

Formation of CaS-MgS in enstatite chondrites and achondrites as a function of redox conditions and temperature: constraints on their evolution in a planetesimal and in a proto-planet.

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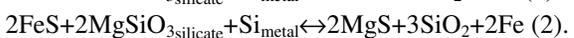
Introduction. The cubic monosulfide series with the general formula (Mg,Mn,Ca,Fe)S are common phases in the enstatite chondrite (EH) and aubrite meteorite groups. In the Earth's mantle, sulfide minerals are associated with peridotites and eclogites (e.g. [1]). Study of these sulfide mineral systems is of interest for the mineralogy and petrology of planetary mantles. For example, MgS could occur in the primitive Earth [2] and because it remains a low density phase compared to metal, would stay a separate phase during the core formation process, and thus not segregate to the core. (Mg,Ca,Mn,Fe)S sulphides might thus be important phases even in planetary differentiation processes. The importance of such minerals, and their formation, composition and textural relationships for understanding the genesis of enstatite chondrites and aubrites, has long been recognized [3]. The main objective of this experimental study is to understand the formation and evolution of (Mg,Ca,Mn,Fe)S sulphides, particularly the oldhamite CaS and ningerite MgS, with pressure, temperature but also with redox conditions because EH and aubrites are meteorites that formed under reduced conditions. Piston-cylinder (PC) and multi-anvil (MA) experiments at high pressure (HP) and high temperature (HT) have been performed in order to simulate the evolution of these phases in a small planetary body from a planetesimal (with PC experiments) up to a proto-planet (with MA experiments).

Experimental and analytical procedures. The PC experiments were carried out using the Lunar and Planetary Institute QuickPress at the NASA Johnson Space Center (Houston, Texas, USA). All the details of this PC procedure is given by [4]. MA experiments were carried out in the presses of the Bayerisches Geoinstitut, Bayreuth (Germany) under the European HP-HT facility. Details of these experimental procedures are given by [5] and [2]. Samples were analyzed with a Scanning Electron Microscope (SEM) equipped with a energy-dispersive X-ray analyzer (EDX). A CAMECA SX electron probe microanalyzer (EPMA), equipped with wavelength dispersive X-ray spectrometer (WDX) was also used to analyze the samples. The oxygen fugacities of the samples have been calculated relative to the buffer iron/wüstite (IW) like in [4].

Results. At 1 GPa, grains of (Ca, Mg, Fe)S are observed in close association with grains of SiO₂, Fe-

Si alloy and sometimes FeS only when the fO₂ is not too reduced. The silicate phases are pyroxene and melt depending on the temperature (Fig. 1). The first evidence of silicate melt is seen at 1350°C. All the starting material is molten at 1700°C (Fig. 1). At 20 GPa and 2200°C, grains of majorite, which are almost FeO-free, are present with a homogeneous Fe-S-Si alloy, small grains of (Mg,Ca)S, and SiO₂. When no Si is added in the starting material (in PC or MA experiments), the fO₂'s of the samples are close to ΔIW-2 and no (Mg,Ca)S is formed showing that the redox conditions were not enough reduced to form this sulfide. As shown in the Fig.2, the S content of the silicate melt depends strongly on the redox conditions of the samples. If we report the S value found [6] in some aubrite glasses, we obtain a redox value around ΔIW-4.5. The partition coefficients (D in wt% ratios) for Ca, Mg and S between (Mg, Ca, Fe)S sulfide and pyroxene (px), between (Mg, Ca, Fe)S sulfide and silicate melt, and finally between melt and px are reported in the Fig. 3 as a function of the redox conditions and T. The D's of Ca and S depend on the fO₂ (except the D_{sul-melt}), whereas the D's of Mg seem to be more sensitive to T as D^{Ca}_{sul-melt}. Last PC experiments, where the cooling of the samples was controlled and slow, were performed in order to see if the crystallization of (Mg,Ca)S could occur through the cooling as already suggested by [6, 7]. In these samples, a massive crystallization of (Mg, Ca, Fe)S phases from the silicate melt have been characterized. This observation is thus in agreement with the suggestions of [6, 7].

Discussion. Due to the Si added in some starting material, it was possible to reach highly reduced redox conditions for most of the experiments. We obtain a minimum relative fO₂ value around -7 log units below the IW buffer. That means that these samples underwent the same range of fO₂ that prevailed during the formation of enstatite meteorites. Because of these very low fO₂ it was possible to form some (Ca,Mg,Fe)S likely through the following reactions:



The high amount of dissolved S in the silicate melt that range up to 10wt% at ΔIW-7 could be the result of CaS^o and MgS^o complexes occurring in the melt at low fO₂ [6, 7], as suggested by the crystallization of

(Mg, Ca)S phases in the slow quench PC runs. From the Fig. 2, we see that the valence of S above $\Delta IW-5$ is 2. The redox conditions are also an important parameter, which could control the differentiation pattern of Ca and S in EH and aubrites, but also in a growing planetesimal under reduced conditions.

