THE ORIGIN OF NININGERITE IN EH3 SILICA-BEARING CHONDRULES: INSIGHTS FROM MINERAL EQUILIBRIA.

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Introduction: The chalcophile behavior of Mg, Ca, Mn, Cr, Ti, Na, and K in enstatite chondrites is commonly interpreted as the evidence for their formation under highly reduced conditions in a portion of the solar nebula with enhanced C/O~0.8-1 [*e.g*., 1-3]. Calculated condensation sequences for such a nebula [1-8] show that the first condensates, such as SiC, TiC, CaS, MgS, AlN, and FeSi, become unstable below ~1000K and are subsequently replaced by oxides, silicates, metal, and troilite. In such a scenario major silicates (pyroxenes, forsterite, and plagioclase) must be formed by reaction of niningerite, (Mg,Fe,Mn)S, oldhamite, CaS, SiC, and FeSi with gaseous O-bearing species, but no petropgaphic evidence for such reactions has been found so far.
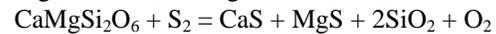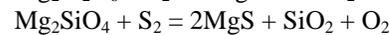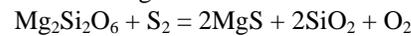
On the contrary, we recently described a suite of SiO_2-bearing chondrules that provide textural evidence for the replacement of enstatite and forsterite by the assemblage of a silica phase and sulfides of Mg, Mn, Fe, and, to a lesser extent, Ca and Na [9]. The accompanying abstract [10] describes these objects in greater detail while here we focus on thermodynamic analysis of the observed mineral reactions.

Summary of Petrographic Observations: Despite substantial textural variations, the SiO_2- and sulfide-bearing mineral assemblages typically have ragged relationships with orthopyroxene and, in places, forsterite grains. This texture suggests substitution of the former for the latter. Silica phase is typically amorphous and porous and contains substantial amounts of Na and S, suggesting that it formed while the chondrules were partially molten [10]. Niningerite and troilite are interspersed within the silica phase in nearly equal proportions. Relatively large grains of both sulfides typically contain silicates as small inclusions. Niningerite is also common on the periphery of rounded enstatite grains enclosed within silica. In some occurrences oldhamite occurs with niningerite and troilite. The niningerite shows minor variations in Mn and Fe contents, with the average composition being $Mg_{0.71}Fe_{0.18}Mn_{0.11}S$. The troilite and oldhamite are nearly pure end-members. The pyroxene displays substantial FeO variations (up to 3 wt.%) and, in places, compositional zoning with FeO decreasing outward. Some low FeO pyroxene grains enclose small blebs of troilite and niningerite. There is no Fe metal in the silica-sulfide assemblage.

Thermodynamics of Mineral Equilibria: The observed mineralogy and mineral chemistry of SiO_2 and

MgS-bearing chondrules requires their formation under relatively oxidizing conditions, similar to those of typical Type I chondrules, followed by exposure to a high-temperature, S-rich environment capable of sulfidizing ferromagnesian silicates. The lack of Fe metal in these chondrules suggests that the chemical potential of S was high enough to make metal unstable.

The observed mineral relationships can be described by the following chemical reactions

$$Mg_2Si_2O_6 + S_2 = 2MgS + 2SiO_2 + O_2$$
$$Mg_2SiO_4 + S_2 = 2MgS + SiO_2 + O_2$$
$$CaMgSi_2O_6 + S_2 = CaS + MgS + 2SiO_2 + O_2$$
$$2CaMgSi_2O_6 + S_2 = 2CaS + Mg_2Si_2O_6 + O_2$$

which did not go to completion, thus preserving both the reactants and products. Similar reactions can be written for the Fe and Mn end-members of silicate solid solutions. FeSi is known to be stable at reducing conditions, so the reaction $SiO_2 + Fe = FeSi + O_2$ can be used to constrain oxygen fugacity (f_{O2}) during sulfidation. Likewise, the mineral equilibrium involving Fe metal and troilite, $Fe + 0.5S_2 = FeS$, can constrain f_{S2}. Although in H-rich nebular environments H_2S and H_2O are the major gaseous species of S and O, respectively, their fugacities are linked to f_{S2} and f_{O2} as $f_{S2}=sqrt[f_{H2S}/(f_{H2}*K_{eq})]$ and $f_{O2}=sqrt[f_{H2O}/(f_{H2}*K_{eq})]$, where K_{eq} is the equilibrium constant of the corresponding reaction. Therefore, if a gaseous phase is in internal equilibrium, as is the case of all full-equilibrium calculations used here, then one can utilize either set of fugacities.

The phase boundaries of the above reactions were calculated using the computer codes and thermodynamic databases of [11]. The results are plotted in Figs. 1-3, with details given in the figure captions.

Results and Discussion: In principle, shifting sulfidation reactions towards products (SiO_2 and sulfides) can be done by lowering f_{O2}, increasing f_{S2}, or a combination of both.

The customary case of sulfide stabilization by lowering f_{O2} is to assume a nebular model with an enhanced C/O ratio. Exposure of Type I chondrules to a high-temperature gaseous phase in such a system would result in formation of Mg and Ca sulfides [*e.g*., 3]. Also, instead of silica either FeSi or SiC, or both should form, consistent with thermodynamic calculations and experiments on forsterite sulfidation [12]. However, such mineralogy is inconsistent with our observations.

The alternative to low f_{O2} is to assume increased f_{S2}.

