Experimental Behavior of Sulfur Under Primitive Planetary Differentiation Processes, the Sulfide Formations in Enstatite Meteorites and Implications for Mercury.

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Introduction. Enstatite meteorites are the most reduced naturally-occuring materials of the solar system. The cubic monosulfide series with the general formula $(Mg,Mn,Ca,Fe)S$ are common phases in these meteorite groups. The importance of such minerals, their formation, composition and textural relationships for understanding the genesis of enstatite chondrites (EC) and aubrites, has long been recognized (e.g. [1]). However, the mechanisms of formation of these sulfides is still not well constrained certainly because of possible multiple ways to produce them. We propose to simulate different models of formation in order to check their mineralogical, chemical and textural relevancies. The solubility of sulfur in silicate melts is of primary interest for planetary mantles, particularly for the Earth and Mercury. Indeed, these two planets could have formed, at least partly, from EC materials (e.g. [2, 3, 4]). The sulfur content in silicate melts depends on the melt composition but also on pressure (P), temperature (T) and oxygen fugacity fO_2. Unfortunately, there is no model of general validity in a wide range of P-T-fO_2-composition which describes precisely the evolution of sulfur content in silicate melts, even if the main trends are now known. The second goal of this study is to constrain the sulfur content in silicate melts under reducing conditions and different temperatures.

Experimental and analytical procedures. The starting materials of these experiments were a mixture of a silicate glass, a troilite FeS, and a pure metallic Si. To simulate the different models of the sulfide formation, we have performed piston-cylinder (PC) experiments at 1 GPa and between 1000 and 2000°C. The samples of this study have been quenched with two different ways: rapidly and slowly. A slow and controlled cooling allows to test the ideas of: (i) [5] who proposed that oldhamite or niningerite could crystallize from a reduced silicate melt upon cooling, and (ii) [6] who suggested that keilite might be the result of a fast quench product while some niningerites could be the result of a high-temperature impact followed by a slow cooling: under these conditions the keilite would exsolved troilite and form niningerite. The experiments were performed with an end-loaded and a non-end loaded piston-cylinder apparatus (at the Ecole Normale Supérieure de Paris, France and at the LPI-NASA Johnson Space Center, Houston, Texas, USA, respectively). All the experimental details of these piston cylinder procedures are given by [7, 8]. Samples were analyzed with a Scanning Electron Microscope (SEM) equipped with a energy-dispersive X-ray analyzer (EDX). A CAMECA SX electron probe microanalyzer, equipped with wavelength dispersive X-ray spectrometer was also used to analyze the samples. The oxygen fugacities of the samples have been calculated relative to the buffer iron/wüstite (ΔIW) like in [9].

Results. The initial pure Si metal of the samples has totally reacted with FeS and/or the silicates since pure Si metal is not observed in the run products of this study. The metallic phase is most often of quasi-spherical shape within the silicate matrix. The sulfides found in our samples are in close association with metallic grains, but sometimes alone in the silicate matrix. We observe two different kind of sulfides in the samples: troilite and grains of solid solution of $(Mg, Fe, Ca)S$. The silicate begins to melt at 1350°C and is totally molten as soon as the temperature reached 1665°C. Below 1350°C, grains of pyroxene and SiO_2 are characterized. Generally, the Fe content of the silicates is very low showing that the silicate glass of the starting material has been reduced during the experiments. Textural and chemical differences are observed between the slowly and rapidly quenched samples. The most striking difference in sulfides grains is the exsolutions observed in troilite or in $(Mg, Ca, Fe)S$ sulfides in the slowly quenched samples, which were heated from 1200°C up to 600°C, below the melting point. FeS or CaS exsolution formed in $(Mg, Ca, Fe)S$ grains with the consequences to decrease the Fe content in these sulfides compared to the sulfides of fast quenched samples. These exsolution have different shapes: either small roundish droplets (around 1 μm) inside the grain or as thin veins. Finally, the most spectacular textures are observed in a slowly quenched sample, which was cooled from 1700°C to 1400°C (Fig. 1). Grains of enstatite with numerous $(Mg, Fe, Ca)S$ cylindrical crystals are characterized. These cylinders are spread

homogeneously in enstatite, while the sulfur-rich glass is totally void of them.

