

SULFIDATION OF ENSTATITE IN THE FINE-GRAINED MATRIX OF EH3 SAHARA

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Introduction: The origin of the Mg-sulfide niningerite in EH3 meteorites is controversial. It is thought to have condensed from a highly reduced (C/O~1) nebular gas [1-3] and, alternatively, to have formed by the sulfidation of Mg-silicates [4-8]. EH3 chondrites contain silica-sulfide-rich chondrules in which ferromagnesian silicates display replacement texture with silica, troilite, and niningerite [6-8], consistent with sulfidation via reactions such as $(\text{Fe}_x\text{Mg}_{2-x})\text{Si}_2\text{O}_6 + \text{S}_2 = 2-x\text{MgS} + x\text{FeS} + 2\text{SiO}_2 + \text{O}_2$. Based on the mineralogy of these chondrules, thermodynamic analysis of phase equilibria suggests silicate sulfidation could have occurred at 1400 to 1600K under near-nebular redox conditions in a H-depleted, dust-enriched, environment, with the $f\text{S}_2$ controlled by molten metal-sulfide assemblages [8, 9].

To further explore this idea, we looked for evidence of sulfidation in the fine-grained matrices of EH3 chondrites. They contain between 2 and 15 vol % matrix (grain diameters <~5 μm) [10, 11]. This matrix occurs widely distributed between chondrules, metal-sulfide nodules (MSN), and large clasts, and it is commonly concentrated in chondrule embayments [12, 13] (Fig. 1). Here we report TEM results of the occurrence of a S-enriched area where niningerite and silica occur surrounded by enstatite.

Methods: TEM sections were extracted using a focused-ion beam (FIB) from polished thin sections of EH3s Sahara 97072, ALH 84170, and LAR 06252. TEM, STEM, EDS, EELS, and electron diffraction were performed with a JEOL 2010F microscope. EDS data were quantified using the Cliff-Lorimer thin-film approximation with theoretical k-factors. Due to the extremely fine-grained nature of the material, many analyses were of mixtures. In order to understand what minerals could reasonably represent the S-rich mixtures, our normative calculations apportioned atomic percentages as follows: all Mn was assigned to MnS, the Mg/Mn ratio from electron microprobe analyses of niningerite was used to assign the proportion of Mg as MgS since this ratio is nearly constant within individual EH meteorites [14], and the remaining S was assigned to Fe. Excess Fe was assigned to FeNi metal, Si to silica if there was sufficient O, and excess Mg to enstatite when Si and O were sufficient. Thus the minerals reported as mixtures are estimates. The FeS-MgS solid solution has been divided into niningerite and keilite based on the Fe/Mg ratio [15]. Niningerite contains at% Fe < at% Mg, and keilite contains at% Fe > at% Mg.

TEM observations: EH3 matrix contains 50 to 80 vol% silicates dominated by enstatite, ~20 to 40 vol% silica, and from <5 to 20 vol% metal and sulfide (Fig. 2). Com-

mon matrix minerals in order of abundance are enstatite, silica, troilite, kamacite, niningerite, oldhamite, djerfisherite, graphite, and schreibersite. The FIB section contains polycrystalline enstatite interspersed with amorphous silica ~100nm in diameter, similar-sized kamacite grains, and smaller sulfides which are predominantly troilite (Fig. 2). Within this section there is a S-rich area that contains amorphous C, silica, niningerite, and veins of keilite + kamacite. The veins connect to kamacite containing 5 at% Ni and 3 at% Si. Adjacent to these veins amorphous silica with a mottled texture is mixed with C, kamacite, and niningerite, which has a gradational contact with enstatite (Fig. 3).

Discussion: We interpret the S-rich area as an example of sulfidation of enstatite producing niningerite/keilite and silica. The FeS contents of niningerite/keilite indicate the minimum temperature of formation was at least ~1000K [16]. Thermodynamic analysis [8, 9] shows that the $f\text{S}_2$ necessary for sulfidation can be maintained by a metal-sulfide assemblage near the redox conditions of CO-CO₂ buffer (Fig. 4). The Si content of the kamacite (3 at%) constrains the conditions under which enstatite, silica, niningerite, and metal are in equilibrium. These minerals point to reactions of silicates and FeNi metal with a gaseous phase dominated by S₂ and CO between ~1000 and 1100K, in agreement with temperatures calculated from the FeS content of the niningerite/keilite.

