ALTERATION OF COARSE-GRAINED FE AND FE,NI SULFIDES IN THE MIGHEI CM2 CARBONACEOUS CHONDRITE: EVIDENCE FOR THE INSTABILITY OF PRIMARY PYRRHOTITE-PENTLANDITE GRAINS DURING AQUEOUS ALTERATION Adrian J. Brearley, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM87131, USA. e-mail: brearley@unm.edu

Introduction: Details of the complexity of aqueous alteration processes in CM chondrites have come from a variety of different mineralogical and isotopic studies. These studies have focused on understanding the progressive sequence of alteration observed in CM2 chondrites [1-4]. Mineralogically, this sequence is defined first by the alteration of Fe,Ni metal, chondrule mesostasis and later by the pseudomorphic replacement of primary chondrule silicates by hydrous phases such as Mg-Fe serpentine.

A key aspect of the alteration of CM chondrites that is currently poorly understood concerns the role of sulfides in the alteration sequence. The general viewpoint is that primary sulfides, such as troilite, are altered early [5] and are involved in reactions that result in the formation of a major phase in CM chondrites, tochilinite. Other sulfide phases such as pentlandite and pyrrhotite are also considered to be of secondary origin and may have formed by replacement of troilite and/or metal [5,6,7,8]. However, we have recently shown that pentlandite and pyrrhotite that is primary in origin and is derived from type IIA chondrules [9,10] are the most common coarse-grained sulfide phases in the weakly altered CM chondrite TIL 91772. Our more recent investigations [11] also show that similar sulfides are present in Crescent, another CM chondrite that exhibits a relatively modest degree of alteration.

In this study, we describe SEM and TEM observations of similar coarse-grained sulfides from the moderately altered CM2 chondrite Mighei, which show clear evidence that they are unstable during aqueous alteration and are undergoing the earliest stages of replacement. The behavior of these sulfides has potential to provide a sensitive indicator of aqueous alteration of CM2 chondrites.

Techniques: A thin section of the CM chondrite Mighei was studied with SE and BSE imaging using a FEI Quanta 3D FEGSEM. Individual sulfide grains were located using mineralogical modal abundance maps collected using a QEMSCAN instrument as described by [1]. A total of 10 composite pyrrhotite-pentlandite grains were studied, ranging in size from 20 - > 50 µm in size. Qualitative EDS spectra were obtained from individual grains using an EDAX Apollo 40 SDD EDS detector. Electron-transparent FIB sections for TEM analysis were prepared from individual sulfide grains using a FEI Quanta 3D DualBeam® FEGSEM/FIB. The FIB-prepared samples were removed from the thin sections using the in situ lift out technique with an Omniprobe 200 micromanipulator.

Results: The composite pyrrhotite-pentlandite grains in Mighei are textural similar to those in Mighei. They typically occur as either isolated grains in the matrix (Figure 1) or within type IIA chondrules. Volumetrically the grains are dominated by pyrrhotite, Pentlandite grains, 5-20 microns always occur on the periphery of the pyrrhotite grains, but are clearly an integral part of the composite grain. Sometimes, the

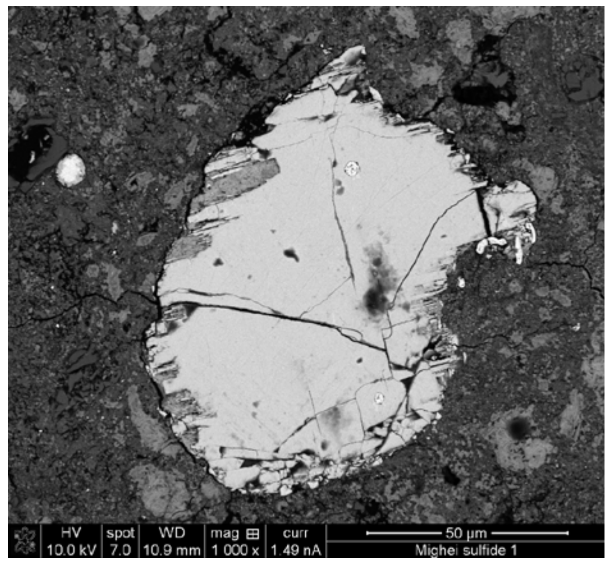

Figure 1. FEGSEM BSE image of partially altered submicron pyrrhotite grain in the Mighei CM carbonaceous chondrite. Elongate embayments filled with phyllosilicate minerals are present around the periphery of the grain.

pentlandite occurs as a thin, partial rim around the exterior of the pyrrhotite grain. The largest of these composite grains occur as isolated grains in the matrix and are usually irregular in shape but can show partially rounded morphologies. Where the grains occur in chondrules they are usually smaller, but are more commonly rounded to subrounded in morphology. SEM studies show that all the grains contain extremely fine-grained exsolved blebs or lamellae of a Ni-rich phase within the pyrrhotite, identical to those we have previously described in TIL 91722. Eight of the 10 composite grains that we studied show distinctive evidence of pseudomorphic replacement by secondary phases. The extent of replacement is highly variable, but the style of replacement is essentially identical in all cases. Figure 1 shows a typical example of this replacement texture. Elongate embayments are present at numerous places on the periphery of the grains that are filled with a fibrous phase. The size of these embayments varies in depth and width, but the largest can extend for up to 20 µm into the grain and be 5-10 µm in width. The parallel sides of the replaced zones in the crystals indicate that the replacement is crystallographically controlled. Where fine exsolution lamellae are present within the pyrrhotite adjacent to the alteration zones, it is clear that they have also undergone replacement. However, the pentlandite appears to be more resistant to alteration and sometimes relicts of pentlandite lamellae still occur within the altered regions of the pyrrhotite grains.

