EVIDENCE OF HIGH-TEMPERATURE FORMATION OF SULFIDE PHASES OF CHONDRULES.

Y. Marrocchi[1] and G. Libourel[1], [1]CRPG-CNRS, 15 rue Notre Dame des Pauvres, BP 20, F-54501 Vandoeuvre-Lès-Nancy, France (yvesm@crpg.cnrs-nancy.fr; libou@crpg.cnrs-nancy.fr).

Introduction: Sulfur, the tenth most abundant element in the solar system, is present in primtitive chondrite with an average concentration of around 2 wt%. It occurs almost exclusively as stoichiometric iron sulfide troilite (FeS) blebs that are located within or near the edge of chondrules. The origin of these troilite blebs is still a matter of debate. If the FeS phases are primary (i.e., they were present in the chondrule precursors), they would have crystallized from an immiscible sulfide melt during cooling of a chondrule melt [1]. However, experimental studies suggest that troilite should have been vaporized under thermal conditions expected for chondrules formation [2]. Hence, it has been proposed that sulfur would have recondensed as sulfides veeners on the surface of the solidified chondrules [3]. However, the sulfur isotopic composition of putative primary troilite preserved within chondrules and sulfides veeners do not show any measurable isotopic differences contrary to what would be excepted for such a process [4]. Thus, it is generally proposed that sulfur underwent important secondary redistribution in the solar nebula and/or during parent-body processes [3]. However, the origin of sulfides remains poorly constrained despite their importance in understanding the nature, the kinetic and the chronology of the processes that affects chondrules formation and evolution. Here we report a systematic petrographic and mineralogical study of sulfides in type I chondrules of the carbonaceous chondrite Vigarano (CV3) in order to establish the conditions under which they formed.

Methods: We surveyed all the type I chondrules in two thin sections of Vigarano (CV3), using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectral (EDX). We also acquired multi-elements EDX maps of 25 selected chondrules of all petrological types. Based on the compilation of Mg, Si, Fe, Ni and S maps, we determined the modal abundances of the different silicate phases (olivine, pyroxene & mesostasis) and the metallic phases (Fe-Ni metal and sulfides). Quantitative analyses for the mineralogical composition of chondrules were performed with a CAMECA SX-50 electron microprobe, paying special attention to the sulfur content determination.

Results: The vast majority of the type I chondrules we observed present a radial zonation in their mineralogical assemblages with olivines and mesostasis being located in the inner part of the chondrules while the outer zone is dominated by low-Ca pyroxenes (i.e., enstatie) parallels to the surface.

Most sulfides in type I porphyritic chondrules of Vigarano are present as opaque phases composed entirely of troilite. In some cases, they appear to be associated with magnetite either as spherules or within complex liquid-shape structures. FeS associated with Fe-Ni metal are also observed in Vigarano but in very low abundance comparing to ordinary chondrites [1].

Our detailed survey of porphyritic chondrules using EDX mapping reveals however that troilites are mainly located within the low-Ca pyroxene outer zone, and that the amount of troilite blebs increases with the abundance of low-Ca pyroxenes. This trend is confirmed by the observed correlation between the percentage of sulfides and low-Ca pyroxenes determined from image processing of the EDX maps of 25 chondrules of all petrological types (Fig. 1). Our observation shows in addition that troilites are very often poikilitically enclosed in the low-Ca pyroxene and not in olivines.
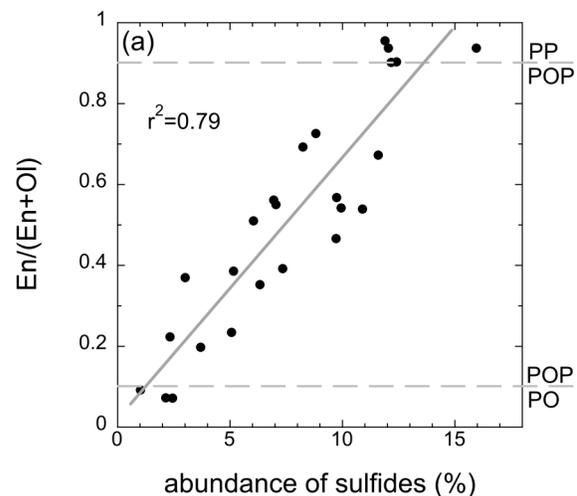

Fig.1: modal abundance of sulfides reported versus modal abudance of low-Ca pyroxene (enstatite) for 25 type I chondrules of Vigarano.

