

THE ORIGIN OF NININGERITE IN EH3 SILICA-BEARING CHONDRULES. S. W. Lehner¹, M. I. Petaev², M. Zolotov¹, P. R. Buseck¹; ¹School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, (slehner@asu.edu, pbuseck@asu.edu); ²Department of Earth & Planetary Sciences, Harvard University, Solar, Stellar, & Planetary Sciences, Harvard-Smithsonian CfA.

Introduction: EH3 chondrites have a population of silica-bearing chondrules that contain abundant sulfides, a feature that distinguishes them from silica-bearing chondrules in other chondrite groups [1, 2]. These chondrules are enriched in Al, S, Na, Mn, and Si relative to CI chondrites and contain evidence that niningerite (Mg,Fe,Mn)S formed from pyroxene and olivine via silicate sulfidation reactions (Figs 1, 2). Furthermore, the most primitive EH3 chondrites contain numerous metal-sulfide nodules that appear to have been remelted [3, 4]. Metal-sulfide melt may be capable of generating sufficient S vapor pressure to drive sulfidation under certain circumstances [5]. The formation of niningerite during secondary processing of silicates is in contrast to models calling for direct condensation of the lithophile sulfides in ECs from a nebular gas with enhanced C/O ratio [6].

Methods: Initial observations and measurements with electron microprobe, scanning electron microscopy, and petrographic microscopy were previously reported [1]. Additional work involved transmission electron microscopy (TEM) sections extracted with a focused ion beam (FIB) instrument and chemical equilibrium calculations.

Results: Most chondrules have pyroxene mantles, with cores containing a silica phase and sulfides (Fig. 1), although some have silica-rich rims. In many cases Raman spectroscopy indicated silica was amorphous or possibly cryptocrystalline tridymite or cristobalite. In a few cases silica with low impurities produced Raman spectra indicating cristobalite. We use the generic name silica when referring to a phase and SiO₂ when referring to a component. Many SiO₂-rich regions within the chondrules (70 to 93 wt% SiO₂) are porous and contain Na and S. Niningerite occurs in approximately equal proportions with troilite, and both are interspersed within silica. Large grains of both sulfides commonly contain silicates and Si-bearing mixtures as small inclusions. Similar mixtures with compositions intermediate between sulfides and silicates occur between pyroxene and niningerite. Niningerite is also common on the peripheries of rounded enstatite grains enclosed within silica.

The average enstatite and olivine compositions are En₉₉ and Fo₉₈, respectively. However, pyroxene in these chondrules contains up to 2.2 mol% FeO, which in many cases is zoned with highest concentration in the center of the grains (Figs 3, 4). For example, the chondrule shown in Figs 1-4 has a bimodal FeO distribution, with the higher-FeO concentration ~ 1 mol% (Fig. 4). The low-FeO pyroxene (<0.2 mol% FeO) contains small blebs of troilite and niningerite (Fig. 3) that are absent from the high-

er-FeO pyroxene.

Discussion: The assemblages of enstatite, niningerite, and silica can be explained in terms of both gas-solid sulfidation of silicates and sulfidation during chondrule remelting. Some chondrules were partially remelted, leaving large olivine and enstatite grains, including partially sulfidized grains, intact (Fig. 1). Sulfides and small pyroxene grains were melted. The melted fraction (rich in S, Si, Fe, Na, and Mn) formed niningerite, silica phases, S-containing silicates, and troilite, all of which must have formed under high fS_2 as indicated by the lack of Fe metal. The occurrence of mixtures with compositions intermediate between known sulfides and silicates is evidence for exchange of elements between these mineral groups during remelting. Other assemblages are consistent with gas-solid sulfidation of magnesian silicates forming silica and MgS within niningerite.

Sulfide-silicate equilibria can be shifted toward sulfide stability in environments with significantly lower than nebular fO_2 , significantly higher than nebular fS_2 , or both. It also remains to be determined whether such reactions occurred in the nebula or in a H-depleted environment. Injecting FeO-bearing silicates into a nebular system with low fO_2 , resulting from extremely dry conditions or an influx of C, can explain sulfidation by raising the (H₂S+SiS)/H₂O ratio; however, other reactions, which would be expected under such reducing conditions, such as complete reduction of FeO in silicates, are not observed. Also, silica stability suggests fO_2 near solar values [5]. At temperatures above ~ 1500 K, fS_2 supplied by a Fe-Ni-S melt is sufficient to drive sulfidation reactions even in a system with nominally solar fO_2 if the system is depleted in H and enriched in C [5].

Conclusions: The FeO content of silicates and presence of silica indicate sulfidation in the silica-bearing chondrules occurred in a region with nominally solar fO_2 . Thermodynamic calculations suggest silicate sulfidation reactions are possible at high temperature and near nebular fO_2 in a H-depleted, C-buffered environment, with fS_2 generated by melting of metal-sulfide nodules.

