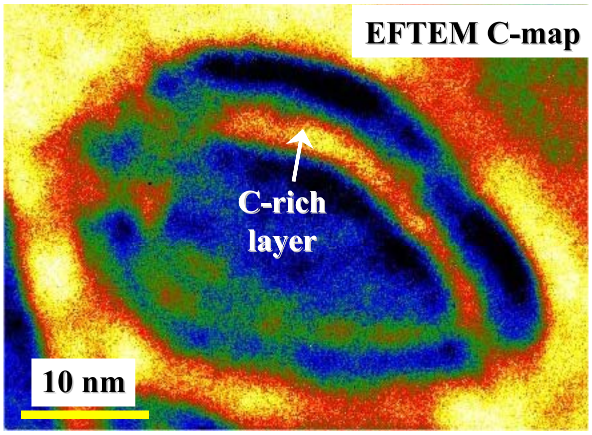

Figure 2. Energy filtered TEM carbon map of grain shown in Fig. 1 illustrating the presence of a carbon-rich layer between the core kamacite and magnetite rim. The grain itself is embedded in C-rich material.

References: [1] Zolensky, M.E. and McSween, H.Y. (1988) In '*Meteorites and the Early Solar System*' pp. 114-143. [2] Browning, L.B. et al. (1996) *GCA* **60**, 2621-2633. [3] Brearley, A.J. (1995) *GCA* **59**, 2291-2317. [4] Hanowski, N.P. and Brearley, A.J. (2000) *MAPS* **35**, 1291-1308. [5] Metzler, K. et al. (1992) *GCA* **56**, 2873-2897 [6] Bischoff, A. (1998) *MAPS* **33**, 1113-1122. [7] Zolensky, M.E. et al. (1993) *GCA* **57**, 3123. [8] Chizmadia, L. J. and Brearley, A.J. (2002) MAPS Suppl. 37, A33. [9] Lauretta, D. et al. (2000) GCA **64**, 3263. [10] Brearley, A.J. and Geiger, T. (1991) *Meteoritics* **26**, 323. [11] Brearley, A.J. (2002) **XXXIII**. Abstract CD ROM, Abs # 1388. **Acknowledgements.** Supported by NASA grant NAG5-9798 to A.J. Brearley (PI).