PROCESSING OF SILICATES IN S-RICH SYSTEMS: IMPLICATIONS FOR THE ORIGIN OF ENSTATITE CHONDRITES.

M. I. Petaev[1], S. W. Lehner[2], P. R. Buseck[2]; [1]Department of Earth & Planetary Sciences, Harvard University, Solar, Stellar, & Planetary Sciences, Harvard-Smithsonian CfA, Cambridge, MA 02138, (mpetaev@fas.harvard.edu); [2]School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, (slehner@asu.edu, pbuseck@asu.edu).

Introduction: The hallmark of enstatite chondrites is the chalcophile behavior of Mg, Ca, Mn, Cr, Ti, Na, and K. Since the pioneering work of Larimer [1], the Ca, Mg, and Mn sulfides together with nearly pure enstatite, Si-bearing Fe,Ni metal, perryite, silica phases, and Cr,Ti-bearing troilite in E chondrites [*e.g.*, 2] was and still is interpreted as evidence of their formation in a nebular system with enhanced C/O ratio of ~1, resulting in f_{O_2} values orders of magnitude lower than those of a nominal solar nebula with C/O ratio of ~0.5 [3]. Calculated condensation sequences for a reduced nebula [3-11] predict that the first condensates, such as SiC, TiC, CaS, MgS, AlN, and FeSi, become unstable below ~1000K and upon cooling are replaced by oxides, silicates, metal, and troilite. Such an idealized model was adequate, at least qualitatively, for explaining the mineralogy of metamorphosed E4-6 chondrites. However, the model fails to account for the mineralogy and mineral chemistry of the most primitive EH3 chondrites.

First, neither refractory carbides nor large amounts of graphite predicted by the 'reduced nebula' models are found in the EH3 chondrites while these phases do occur in the C-rich presolar dust grains, consistent with the predicted condensation sequence of a C-rich gaseous phase [*e.g.*, 12]. Second, no substitution of Ca and Mg sulfides by silicates has been observed, while the substitution of silicates by sulfides was recently documented [13,14]. Perhaps the largest discrepancy between the 'reduced nebula' models and EH3 chondrites is the occurrence of FeO-rich silicates in the latter [*e.g.*, 15-21], indicative of their formation under highly oxidizing conditions incompatible with the stability of Ca and Mg sulfides.

In EH3 chondrites the Ca and Mg sulfides, oldhamite and niningerite, respectively, occur everywhere, including in the abundant metal-sulfide nodules (MSN) [*e.g.*, 22-26] also called layered sulfide-metal-rich chondrules [27]. Some of these nodules contain oldhamite and niningerite in their cores which was interpreted as evidence for condensation of these sulfides as well as the nodules themselves in a nebular system with high C/O ratio [22,24,25]. However, the detailed textural relationships of Ca and Mg sulfides with other minerals of the nodules, the FeO-bearing silicates in them [23], and the trace element chemistry of sulfides [28-31] call into question their origin as nebular condensates.

Recently we proposed an alternative model for formation of Ca, Mg, and Mn sulfides in EH3 chondrites by sulfidation of silicates [32], based on the observed mineral relations in the sulfide and silica-rich chondrules [13,14]. Here we apply this model to silicate-bearing MSNs and sulfidized CAIs [33], evaluate physicochemical conditions of sulfidation, and discuss implications for the origin of enstatite chondrites.

Observations of silicate sulfidation: A suite of silica-bearing chondrules that contain abundant troilite, niningerite and minor oldhamite replacing pyroxenes and olivine was recently described [13,14]. The chondrules show large variations in mineral abundances, indicative of different degrees of silicate sulfidation. Similar objects (silica-niningerite-enstatite clasts) were described earlier from other EH chondrites [34,35].

Silicates have commonly been reported in the metal-sulfide nodules [22-26], but their significance has been overlooked. Only [23] provides several dozen analyses of silicates grains from a number of nodules and describes their modes of occurrence. The ferromagnesian silicates occur as single euhedral (roedderite, enstatite) or rounded (enstatite) grains or aggregates (enstatite, forsterite) and typically contain > 1wt. % FeO. In the accompanying abstract [36] we report on the occurrence of MSNs within silicate chondrules and sulfidized silicates within MSNs. The similarity in mineral chemistry of silicates and opaque minerals from the MSN and silica-sulfide-rich chondrules suggests that both objects might have formed under similar physicochemical conditions via sulfidation of FeO-bearing silicates.

The Sahara 97159 EH3 chondrite contains many extensively altered CAIs [33], with the Ca,Al-rich silicates nearly completely replaced by feldspathoids and albite. The low FeO contents in spinel and silicates were interpreted as evidence of alteration under highly reducing conditions [33]. In addition, some CAIs contain Ti-bearing trolite. Of particular interest is a spinel-rich spherule containing small grains of a Ti,V-monosulfide (> 80 mol % TiS) associated with rutile and perovskite which constrain f_{O_2} and f_{S_2} during alteration.

