

**THE FORMATION CONDITIONS OF CV CHONDRULES: CLUES FROM DISTRIBUTION AND ISOTOPIC COMPOSITIONS OF SULFIDES.** Y. Marrocchi<sup>1</sup>, G. Libourel<sup>2</sup>, L. Piani<sup>3</sup> and M. Chaussidon<sup>4</sup>, <sup>1</sup>CRPG-CNRS, 15 rue Notre Dame des Pauvres, BP 20, F-54501 Vandoeuvre-Lès-Nancy, France (yvesm@crpg.cnrs-nancy.fr), <sup>2</sup>Géoazur, OCA, CS 34229, 06304 Nice, France, <sup>3</sup>Department of Natural History Sciences, Hokkaido University, Sapporo 060-0810, Japan, <sup>4</sup>Institut de Physique du Globe, 75235 Paris, France.

**Introduction:** Chondrules are one of the major high-temperature components in primitive meteorites. They represent direct witnesses of the formation of the solar system and provide important constraints on both the conditions and thermal history of the inner solar system. Although the mineralogy, petrography, bulk chemical and isotopic compositions of chondrules are well-documented, the nature of the chondrule-forming events remain enigmatic. More specifically, the origin of sulfides (FeS) 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 FeS should have been vaporized under thermal conditions expected for chondrules formation [2]. Hence, it has been proposed that sulfur would have recondensed as sulfides veinners on the surface of the solidified chondrules [3]. However, the sulfur isotopic composition of putative primary FeS preserved within chondrules and sulfides veinners do not show any measurable isotopic differences contrary to what would be expected 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 affect chondrules formation and evolution. Here we report a systematic petrographic, mineralogical and isotopic study of sulfides in type I chondrules of the Vigarano and Kaba CV3 carbonaceous chondrites in order to establish the conditions under which they formed.

**Methods:** We surveyed all the type I chondrules in two thin sections of Vigarano and Kaba (CV3), using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectral (EDX). We also acquired multi-elements EDX maps 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. We also used the Cameca ims 1280 HR2 multicollector

ion microprobe at CRPG-CNRS (Nancy, France) to determine the sulfur isotopic compositions of chondrule sulfides in chondrules of the Vigarano and Kaba CV3 chondrites.

**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., enstatite) parallels to the surface (pale green, Fig. 1). Our detailed survey of porphyritic chondrules using EDX mapping reveals however that troilites are mainly located within the low-Ca pyroxene outer zone (purple, Fig. 1), and that the amount of troilite blebs increases with the abundance of low-Ca pyroxenes [5]. Our observation shows in addition that troilites are very often poikilitically enclosed in the low-Ca pyroxene and not in olivines.

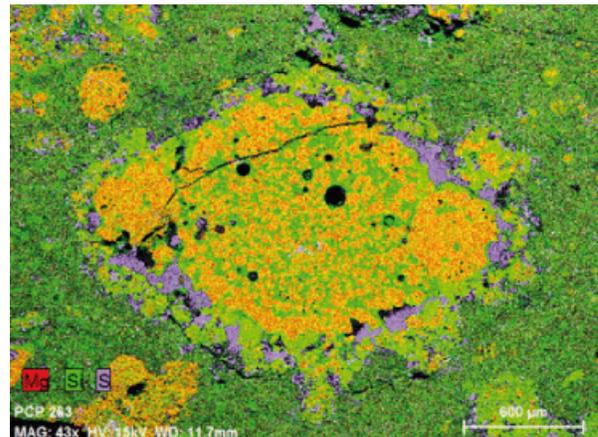


Fig.1: Compiled EDX map of Si, Mg, and S (purple) of a chondrule from Kaba. This map shows that sulfides are mainly associated with low-Ca pyroxenes (pale green) in the outer zone of chondrule.

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 [6]. 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 [5]. All sulfides show homogeneous sulfur

isotopic compositions center to 0 ‰ with  $\delta^{34}\text{S}_{\text{CDT}}$  and  $\delta^{33}\text{S}_{\text{CDT}}$  ranging from -1.0 ‰ to +1.4 ‰ and from -0.6 ‰ to 0.8 ‰, respectively (Fig. 2). Within error bars, no significant mass-independent fractionation effects have been detected (Fig. 2).

