Melt-sulfide Rare Earth Elements distribution under reduced conditions

N. J. INGRAO*[1], T. HAMMOUDA[1], M. BOYET[1], I.VLASTELIC[1], J.-L. DEVIDAL[1], B. N. MOINE[2], O. MATHON[3]

[1] Laboratoire Magmas et Volcans, UCA, Clermont-Ferrand, France (*N.Ingrao@opgc.univ-bpclermont.fr)
[2] Laboratoire Magmas et Volcans, UJM, Saint-Etienne, France.
[3] European Synchrotron Radiation Facility, Grenoble, France

Oldhamite (CaS) is a key mineral in rare earth element (REE) budget of enstatite chondrite (EC). REE are important for tracing and dating cosmochemical processes, and a precise knowledge of their behavior in the EC formation conditions is essential. Mixtures of natural EC (Hvittis, EL6) chondrite doped in REE and CaS were placed in graphite crucibles and run in evacuated pure silica tubes at 1300°C or 1400°C, and at oxygen fugacities between IW-4 and IW-6 (IW refers to the Fe-FeO equilibrium). Sulfides and silicate melt have been analyzed by electron microprobe for major elements and with Laser Ablation ICPMS for trace elements.

In the CaS/silicate melt system, Light-REE and Heavy-REE are moderately incompatible whereas Middle-REE are moderately compatible. We note positive anomalies for Eu and Yb partition coefficients. These results are in agreement with literature data [1,2] but provide a more complete dataset.

Here positive anomalies seem to be caused by the reduction of Eu and Yb to Eu^{2+} and Yb^{2+}. X-ray Absorption Near Edge Spectroscopy analysis confirms the presence of Yb^{2+} in the system. Another experiment at higher fO_2 (IW-1.6, and 5 GPa) resulted in the absence of Yb anomaly and a reduced Eu anomaly. That observation confirms that fO_2 affects the valence state of Yb and its substitution into the sulfide crystals (and to a lesser extent Eu behavior, in the presently investigated range).

The obtained partition coefficients cannot explain the observed high (100 to 1000 x CI) REE abundances in EC CaS [3,4]. The negative Eu anomalies in the REE patterns of some EC [3] are also inconsistent with the experimental data. The highly reducing character of EC being beyond doubt, the natural REE patterns cannot be explained by CaS crystallization on the liquidus, and another process must be involved.

[1] Lodders et al. (1996) *MAPS*, **31**, 749-766. [2] Dickinson et al. (1997) *MAPS*, **32**, 395-412. [3] Floss et al. (2003) *GCA*, **67**, 543-555; [4] Gannoun et al. (2011) *GCA*, **75**, 3269-3289