

REDOX STATE OF PARTLY SULFIDIZED EH3 CHONDRULE CONSTRAINED BY FE EXSOLUTION FROM OLIVINE S. W. Lehner¹, P. Nemeth¹, M. I. Petaev², P. R. Buseck¹; ¹School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, (slehner@asu.edu, pbuseck@asu.edu); ²Dept. of Earth & Planetary Sciences, Harvard University, Solar, Stellar, & Planetary Sciences, Harvard-Smithsonian CfA, Cambridge, MA 02138 (mpetaev@cfa.harvard.edu)

Introduction: EH chondrites experienced gas-solid sulfidation reactions that resulted in the partial re-placement of ferromagnesian silicates by silica, niningerite, troilite, and oldhamite [1-5]. The strongest evidence for these reactions comes from a subset of EH3 ferromagnesian chondrules that contain assemblages of cristobalite, porous S-rich silica, niningerite, and troilite replacing olivine and pyroxene (Fig. 1) [4]. Thermodynamic analysis of the likely sulfidation reactions inferred from the mineralogy of the sulfidized chondrules points to their occurrence during transient heating events in a H-depleted, S- and dust-enriched environment [4,6,7], with the fS_2 buffered by the Fe-FeS assemblage [8,9] and redox conditions on the order of $\log fO_2$ IW-6. Here we present observations of Fe-metal and chromite exsolving out of olivine was been partly replaced by pyroxene, silica, niningerite, and troilite. The phase relations among the Fe-metal, chromite, and olivine constrain the redox conditions of silicate sulfidation.

Methods: A partly sulfidized chondrule from EH3 Sahara 97072 was studied using petrographic microscopy. Chemical mapping and EDS analyses were performed with an FEI XL-30 FEG SEM. A TEM section was extracted from dusty olivine using a focused-ion beam (FIB) from an FEI NOVA dual-source SEM. TEM, STEM, EDS, EELS, and SAED were performed using standard JEOL 2010F, 2000, and 4000 transmission electron microscopes plus a JEOL ARM aberration-corrected microscope. EDS data were quantified using the Cliff-Lorimer thin-film approximation with theoretical k-factors. For analysis of phase equilibria we used the GRAINS code and its thermodynamic database [10]. All solid solutions were treated as ideal.

Petrographic observations: The partly sulfidized chondrule (Fig. 1) has sharp boundaries with the matrix. The outer two thirds of this chondrule, occurs as a sulfide-free, mantle consisting of subhedral enstatite grains and interstitial mesostasis of crystalline silica, albite, and albitic glass. The chondrule interior contains a large opaque dusty olivine megacryst (Figs. 1A, B) that has been partly replaced by pyroxene, niningerite, troilite, and porous silica. Toward the chondrule center, the olivine contains sub-micron Fe-metal grains (Fig. 1C). The pyroxene that partly replaces the olivine contains even smaller Fe-metal grains within SiO_2 -enriched melt inclusions (not shown).

TEM observations: The olivine, nearly pure end-member forsterite, contains euhedral-to-subhedral Fe metal blebs and picrochromite, nearly pure $MgCr_2O_4$, along the [100] olivine direction (*Pnma* setting) (Fig. 2A). Most Fe metal grains contain Cr. The picrochromite occurs as fine lamellae that apparently cross-cut metal grains, suggesting that the picrochromite exsolved first. HRTEM imaging indicates the picrochromite is associated with

amorphous silica.

Phase equilibria: To constrain conditions and determine the sequence of chromite and metal exsolution from olivine we considered reactions among the Cr, Fe, and Mg end-members of olivine ($Cr_{0.005}Fe_{0.005}Mg_{0.99}O_4$), the Cr and Fe end-members of metal ($Cr_{0.01}Fe_{0.99}$) and pure $MgCr_2O_4$ as a function of temperature and fO_2 . The results are plotted in Fig. 3 along with the phase boundary for the reaction of olivine sulfidation buffered by the Fe-FeS assemblage [4]. The upper limit of fS_2 , evaluated from the reaction $Cr(ss) + 0.5 S_2(g) = CrS(ss)$, suggests that the preservation of metallic Cr requires fS_2 many orders of magnitude lower than the values buffered by the Fe-FeS assemblage, indicating physical isolation of the metal in solid olivine.