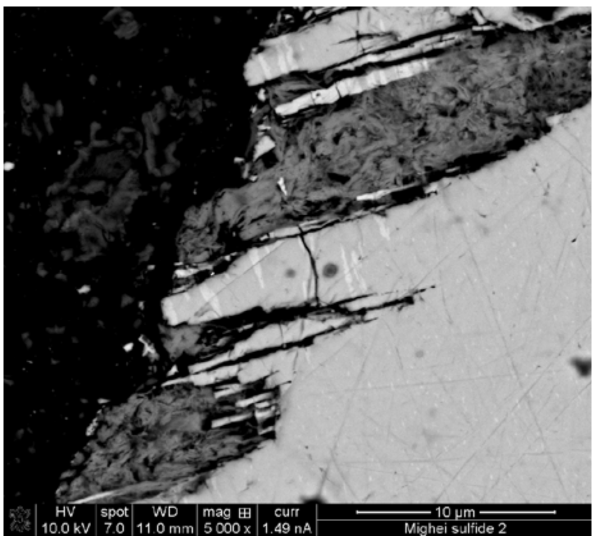

Figure 2 FEGSEM BSE image showing a closeup of an altered region of the pyrrhotitte grain shown in Figure 1. Crystallographically-oriented embayments filled with fibrous phases occur at several places within the grain. Fine exsolution lamellae within the pyrrhotite are truncated at the boundary with the alteration zone.

The FIB section studied so far by TEM was cut normal to a small region of elongate embayments close to the edge of the grain in order to examine the microstructure of the alteration zone. Figure 3 shows a TEM image of the altered region. Alteration of the pyrrhotite appears to occur by two different mechanisms. In the first case, pyrrhotite undergoes direct dissolution, preferentially on (0001) planes resulting in a highly facetted interface with a fibrous oxysulfide that has yet to be identified definitively. In the second case, pyrrhotite has undergone oxidation and loss of sulfur to form small grains of a Fe-oxide, probably magnetite, along fractures which then appears to have undergone dissolution as well. Islands of unaltered pyrrhotite with highly faceted morphologies remain within the regions of secondary oxysulfide.

Conclusions. Pyrrhotite-pentlandite grains in Mighei show many similarities to those found in TIL 91722. These include the presence of larger grains of pentlandite around the periphery of the grains, with widespread submicron blebs and lamellae of an exsolved Ni-rich Fe sulfide within the pyrrhotite. However, unlike TIL 91722, many of these grains exhibit clear evidence of secondary alteration. The pyrrhotite and pentlandite have been replaced by an as yet unidentified oxysulfide phase. The replacement of pyrrhotite can also involve the formation of a transitional Fe-oxide phase. The reaction is strongly crystallographically controlled occurring parallel to (0001) planes of hexagonal pyrrhotite. These observations demonstrate that contrary to previous views, pentlandite and pyrrhotite in CM chondrites are not necessarily secondary alteration products, but are clearly unstable during alteration, altering by a step wise mechanism to form an oxysulfide phase.

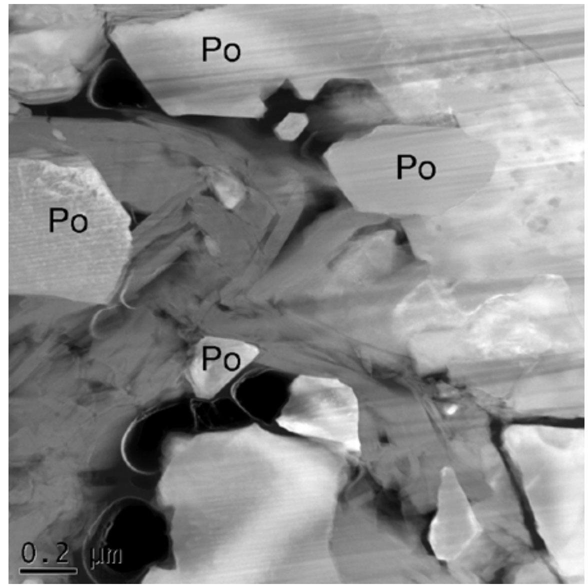

Figure 3 Dark field STEM image of alteration zone in pyrrhotite (po). Grains of a fibrous oxysulfide occur replacing the po with islands of unaltered po remaining within the fibrous phase.

References [1] Browning, L. B. et al. (1996) *GCA 60*, 2621–2633.; [2] Rubin, A.E. et al. (2007) *GCA 71*, 2361-2382. [3] Howard K.T. et al. (2009) *GCA* 73, 4576-4589. [4] Brearley, A.J. et al. (2009) *MAPS* 44, A40. [5] Hanowski, N.P. and Brearley, A.J. (2001). GCA 65, 495. [6] Zolensky, M.E. and Lie, L. (2003) *LPS XXXIV*, 1235. [7] Bullock et al. (2007) *LPS XXXVIII*, 2057. [8] Fuchs, L.H. et al. (1973) *Smithson. Contrib. to the Earth Sci*, 10, 1–39. [9] Brearley, A.J. and Martinez, C. (2010) LPI Contribution No. 1533, 1689. [10] Brearley, A.J. (2010) MAPS, 45, 5159 . [11] Maldonado, E.M. and Brearley, A.J. (2011) This volume.

Acknowledgements: Funded by NASA Grant NNG06GG37G to A.J. Brearley (PI).