Two different mechanisms of formation have been characterized for CaS-MgS phases: (i) a crystallization through process (1) or (2) where no melting is required, (ii) crystallization of CaS-MgS from a silicate melt through a slow cooling. The distribution coefficients of U and Nd between metal and CaS have been measured at 20 GPa. Our first result indicates that Nd prefers CaS, even stronger than U does. To finish, it is interesting to note that these observations are in agreement with previous observations done on EH [8,9].

References: [1] Sharp 1996 *Nature*, 211, 402-403. [2] Siebert et al., 2004, *Phys. Earth Planet. Int.*, 144, 421-432. [3] Keil, 1989 *Meteoritics*, 24: 195-208. [4] Musselwhite, D.S., H.A. Dalton, W.H. Keifer and A.H. Treiman (2006) *Meteoritics and Planet. Sci.* 41, 1271-1290. [5] Malavergne V, Siebert J, Guyot F, Hammouda T, Gautron L, Combes R, Borensztajn S, et Frost D (2004) *GCA*, 68, 4201-4211 [6] Fogel 2005 *Geochim. Cosmochim. Acta* 69, 1633-1648 [7] Mc Coy et al. 1999 *Meteoritics* 34,735-746. [8] Furst et al. 1982 *Geophys. Research Lett.* 9, 41-44. [9] Murrell and Burnett 1982 *Geochim. Cosmochim. Acta* 46, 2453-2460.

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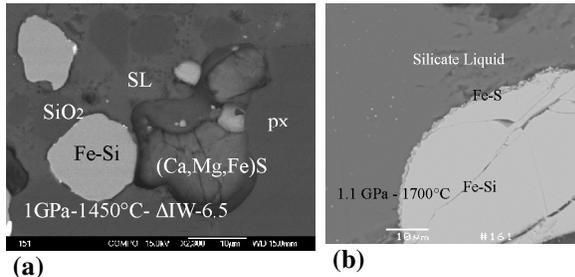


Fig. 1 : BSE images of two PC runs :1 GPa-1450°C (a), 1.1 GPa-1700 °C (b). The scale bar represents 10 μ m. SL : silicate liquid, px : pyroxene

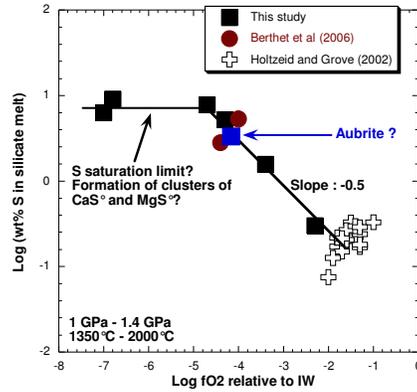


Fig. 2: The S contents in silicate melt, from this study for S and previous work, are plotted vs fO_2 relative to IW at different T.

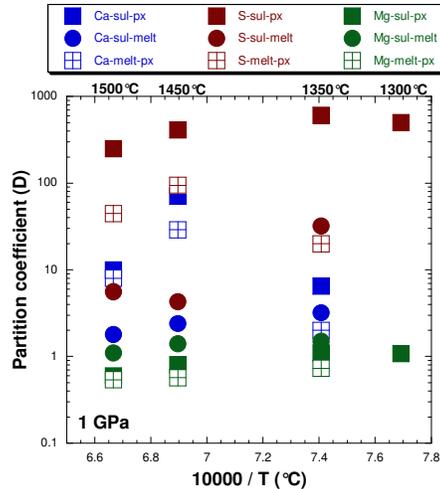
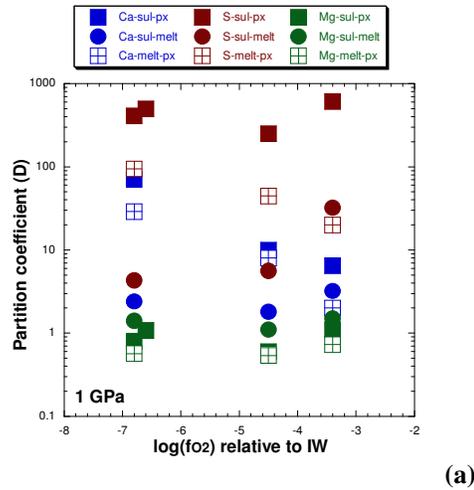


Fig. 3: The partition coefficients for Ca, Mg and S between (Mg, Ca, Fe)S sulfide (sul) and pyroxene (px), between (Mg, Ca, Fe)S sulfide and silicate melt (melt), and between melt and px as a function of the redox (a) conditions and T (b).