Discussion: Figure 3 suggests that exsolution of both picrochromite and metal from olivine occurs at high temperatures but under different redox conditions. The exsolution of picrochromite suggests that the chondrule was annealed under oxidizing conditions, perhaps during the formation of the mantle. The subsequent interaction of the chondrule with a more reducing environment resulted in exsolution of Cr-bearing metal. Whether the exsolution of this metal that was sealed within the olivine and pyroxene was contemporaneous with the olivine sulfidation is difficult to assess with certainty. It is possible that the fO_2 and fS_2 were high enough to sulfidize olivine but not orthopyroxene (Fig. 3).

Conclusions: The exsolution of picrochromite, and Fe metal, from olivine that has been partly replaced by pyroxene, niningerite and silica suggests that the chondrule experienced heating above 1700 K in an environment with variable redox conditions changing from $\log fO_2$ IW-2 to -7.

References: [1] Grossman et al., (1985) *GCA* 49: 1781-1795. [2] Ikeda (1989) Proceeding s of NIPR Symp. on Antarctic Meteorites 2: 109-146. [3] Lehner and Buseck (2010) *LPSC* 41 #1855 [4] Lehner S. W. et al. (2013) *GCA* 101: 34-56. [5] Rubin (1983) *E&PSL* 64: 201-212. [6] Petaev M. I. et al. (2011) *LPSC* 42, #2323. [7] Petaev, M.I., et al. (Nov. 2011) LPI Workshop on form. of first solids in the SS #9095. [8] Guillermet et al., (1981) *Metallurgical Transactions B-Process Metallurgy* 12: 745-754. [9] Petaev et al. (2012) *LPSC* 43 #2229. [10] Petaev, M. I. (2009) *Calphad* 33:317-327

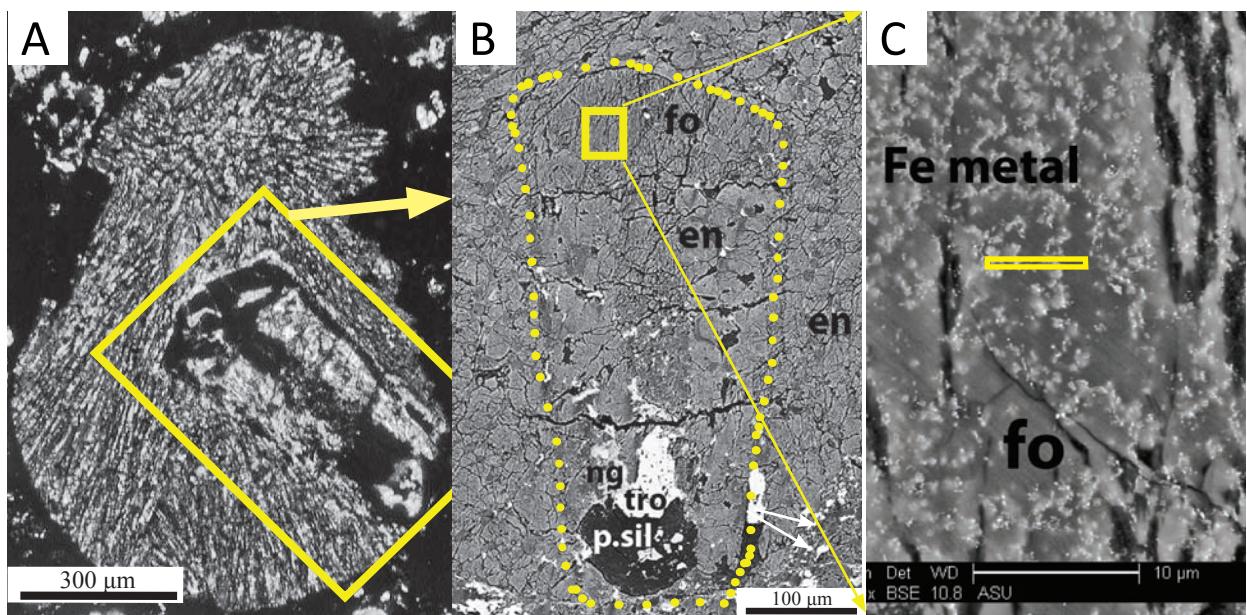


Fig. 1. Large dusty olivine megacryst within a partly sulfidized chondrule. A) Plane-polarized-light image. B) Backscattered electron (BSE) enlargement of the megacryst. C) BSE enlargement of the dusty olivine from the rectangle in B. Yellow rectangle shows the location of the FIB section in Fig 2. fo = forsterite, p. sil = porous silica, ng = niningerite, tro = troilite, en = enstatite.