References: [1] Lehner, S.W. and P.R. Buseck, (2010), *41st LPSC*. [2] Hezel, D.C., et al., (2006), *GCA*, 70, 1548-1564. [3] Weisberg, M.K., et al., (2006), *MAPS*, 41, p. A186-A186. [4] Lehner, S.W., P.R. Buseck, and W.F. McDonough, (2010), *MAPS*, 45, 289-303. [5] Petaev et al. (2011), *42nd LPSC* This volume. [6] Larimer, J.W. and M. Bartholomay, (1979), *GCA*, 43, 1455-1466.

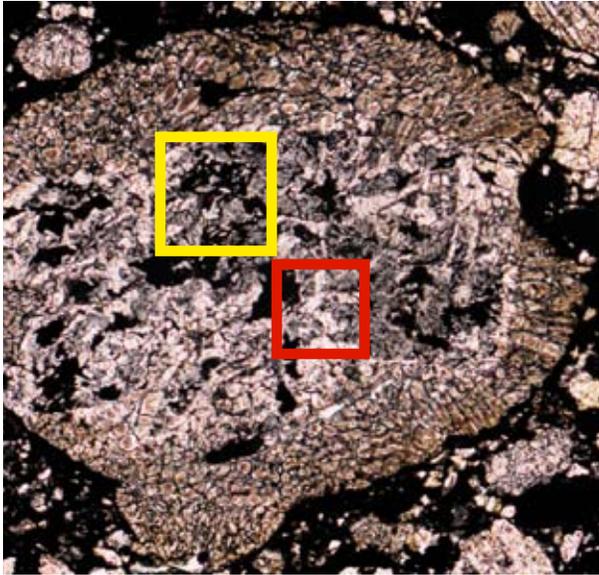


Fig 1. Plane polarized view of a porphyritic pyroxene (px) chondrule with sulfidized interior. Bright areas are high-FeO px and darker areas are low-FeO px containing sulfides. The yellow box is enlarged in Fig. 2. The red box is enlarged in Fig. 3.

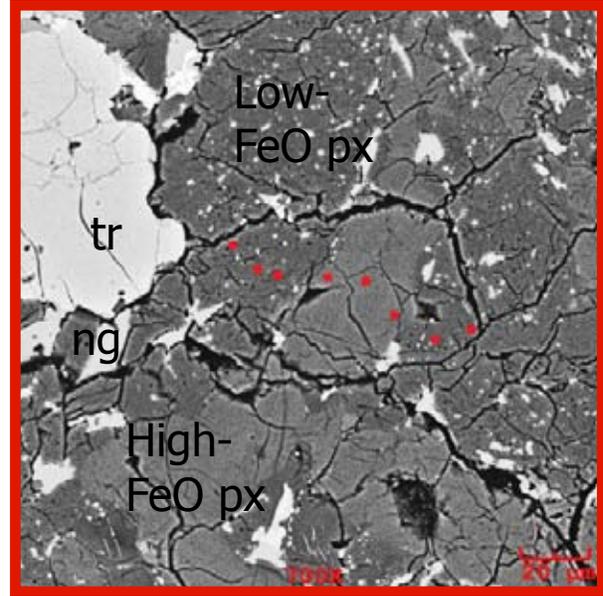


Fig 3. Back-scattered electron image of the area in the red box of Fig. 1. Red dots show the location of a microprobe traverse across an area of high-FeO px. Note the sulfide grains within the low-FeO pyroxene.

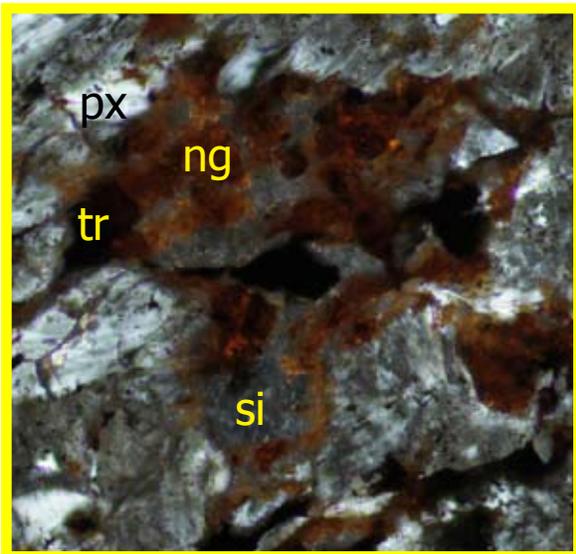


Fig 2. Crossed-polar view of a region where the pyroxene has been altered to niningerite (ng) and silica (si), with inclusions of troilite (tr).

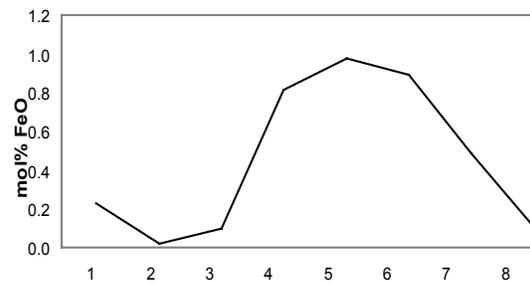


Fig 4. Plot of Fe concentration vs distance corresponding to the red dots in Fig. 3.