The composition of the mesostasis of 5 well-preserved type I chondrules (PO & POP) has been analyzed with the electronic microprobe. The major element concentrations and the compositional trends we obtained are consistent with those generally reported for chondrule mesostasis [5]. Sulfur is present in all mesostasis with

concentrations up to around 1,700 ppm of S. Our results do not show any evidence of compositional zoning of sulfur but we observed a positive correlation with FeO (Fig. 2). It is important to note that the correlation between FeO and S is present in all the chondrules mesostasis we have analyzed but with variable slopes.
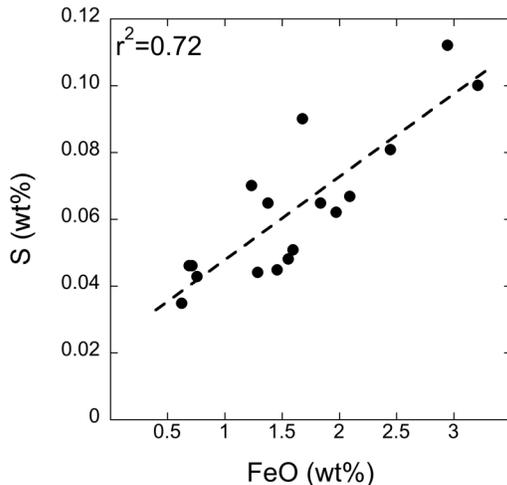

Fig. 2: Concentration of FeO and sulfur (expressed as wt % of S) measured in different zones of a well-preserved mesostasis of a POP chondrule.

Discussion: The abundances of low-Ca pyroxenes relative to olivines increase from PO to POP and PP chondrules. Based on the fact that these zonations involve high-temperature assemblages, it is generally accepted that they have been acquired during chondrule forming events, very likely by SiO nebular gas-melt interactions. That troilites present the same zonation (Fig. 1) and are poikilitically enclosed in low-Ca pyroxene suggests that sulfides are co-genetic with the low-Ca pyroxenes and as a consequence they were probably formed during high-temperature events. This conclusion is supported by the fact that troilites present massive structures, as opposed to those formed by thermal metamorphism [6], hydrothermal alteration [7] and shock metamorphism [8]. In addition, the fact that troilites are not associated with Fe-Ni metal seems also to rule out a possible origin by sulfidization of metallic spherules during cooling of chondrules or of the parent body [9]. In contrast to secondary alteration processes, this set of observations suggests that sulfides in Vigarano type I chondrules were inherited from the high-temperature forming-event of chondrules.

The covariance of S and FeO in the chondrules mesostasis (Fig. 2) is similar to that observed in naturally-occurring sulfur-rich basaltic magmas [10] and in sulfur solubility experiments in Fe-bearing silicate melts [11]. This relationship suggest that high temperature gas-melt interactions control the behavior of sulfur during chondrule formation. The main characteristic of sulfur solubility in silicate melts is the existence of a concentration limit, the sulfur content at sulfide saturation (hereafter SCSS), at which sulfides (solid or liquid) separate from silicate melt [11]. According to experimental studies [11], two main factors control the sulfur solubility in silicate melts: (i) the polymerization state of the liquid; the SCCS decreasing with decreasing the NBO/T of the liquid, and (ii) FeO content of the silicate melt as follows:

$$FeO_{(melt)} + \tfrac{1}{2}\,S_{2(gas)} \Leftrightarrow FeS_{(sulfide)} + \tfrac{1}{2}\,O_{2(gas)}$$

The correlations observed between the S and FeO contents in the chondrule mesostases (Fig. 2) and the amounts of troilites and low-Ca pyroxenes (Fig. 1) can be interpreted within this frame. According to [5,12], gas-melt interactions, via the incorporation of silica, result in dissolution of olivines and formation of low-Ca pyroxenes. During this process and depending on the fS_2 of the surrounding nebular gas, sulfur can be dissolved into the chondrule melt that may or may not reach the SCSS. Thus, as chondrule melts evolve towards more silicic compositions due to the incoming silica from the surrounding nebular gas, the SCSS decreases, leading eventually to the formation of iron sulfides that will be co-crystallized with the low-Ca pyroxenes. In such a scheme, change in the chemistry and mineralogy (silica-rich melt + low-Ca pyroxene ± FeS) of type I chondrules (i.e., PO, POP and PP) could be interpreted as different durations of gas-melt interactions. In this model, the formation of troilites occurred at the periphery of chondrules and migrated inward due to the decrease of the SCSS induced by the increase of the silica activity. If correct, this new finding may place severe constrains on the fS_2 reigning during chondrule formation events.

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