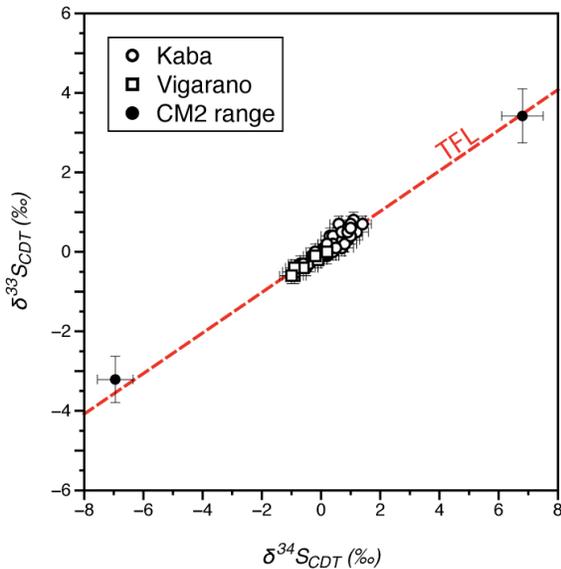


Fig.2: Sulfur isotopic composition of FeS within chondrule of the Kaba and Vigarano CV3 chondrites. All the data fall on the Terrestrial Fractionation Line (TFL). The sulfur isotopic variability observed in FeS of aqueously altered CM chondrites are shown for comparison [7].

**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. That troilites present the same zonation (Fig. 1) and are poikilitically enclosed in low-Ca pyroxene suggests that: (i) sulfides are co-genetic with the low-Ca pyroxenes and (ii) they were formed during the high-temperature chondrule-forming events. Such features put important constraints on the formation conditions of CV chondrules. Due to the volatile behavior of S compared to Mg and Si, the spatial correlation between FeS and low-Ca pyroxenes seems unlikely to have been established during closed-system crystallisation of chondrules. This is supported by calculations that show that large FeS inclusions would evaporate from chondrules within a short period of time ( $\ll 1$  s) [8]. In addition, FeS evaporation is also expected during the chondrule-forming event(s) even under very high degree of dust/gas enrichment and/or extremely fast cooling rates [9]. Such features and the

lack of sulfur isotopic fractionation observed in CV chondrules (Fig. 2) support that significant gas-melt exchanges took place during the chondrule-forming event(s).

Based on the oxygen isotopic composition of olivines and low-Ca pyroxenes, it has been proposed that chondrules formed from an homogenous melt that equilibrated with the ambient gas [10]. However, such model is at odds with the chemical disequilibrium reported in CV chondrules between olivines, low-Ca pyroxenes and glassy mesostasis [7]. This disequilibrium implies that: (i) chondrule mesostases cannot be the parent liquidus of olivines, (ii) olivines should be considered as relict phases and (iii) low-Ca pyroxene formed from the partial resorption of olivine during gas-melt interactions [7]. The latter model is supported by the sulfide characteristics of CV chondrules (Fig. 1) as no specific spatial distribution of FeS would be expected within chondrules if they were formed from homogenous melts. To the contrary, gas-melt interactions result in dissolution of olivines and formation of low-Ca pyroxenes due the incorporation of silica [5, 6]. During this process and depending on the  $f\text{S}_2$  of the surrounding nebular gas, sulfur can be dissolved into the chondrule melt that may or may not reach the Sulfur Content at Sulfide Saturation (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  $\pm$  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.

**References:** [1] Rubin A.E. et al. (1999) *GCA*, 63, 2281-2298. [2] Hewins R.H. (2005) *Chondrites and melts the Protoplanetary Disk*, 341, 286-316. [3] Zanda B. et al. (1995) *MAPS*, 30, 605. [4] Taschibana S. & Huss G.R. (1996) *GCA*, 69, 3075-3097. [5] Marrocchi y. & Libourel G. (2013) *GCA*, 119, 117-136. [6] Libourel G. et al. (2006) *EPSL*, 251, 232-240. [7] Bullock E.S. et al. (2010) *MAPS* 45, 885-898. [8] Uesugi M. et al. (2005) *MAPS*, 40, 1103-1114. [9] Alexander C.M.O.'D. et al. (2008) *Science* 320, 1617-1619. [10] Rudraswami N.G. et al. (2011) *GCA* 75, 7596-7611.