SILICA-RICH CHONDRULES IN ALH 84170 AND SAHARA 97072 EH3 METEORITES: EVIDENCE FOR SULFIDATION OF SILICATES. S. W. Lehner¹ and P. R. Buseck¹, ¹School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, (slehner@asu.edu, pbuseck@asu.edu).

Introduction: Oldhamite (CaS) and niningerite (MgS), both of which are highly reduced phases in EH chondrites, have been proposed to have condensed from a fractionated solar gas with a C/O ratio ~1 [1]. However, this model has been questioned because it does not explain the limited abundance of graphite in E3 chondrites; the need to preserve the sulfides below ~1000 K where, according to the C/O ~1 model, they become unstable [2]; and the high concentrations of volatile elements in oldhamite. An alternative mechanism for the formation of ECs from a nebula of solar composition is provided by the condensation with partial isolation (CWPI) model of Petaev and Wood [3]. However this model requires requires a process other than condensation for the formation of niningerite, which does not appear as a stable phase in the calculations.

Niningerite could have formed via sulfidation of enstatite and olivine during transient heating events [4], and oldhamite could have formed by igneous processes [5]. The sulfidation of olivine has been shown experimentally to form niningerite and enstatite [4] and sulfidation of enstatite was proposed to explain silica-rich clasts in the Adhi-Kot impact-melt breccia, with niningerite as a product [6]. Here we present mineralogical evidence for silicate sulfidation, reporting chondrules rich in silica, niningerite, and troilite in intimate association with enstatite and olivine. This is the first-in depth study of silica-rich chondrules in EH meteorites.

Methods: Thin sections of four EL3 and nine EH3 meteorites were surveyed for silica-rich chondrules using petrographic microscopy. They occur in Sahara 97072, ALH 84170, PCA 91085, and EET 83322, all EHs. Eight silica-rich chondrules from Sahara 97072 and one from ALHA 84170 were chosen for further study. Element maps and backscattered images were made using SEM with EDS. Minerals were analyzed with a JEOL JXA-8600 electron microprobe. Bulk chondrule compositions were measured by either a) rastering a 15-µm electron beam over 300 x 275 µm rectangular areas, or b) obtaining EDS spectra with a FEG SEM over the largest rectangle to fit over a chondrule, or both a) and b). Laser Raman spectra were obtained with a 532-nm laser that had a spot size of ~3 µm. Modal analyses were obtained by pixel counting element maps.

Results: Based on EDS and microprobe analyses, silica is abundant in the chondrules under consideration. In places Raman spectroscopy showed the silica to be tridymite, but more commonly it indicated amorphous or possibly cryptocrystalline tridymite. We therefore use the generic name silica rather than a specific mineral.

Chondrules range from being dominated by silica (Fig. 1) to consisting of enstatite with enclosed silica, troilite, and niningerite. Other chondrule regions contain between 70 and 95 wt % SiO₂ but also contain up to 5 wt % S and significant Ca or Na. These areas yield low totals in microprobe analyses, are relatively dark, and appear fibrous in electron backscattered images, suggesting they are either porous, have high volatile content, or unidentified light elements such as C. Most chondrules contain Al-rich phases, identified as plagioclase, augite, or both with Raman spectroscopy. All chondrules contain enstatite, most of which is clinoenstatite (avg. En₉₉), and >50% contain minor forsterite (avg. Fo₉₈). Troilite and niningerite occur in approximately equal proportions interspersed within the silica. Most chondrules have enstatite rims and their cores contain silica and sulfides, although some have silica rims with a mixture of enstatite and silica in their cores. Some chondrules contain oldhamite, but more commonly Ca is in the pyroxene and silica-rich regions. Kamacite occurs in the matrix but is absent from the chondrules.

The bulk compositions of the SiO₂-rich chondrules are similar to the Al₂O₃-rich [7, 8] and SiO₂-rich chondrules in ordinary chondrites [9], except for containing \sim 5 to 10 wt% S. Al₂O₃ ranges from <1 up to \sim 8 wt %, CaO from <1 to nearly 3 wt %, and Na₂O from <1 to \sim 4 wt %. Molar volume ratios of silica to niningerite and troilite are \sim 2:1:1 respectively for all nine chondrules.

Discussion: Silica occurs with enstatite in all chondrules and with olivine in several (Fig. 2). The molar volume ratios of silica to troilite and niningerite are consistent with the following reactions:

$$\begin{split} &Mg_{2}SiO_{4}+3H_{2}S(g)+3SiO(g)+Fe=MgSiO_{3}+2SiO_{2}\\ &+MgS+FeS+SiS(g)+3H_{2}(g),\Delta Grxn\ \ \text{-}2685\ kJmol^{-1};\\ &and \end{split}$$

$$\begin{split} MgSiO_3 + 2H_2S(g) + SiO(g) + Fe &= 2SiO_2 + MgS + FeS \\ &+ 2H_2(g), \end{split}$$
 $\Delta Grxn -603 \text{ kJmol}^{-1}.$

Both reactions produce products with the same silica/sulfide ratios observed in the chondrules. The reactions as written and the ΔG_{rxn} are based on 1 atm pressure. The actual ΔG for these reactions in the solar nebula would depend on the relative fugacities of the gas species on both sides of the equations. High partial pressures of SiO gas could have resulted from volatilization events in regions with a high dust/gas ratio [10], particularly under highly reducing conditions. Under such a scenario, high partial pressure of H_2S could have resulted from volatilization of FeS.

Conclusions: Our evidence suggests that at least some niningerite could have formed by sulfidation of

enstatite and olivine, lending support to the CWPI condensation model [3] for the formation of the EC mineralogy.

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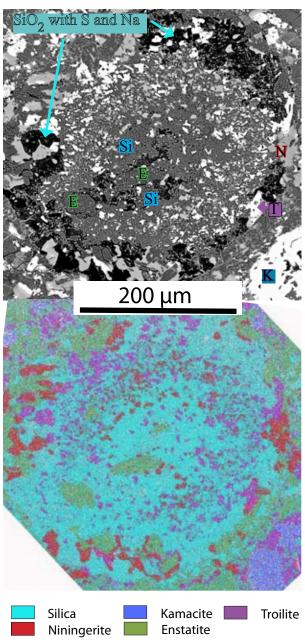


Fig.1. Top: BSE image of a silica-rich chondrule. E is enstatite, Si is silica, N is niningerite, T is troilite, and K is kamacite. The black areas are rich in Si, contain S and Na, and yeild low microprobe totals. Bottom: Element maps of Fe, S, Si, Mg, and Mn overlain on one another.

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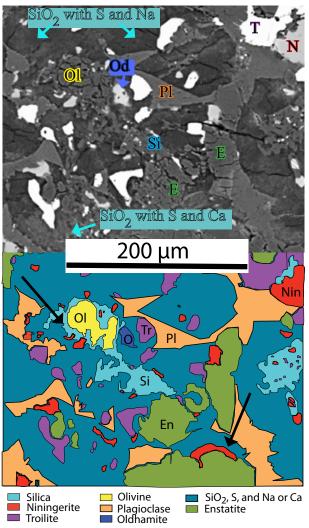


Fig. 2. Top: BSE image of the central region of a silica-rich chondrule showing possible reaction textures between olivine or enstatite with silica and niningerite (arrows). Ol is olivine, Od is oldhamite, the others are the same as in Fig. 1. Bottom: Color-coded map of mineralogy in top image.