

CHEMICAL FRACTIONATION DURING PROCESSING OF SILICATES IN S-RICH SYSTEMS: IMPLICATIONS FOR THE ORIGIN OF ENSTATITE CHONDRITES. M. I. Petaev¹, S. W. Lehner², P. R. Buseck²; ¹Department of Earth & Planetary Sciences, Harvard University, Solar, Stellar, & Planetary Sciences, Harvard-Smithsonian CfA, Cambridge, MA 02138, (mpetaev@fas.harvard.edu); ²School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, (slehner@asu.edu, pbuseck@asu.edu).

Introduction: Since the pioneering studies of Keil [1] and Larimer [2], the chalcophile behavior of Mg, Ca, Mn, Cr, Ti, Na, and K in enstatite chondrites 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]. The calculated condensation sequences for a reduced nebula [3-12] predict formation of SiC, TiC, CaS, MgS, AlN, and FeSi as the first condensates, but these become unstable below ~1000K and upon cooling should be replaced by oxides, silicates, metal, and troilite. This assemblage is inconsistent with the mineralogy and mineral chemistry of the most primitive EH3 chondrites.

In particular, no substitution of Ca and Mg sulfides by silicates has been observed. In contrast, the substitution of silicates by sulfides is documented in the ‘silica-niningerite-enstatite clasts’ [13,14], a suite of silica-sulfide-bearing chondrules [15,16], metal-sulfide nodules (MSN) [17,18,19], and the fine-grained matrix [20]. Moreover, similar textural and chemical characteristics of silicates and sulfides in the silica-sulfide-bearing chondrules and MSN show that these objects apparently represent a continuous series formed under similar physicochemical conditions.

Perhaps the largest discrepancy between the ‘reduced nebula’ models and EH3 chondrites is the common occurrence of FeO-rich silicates in the latter [e.g., 21-27], indicative of their formation under oxidizing conditions incompatible with the stability of Ca and Mg sulfides. The replacement of many FeO-rich silicate grains by the assemblages of less ferrous silicates, Ni-free metal, and troilite [e.g., 22-25], and, in places, by niningerite and silica ± oldhamite [13-16] implies a secondary origin of the Fe, Ca, and Mg sulfides and silica in an environment with high f_{S_2} maintained by the Fe-FeS buffer.

Recently we proposed a model for the formation of Ca, Mg, and Mn sulfides in EH3 chondrites by sulfidation of silicates [28,29] that is based on the mineral relations in the silica-sulfide-bearing chondrules [15,16], MSN [18,19], and sulfidized CAIs [30]. Here we use this model to evaluate physicochemical conditions of chemical fractionation observed in sulfidized chondrules [31] and discuss its implications for the origin of EH chondrites.

Chemical fractionation in sulfidized chondrules: Bulk chemical compositions of nine silica-sulfide-

bearing chondrules were measured using EPMA and SEM EDS with a defocused beam [31]. Based on the relative abundance of silica and enstatite, the chondrules were divided into three groups – enstatite-rich minimally sulfidized, silica-rich fully sulfidized, and partially sulfidized with approximately equal abundances of enstatite and silica. The groups show large variations (Fig. 1) indicative of significant chemical fractionation during silicate sulfidation. In general, the Si content in the chondrules essentially does not change whereas S, Fe, Mn, Na, and K are gained and Mg is lost as sulfidation of silicates progresses. A slight correlated depletion of the fully sulfidized chondrules in Fe, Mn, Mg and S relative to the partially sulfidized chondrules testifies to a partial loss of the niningerite perhaps due to its expulsion from the partially molten chondrules as observed in melting experiments of the EH4 chondrite Indarch [32].

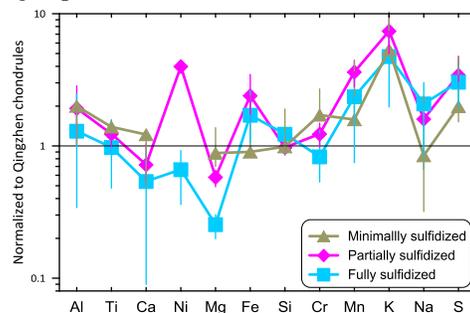


Fig. 1. Chemical variations among different groups of sulfidized chondrules normalized to the average composition of the ferromagnesian chondrules from the EH3 chondrite Qingzhen [33]. Error bars are 1σ standard deviations of the mean (three chondrules in each group).