Discussion. Due to the Si added in the starting material of this study, it is possible to reach highly reducing conditions for most of the experiments, with a minimum relative fO_2 value around 6 log units below the IW buffer. These samples underwent the same range of fO_2 that prevailed during the formation of EC and aubrites (e.g. [5, 10, 11]). Our experiments reproduce the mineralogy, the main chemical characteristics (e.g. [1]) and even some typical textures (e.g. the association of troilite, kamacite and niningerite or oldhamite, sulfide exsolution) of enstatite meteorites showing the relevance of our samples for this kind of systems. Fig. 1 illustrates the fact that enstatite can not keep as much sulfur as the melt does, producing the crystallization of sulfides upon the cooling of the silicate melt. This sulfides formation during the cooling can also be helped by the result of CaS° and MgS° complexes occuring in the melt at low fO_2 [10]. The textures shown in Fig. 1 favor this interpretation. This slow quenched sample demonstrates that reduced silicate melts can crystallize grains of oldhamite or niningerite upon cooling. The second series of the slow quenched samples (heated from 1200°C up to 600°C) allow to conclude that (Mg, Fe, Ca)S sulfides can lose part of their FeS or CaS component during the cooling as exsolution. This observation is thus in agreement with the proposition of [6] about the formation and possible evolution of keilites (Fe$_{>0.5}$ Mg$_{<0.5}$)S, the iron-dominant analog of niningerite. To finish, the evolution of the sulfur content in silicate melt around 1 GPa depends strongly on fO_2 but also on T (Fig. 2). These results allow to propose two possible important features about planetary differentiation. First, if the linear increase of the sulfur content in silicate melts with ΔIW ranging from -2 to -1 remains valid at very high temperatures, then around 2500°C, the sulfur solubility limit will be reached. This means that there is no need of extremely reducing conditions to keep large amount of sulfur (several wt%) in a molten mantle, since very high temperatures could be enough. Secondly, a planetary body made mainly of enstatite chondrites (like it might be the case for the proto-Earth or Mercury, [2, 3, 4]), which undergoes a large melting impact event (like the Earth with the Moon formation, or maybe like Mercury with the lost of a part of its mantle, e.g. [12, 13]) could keep a large amount of sulfur in its molten mantle. This silicate melt will cool and will remove the main part of its sulfur during its crystallization stage (Fig. 1). Then, CaS-MgS monosulfides could form and thus provide a reservoir of sulphur in the mantle and superficial planetary envelopes as it has been observed at the surface of Mercury as shown by the results from MESSENGER [14].

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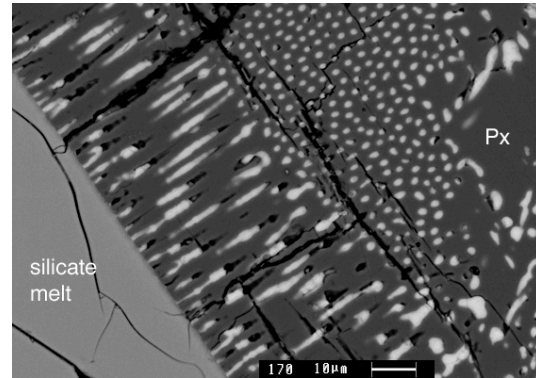

Fig. 1 : BSE image of a sample heated at 1700°C followed by a slow quench up to 1400°C. The silicate melt has crystallized into enstatite and (Mg, Fe, Ca)S sulfides. Part of the melt stayed as a glass.
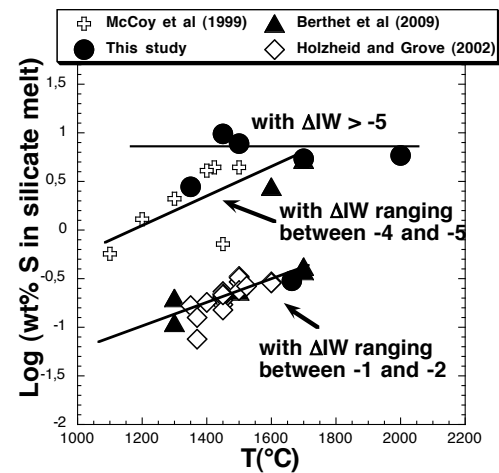

Fig. 2: The S contents in silicate melts, from this study and previous works, are plotted vs T at different fO_2 relative to IW.