Physicochemical conditions of sulfidation: The sulfidation reactions recorded in the silica-bearing, sulfide-rich chondrules [14] require interaction of ordinary ferromagnesian chondrules with an external S-rich, H-poor gas at temperatures exceeding the Fe-FeS eutectic [32]. Details of the thermodynamic analysis of relevant mineral equilibria are discussed in [32,37]. We used a similar approach to assess physicochemical conditions of metal-silicate-sulfide assemblages of MSNs. The Si-bearing metal in the MSNs allows narrowing of the range of f_{O_2} consistent with their mineralogy by consi-

dering the Si-SiO$_2$ equilibrium instead of the FeSi-SiO$_2$ used for placing the lower f_{O2} limit for metal-free chondrules.

The results (Fig. 1) are stability fields of mineral assemblages such as Di (diopside) – Fo (fosterite) – En (enstatite), En – Fo – Old (oldhamite), En – Old – Nin (niningerite), Old – Nin – Sil (silica represented by cristobalite), and Old – Nin – Metal (3.5 wt. % Si dissolved in Fe,Ni metal). The redox conditions of EH CAI sulfidation are estimated from the TiO$_2$ (rutile) – TiS (wassonite) equilibrium.

Details aside, the overall conclusion of Fig. 1 is that the f_{S2} and f_{O2} recorded in mineral assemblages of sulfidized chondrules, silicate-bearing MSNs, and sulfidized CAIs are all consistent with each other, implying that they can result from an interaction of 'normal' chondrules and CAIs with a common S- and C-rich and H-poor gaseous reservoir.

Implications for the origin of enstatite chondrites: The textural, mineralogical, and chemical characteristics of sulfidized chondrules and MSNs suggest that their Ca and Mg sulfides are secondary products formed during high-temperature processing of ordinary ferromagnesian chondrules in a gaseous reservoir enriched in S and C and severely depleted in H. The high f_{S2} necessary for sulfidation of silicates was supplied by the molten metal-sulfide assemblage, while the near nominal solar nebula redox conditions were most likely supported by the increased C abundance that was probably added in the form of organic matter. Such a scenario provides a viable alternative to the condensation origin of oldhamite and niningerite as well as other unusual minerals of enstatite chondrites.

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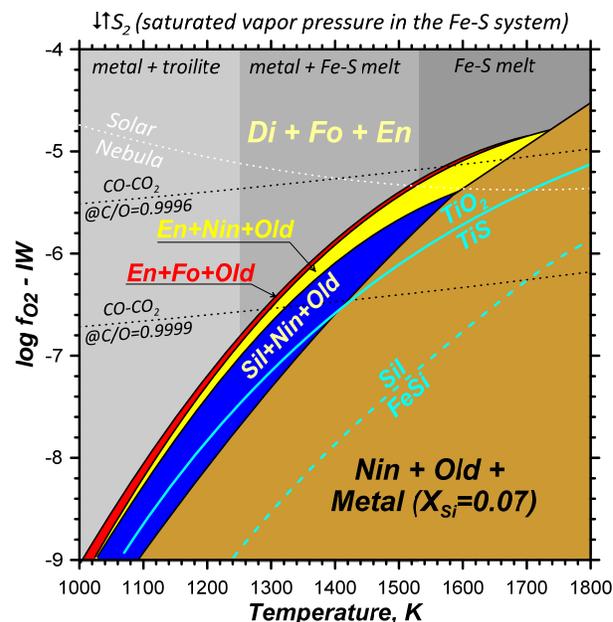
Fig.1. Stability fields of mineral assemblages of sulfidized chondrules and MSNs. The TiO$_2$-TiS equilibrium (solid cyan line) denotes redox conditions of CAI sulfidation. The metastable SiO$_2$-FeSi equilibrium (dotted cyan line) is shown for comparison. All solid solutions, except for Si in Fe,Ni metal, were treated as ideal, with the mole fractions of MgS in niningerite equal to 0.3. The thermodynamic data and activity coefficients of Si in Fe,Ni metal are from [38]. Following [32], the f_{S2} at any given temperature is assumed equal to the S$_2$-saturated pressure in the Fe-S system [39]. Gray shades show phase changes in the Fe-S system. The f_{O2} values for the nominal solar nebula (white dotted line) are calculated at a nebular pressure of 10^{-5} bar with the GRAINS code [38] assuming full equilibrium. Also plotted are the f_{O2} values for the CO-CO$_2$ (black dotted lines) buffer at a C/O ratio of ~1. 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.