

REE PARTITIONING BETWEEN SILICATE LIQUID AND IMMISCIBLE SULFIDE LIQUID: THE ORIGIN OF THE NEGATIVE Eu ANOMALY IN AUBRITE SULFIDES; Tammy L. Dickinson, Gary E. Lofgren and Gordon. A. McKay, SN2, NASA Johnson Space Center, Houston, Tx. 77058.

Aubrites have flat to bowed (LREE and HREE depleted) REE patterns with negative Eu anomalies. Oldhamite (CaS) has been shown to be the main carrier of REE in aubrites (1,2). A large (2cm) crystal of oldhamite with inclusions of alabandite, troilite, daubreelite, caswellsilverite and metallic NiFe has recently been described in an igneous clast from the Norton County aubrite (3). The sulfide portion of this clast apparently formed as an immiscible sulfide liquid within the silicate parent magma. Ion microprobe studies of this unusual clast show that the oldhamite has a bowed REE pattern at about 200 times CI, with a negative Eu anomaly (Eu/Gd ratio 0.5). Two hypotheses have been proposed for the origin of the negative Eu anomaly in oldhamite: it may be inherited from the parent magma or it may be produced from a melt with no Eu anomaly as a result of the REE partitioning during separation of immiscible sulfide melts from silicate melts (3). We have begun experiments on REE partitioning between Ca-rich sulfide liquid and silicate liquid in order to distinguish between these hypotheses.

Experimental We have obtained preliminary results for the partitioning of REE between immiscible sulfide and silicate liquids. Experimental charges consist of a mixture of oxides of Si, Al, Ca, Mg, and Fe, approximating a eucritic composition, powdered metallic Fe and Ni, and FeS₂. Aluminum foil or powdered Al metal was added as an oxygen getter to keep the charge at the Al-Al₂O₃ buffer. Experiments using powdered Al metal produced more homogeneous charge than did the Al-foil. Experiments to study Eu and Gd partitioning were conducted with Al-foil, while Al metal powder was used for the remaining REE. Samples were doped with wt % levels of REE. The REE were grouped (Eu, Gd) and (Nd, Sm, Yb) in order to avoid peak overlap during microprobe analyses. The charges were placed in Al₂O₃ crucibles, sealed in evacuated silica tubes, and suspended in air in a Deltech furnace. All charges were homogenized at 1350°C for two hours and then rapidly cooled to the run temperature (1250, 1000, and 800°C) and held for approximately 48 hours. The initial experiments, those with Eu and Gd, were quenched in water. However, since CaS hydrates very quickly, later experiments were quenched using compressed air. Microprobe analyses of phases in the later experiments gave better results as judged by the totals of the analyses. The Al₂O₃ crucibles containing the charges were mounted in epoxy, cut in half and polished. All sample processing was done in oil or alcohol to minimize alteration of CaS. Charges were analyzed with the JSC Cameca automated electron microprobe using standard procedures for our laboratory.

Results The 1350°C charges contained only metallic NiFe and silicate glass, but no sulfide. The 1250° charges contained sulfide, metallic NiFe and silicate glass. In all cases the sulfide occurred as partial rims on the metallic NiFe. In

general, the 1000 and 800°C charges contained distinct spheres of sulfide which were not associated with metallic NiFe.

Abundances in the quenched silicate glass are approximately equal for all REE and do not appear to depend on Ca abundance. In contrast, the REE concentration of the sulfide is correlated with Ca concentration and temperature. The experimentally produced sulfide is generally less calcic (<30% Ca) than naturally occurring oldhamite (50% Ca). Although abundances are correlated with Ca content and temperature, the DS(Eu)/DS(Gd) ratio is constant. Thus, the absolute D's may vary with temperature, but the relative pattern does not. Values for $D(\text{REE})_{\text{sulfide/silicate}}$ (DS) decreases with decreasing temperature (Fig. 1). At all three temperatures there is a negative Eu anomaly.

Due to the amount of Al metal added to the charges as a reducing agent, all charges contained Al_2O_3 intimately associated with the silicate glass. Thus, it was difficult to obtain good analyses of the glasses. Some charges contained plagioclase laths due to the Al enrichment. Since Eu is compatible in plagioclase, the timing of plagioclase crystallization is important to the interpretation of the measured sulfide/silicate distribution coefficients. For instance, if plagioclase grew after the separation of the sulfide from the silicate melt, and if the sulfide subsequently failed to equilibrate with the Eu-depleted silicate melt, then $DS_{\text{apparent}}(\text{Eu}) > DS_{\text{actual}}(\text{Eu})$ and $DS_{\text{apparent}}(\text{REE}^{+3}) < DS_{\text{actual}}(\text{REE}^{+3})$. Thus, we can look at the limiting case for our data, where $DS(\text{REE}^{+3})$ is a lower limit and $DS(\text{Eu})$ is an upper limit. If such limits are placed on the data, at 1250°C the magnitude of the Eu anomaly decreases. At 1000°C the pattern becomes rather flat and at 800°C a small positive Eu anomaly is produced. However, the fact the $D(\text{Eu})/D(\text{Gd})$ ratio does not vary with temperature or from one sulfide spot to another argues against this. Thus, we believe that the negative Eu anomaly is real.

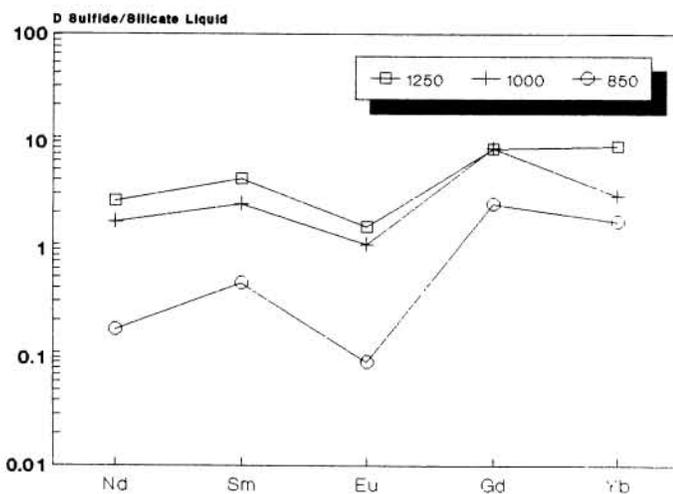


Fig. 1

Future experiments will be with starting compositions that minimize the crystallization of plagioclase, and hopefully substitute a mineral that will not effect the REE, such as enstatite. Since crystallization of plagioclase competes with the sulfide for Ca, we believe that this allow us to grow more calcic sulfide.

REFERENCES (1) Larimer J. W. and Ganapathy R. (1987) EPSL 84, 123-124. (2) Lundberg L. L. and Crozaz G. (1988) Met. 23, 285-286. (3) Wheelock M. M. et al. (1989) Met., in press.