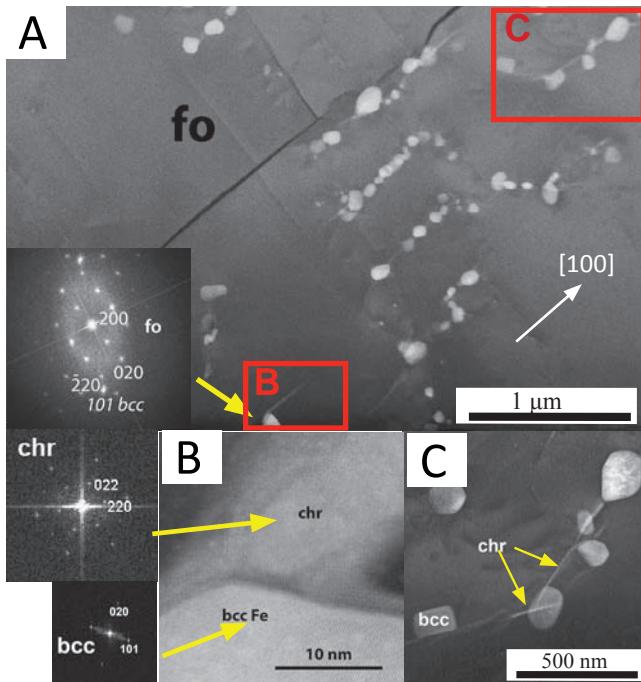


Fig. 2. A) Annular dark-field STEM image of a portion of the FIB section. The inset shows the orientation of kamacite in relation to the olivine. B) Enlargement of metal bleb and chromite lamellae from the red rectangle labeled 'B'. Diffraction patterns show chromite and kamacite. C) Enlargement of red rectangle labeled 'C'. Note the relation of chromite lamellae to Fe-metal blebs. bcc = BCC iron, chr = chromite; other abbreviations as in Fig 1.

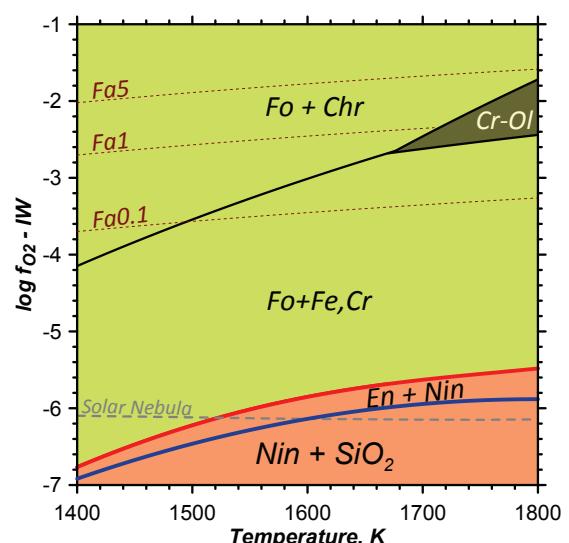


Fig. 3. Diagram of phase stability fields in the S-free (light green, minerals occurring within olivine and pyroxene) and S-rich (peach, partly sulfidized silicates with the fS_2 buffered by Fe-FeS) portions of the Mg-Fe-Cr-Si-O-S system. Chr = $MgCr_2O_4$, Fo = Mg_2SiO_4 , Cr,Fe = Cr bearing metal, Cr-Ol = Cr and Fe-bearing olivine (see text), Fa = fayalite content in olivine, En = enstatite, Nin = niningerite, $(Fe,Mg)_S$, SiO_2 = silica. The fO_2 curves for the metal-olivine (Fa#) and solar nebula equilibria [4] are shown for reference.