Conclusions: The mineralogy and compositions of this S-rich area can be explained by reaction of enstatite and FeNi metal with a gas composed primarily of S₂ and CO at a temperature between ~1000 and 1100K that produced silica and niningerite/keilite.

References: [1] Lin Y. & El Goresy A. (2002) *MAPS*, 37, 577-599. [2] El Goresy A. et al. (1988) *Proc. NIPR Symp. Antarctic Meteor.*, 1, 65-101. [3] Kimura, M. *Proc. NIPR Symp. Antarctic Meteor.*, 1, 51-64. [4] Rubin A. E. (1983) *E&PSL* 64: 201-212. [5] Ikeda Y. (1989) *Proc. NIPR Symp. Antarctic Meteor.* 2: 109-146. [6] Lehner S. W. & Buseck P. R. (2010) *LPS* 41, #1855. [7] Lehner S. W. et al. (2011) *LPS* 42, #1863. [8] Petaev M. I. et al. (2011) *LPS* 42, #2323. [9] Petaev, M.I., et al. (Nov. 2011) *LPI Workshop on form. of first solids in the SS #9095*. [10] Huss, G. R., et al (2005), in *Chond. and the Protopl. Disk*, ASP, 701-731. [11] Scott, E.R.D. and A.N. Krot (2005), in *Chond. and the Protopl. Disk*, ASP, 15-53. [12] Rubin, A.E., et al., (2009), *MAPS*, 44, 589-601. [13] Lehner, S.W. and P.R. Buseck, 2010, *LPS* 41, Abst 1880. [14] Lin and El Goresy, (2002), *MAPS* 37, 577-599. [15] Shimizu, M. et al. (2002) *The Can. Min.* 40, 1687-1692. [16] Skinner B. J. and Luce F. D., (1971) *Amer. Min.* 56: 1269-1296. [17] Guillermet A. F. et al.

(1980) *Metall. Trans.*, 12B, 745-754. [18] Ebel D. S. & Alexander C. M. O'D. (2011) *P&SS*, DOI 10.1016/j.pss.2011.07.017. [19] Petaev M. I. (2009) *CALPHAD*, 33, 417-427.

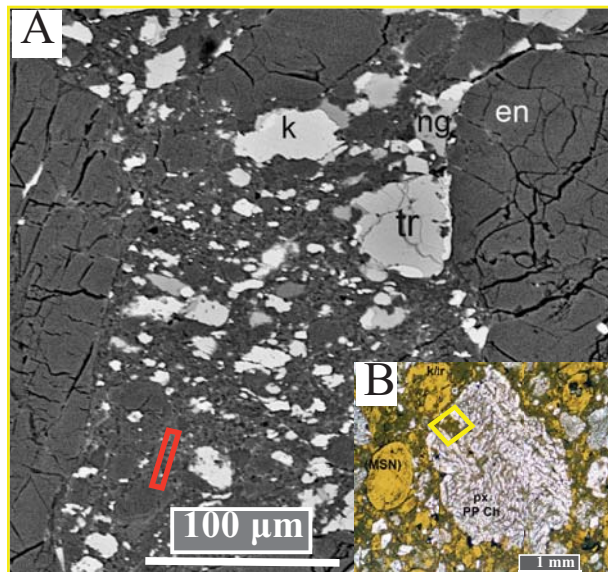


Fig. 1. (A) BSE image of fine-grained material. The red rectangle marks the location of a FIB section (Fig. 2). (B) Combined reflected- and transmitted-light image showing distribution of fine-grained opaque material. Area in the yellow diamond is enlarged in A. k = kamacite, tr = troilite, MSN = metal-sulfide nodule, px = pyroxene, en = enstatite, ng = niningerite, PP Ch = porphyritic pyroxene chondrule.