Physicochemical conditions of sulfidation: The sulfidation reactions recorded in the silica-sulfide-bearing chondrules, MSN, and sulfidized CAIs [29] require interaction of ordinary ferromagnesian chondrules with a S-rich, H-poor gas at temperatures exceeding the Fe-FeS eutectic (Fig. 2). In such a H-poor system, f_{O_2} values required for sulfidation of different silicates were likely maintained by the CO – CO₂ mixture formed via reactions between organic matter and oxygen released from the chondrules. Local variations in the CO₂/CO ratio in the gaseous phase were probably responsible for controlling which elements could have been extracted from silicates into sulfides (Fig. 2). Details of the thermodynamic analysis of mineral equilibria shown in Fig. 2 are discussed in [28,29].

The interaction of Ca and Mg silicates with a S-rich

gaseous phase at relatively reducing conditions (red and yellow fields in Fig. 2) results in substantial changes in volatility of Ca, Mg, and Si. The calculated partial pressures of gaseous Mg, Fe, Ca, Mn, SiO, SiS, S₂, and O₂ in the ambient gas equilibrated with Fe-FeS and enstatite-niningerite-silica assemblages (Fig. 3) are rather high at temperatures >1300K, implying high mobility of Fe, Mg, Mn, and Si during silicate sulfidation. Perhaps the most important is a large increase in Mg volatility as enstatite was being replaced by the assemblage of niningerite and silica.

Implications for the origin of enstatite chondrites: The change of Mg volatility implies that sulfidation of enstatite (and forsterite) would result in evaporative loss of Mg until the Mg saturation (red solid curve in Fig. 3) in the ambient gas is reached. An additional driving force for Mg evaporation from sulfidized chondrules is the large difference in Mg/Fe ratio between the niningerite formed from ferromagnesian silicates (Mg/Fe ~10 or more) and the equilibrium composition of niningerite at high temperatures (Mg/Fe ~ 0.5 at 1200K [34]). During progressive silicate sulfidation, the newly formed Mg-rich niningerite would tend to reach equilibrium composition by losing Mg to and gaining Fe (and Mn) from the ambient gaseous phase, consistent with the chemical fractionation in the sulfidized chondrules (Fig. 1). This fractionation means that the sulfidation of ferromagnesian silicates to form MgS could have been responsible for the low bulk Mg/Si ratios of the enstatite chondrites.

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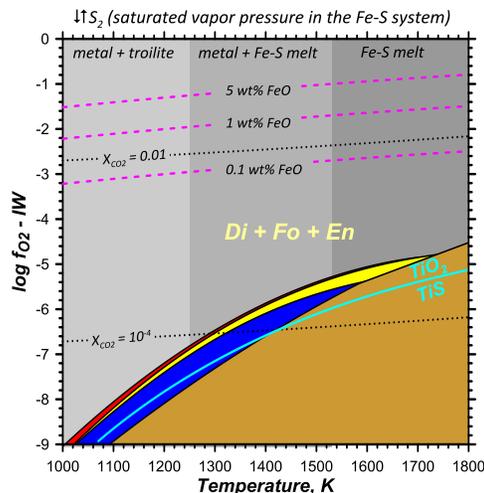


Fig. 2. Physicochemical conditions of silicate sulfidation in EH3 chondrites (modified after [28,29]). Labeled dashed purple lines show FeO content in silicates (olivine or low-Ca pyroxene in 'reduced' chondrules [21-27]) equilibrated with Ni-free metal, troilite, or both. The solid cyan line shows redox conditions of CAI alteration [30]. Labeled dotted black lines show f_{O_2} values buffered by the CO-CO₂ mixtures. Three gray fields show different phases of the Fe-S system coexisting with the assemblage of high-Ca pyroxene (Di), forsterite (Fo), and enstatite (En). Other colored fields show stable assemblages of En+Fo+Nin (red), En+Nin+Old (yellow), Sil+Nin+Old (blue), and Nin+Old+Fe metal with 3.5 wt% Si (brown). Nin – niningerite, Old – oldhamite, Sil – silica.

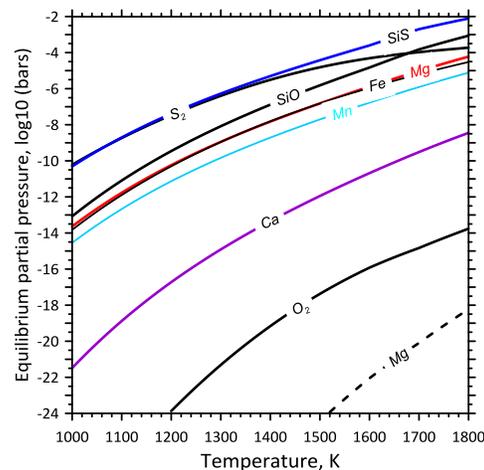


Fig. 3. Partial pressures of gaseous Mg, Fe, Ca, Mn, SiO, SiS, S₂, and O₂ in the ambient gas equilibrated with Fe-FeS and enstatite-niningerite-silica assemblages. The dashed line shows partial pressure of Mg equilibrated with the enstatite-silica assemblage prior to sulfidation.