Our full-equilibrium calculations show that an increase of S abundance by up to 1000× in an otherwise 'solar' system does not stabilize Ca and Mg sulfides because of the high stability of H_2S. Addition of S does increase f_{H2S} by the same magnitude but, without lowering f_{O2}, does not stabilize Mg and Ca sulfides. However, we found that partially or completely molten metal-sulfide nodules, abundant in enstatite chondrites, are capable of generating f_{S2} high enough to shift silicate-sulfide reactions toward the stability fields of SiO_2 and sulfides at nominal solar nebula redox conditions (Fig. 1).

The caveat is the necessity to preserve S_2 gas released from the metal-sulfide nodules from conversion into H_2S through reaction with H_2. Such S_2 preservation can be done in a system depleted in H by ~10,000× (Fig. 2), consistent with current ideas on dust enrichment in chondrule-forming environments [14]. Depletion in H of such a magnitude would make redox conditions in the remaining system highly oxidizing, thus greatly increasing the stability of silicates and making their sulfidation nearly impossible. Therefore, a reducing agent capable of binding O is needed. The most obvious candidate is C, which may have occurred in the chondrule-forming regions as organic matter. Fig. 3 shows that a gaseous phase with a C/O ratio approaching 1 is capable of creating f_{O2} values favorable for sul-

fidation of ferromagnesian silicates.

Concluding remark: Molten metal-sulfide nodules are capable of generating f_{S2} high enough to shift silicate-sulfide reactions toward the stability fields of SiO_2 and sulfides at nominal solar nebula redox conditions. A reheating of ferromagnesian chondrules and metal-sulfide nodules, abundant in enstatite chondrites, would result in formation of textures and mineral assemblages similar to those of the SiO_2-rich chondrules from enstatite chondrites.

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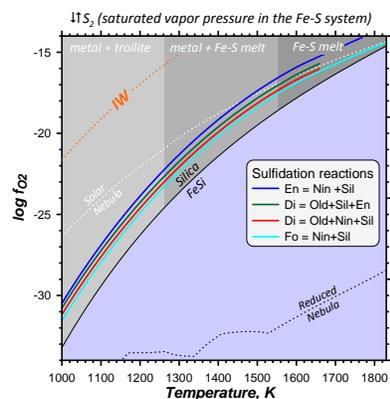

Fig. 1. Phase boundaries of sulfidation reactions involving enstatite (blue), diopside (green and red), and forsterite (cian). The stability fields of silicates are above the corresponding phase boundaries, at high f_{O2}. The f_{S2} values are assumed to be equal to those of the metal-sulfide buffer at each temperature. Data for the Fe-S melt are from [13]. The niningerite solid solutions is treated as ideal, with X_{MgS}=0.7. The f_{O2} values for the nominal (white dotted line) and 'reduced' (C/O=1, black dotted line) are calculated at nebular pressure of 10^{-5} bar with the GRAINS code assuming full equilibrium. Gray shades show phase changes in the Fe-S system. The powder-blue corner shows the stability field of FeSi. The IW buffer curve is shown for reference.
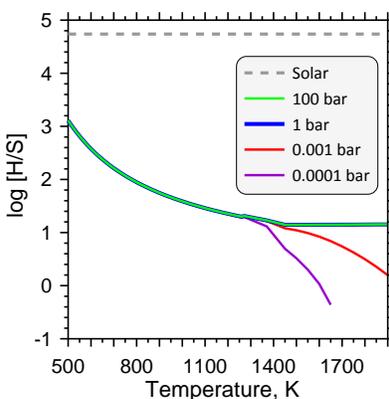

Fig. 2. Atomic H/S ratios in the gaseous phase equilibrated with solid metal-troilite or metal-sulfide melt at different temperatures and pressures. Because of the high stability of H_2S, the S_2 gas released from metal-sulfide nodules would react with H_2 until the equilibrium H_2S/H_2 ratio is reached: $H_2S/H_2 = K_{eq} \times sqrt(f_{S2})$, where f_{S2} is set by the metal-sulfide nodules and K_{eq} is the equilibrium constant of reaction $0.5 S_2 + H_2 = H_2S$. Then the H/S ratio in such a gaseous phase is calculated from the mass balance considerations assuming that the gaseous phase contains only H and S. Thus, the high S_2 and H_2S fugacities necessary for sulfidation of Mg and Ca silicates under near solar redox conditions can only be reached in H-depleted systems.
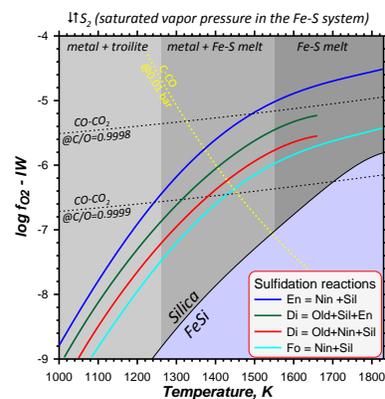

Fig. 3. Phase boundaries of sulfidation reactions (the same as in Fig. 1) plotted against the IW buffer in order to expand the vertical scale. Also plotted are the f_{O2} values for the C-CO (yellow dotted line) and CO-CO_2 (black dotted lines) buffers at a C/O ratio of ~1. The C-CO buffer is pressure-dependent, with decreasing pressure shifting curves towards lower temperatures and making their slopes somewhat steeper relative to the yellow line calculated at 0.01 bars. Note that the f_{O2} values of the CO-CO_2 buffer at C/O~1 are much higher than those of the reduced solar nebula (C/O=1) because the nebula contains large amount of H, an additional reducing agent.