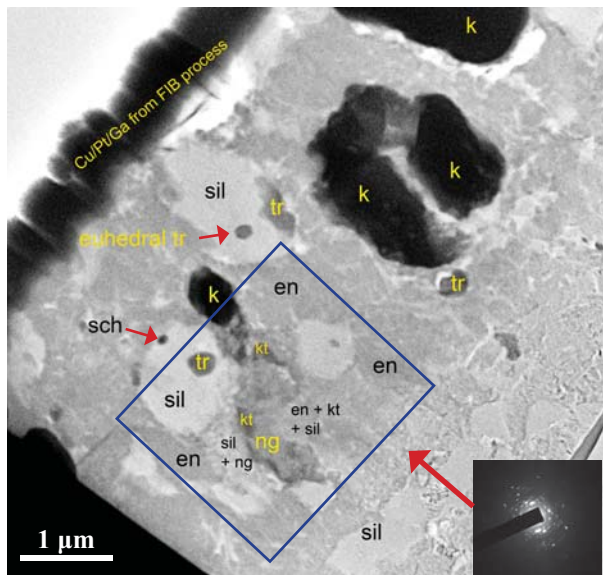


Fig. 2. TEM bright-field image of FIB section lifted from location of red rectangle in Fig. 1. Electron diffraction (lower right) indicates the enstatite is polycrystalline. The area in the blue rectangle is enlarged in Fig. 3 and contains an area rich in S, lacking O where enstatite appears to have been replaced by niningerite or keilite. sil = silica, sch = schreibersite, kt = keilite; other symbols as in Fig. 1

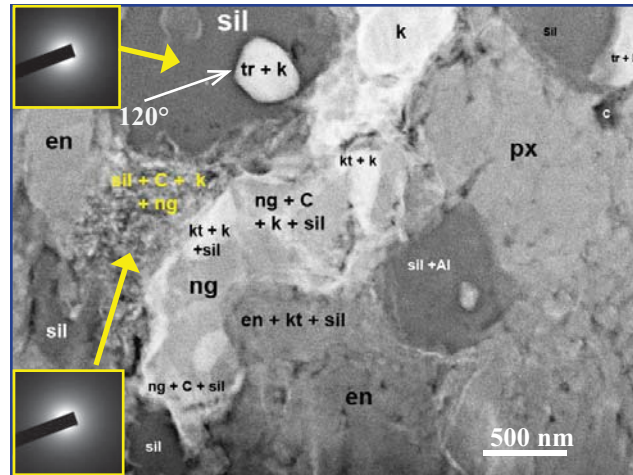


Fig. 3. Scanning TEM annular dark-field image of the area from the rectangle in Fig. 2, which is the S-rich area discussed in the text. The center of this area consists of a C-rich mixture of niningerite, kamacite, and silica that grades into niningerite and is bordered by veins of keilite + kamacite. To the left of these veins silica with mottled texture enclosing minor C, kamacite and niningerite is in contact with enstatite. On the lower right side of the niningerite a mixture of enstatite, keilite, and silica is in contact with enstatite. A mixture (Fe/S=1.2) of Fe-metal and troilite occurs enclosed in amorphous silica to the left of the large kamacite grain.

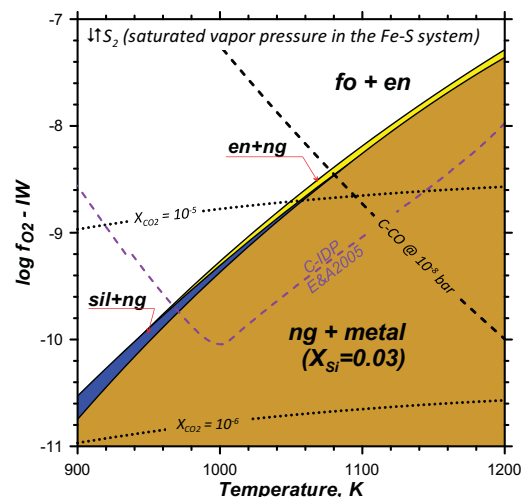


Fig. 4. Stability fields of forsterite (fo), enstatite (en), niningerite (ng), silica (sil) and metal bearing 3 at % Si in equilibrium with Fe-FeS buffer [17]. The black dotted lines show the f_{O_2} values of the CO-CO₂ buffer, with labeled mole fractions of CO₂. The dashed line shows the f_{O_2} values of the C-CO buffer at total pressure of 10⁻⁸ bar. The purple dashed line shows the f_{O_2} values in a system 1000× enriched in cluster interplanetary dust particles (C-IDP) [18] calculated at a nebular pressure of 10⁻⁴ bar with the GRAINS code [19] assuming full equilibrium. The sources of thermodynamic data and activity coefficients are the same as [8, 9]. The mineral assemblages in Figs. 2 and 3 point to reactions of silicates and Fe,Ni metal with a gaseous phase dominated by S₂ and CO at temperatures between ~1000 and 1100K.