

EXPERIMENTAL REE PARTITIONING IN OLDHAMITE: IMPLICATIONS FOR THE IGNEOUS ORIGIN OF AUBRITIC OLDHAMITE

Tamara L. Dickinson¹ and Timothy J. McCoy² ¹Catholic Univ., Mail Code 691, NASA/Goddard Space Flight Center, Greenbelt, MD 20771. ²Code SN4, NASA/Johnson Space Center, Houston, TX 77058.

Introduction. Aubrites (enstatite achondrites) are breccias consisting of FeO-free enstatite and a host of unusual, highly-reduced phases [1]. Among these phases, oldhamite (CaS) has garnered special attention, since it is the major REE carrier in aubrites [2], has a variety of REE patterns comparable to those in unequilibrated enstatite chondrites [3], and has an extraordinarily high melting point as a pure substance (2525°C). These latter two facts have caused some authors [3,4] to assert that much of the aubritic oldhamite is an unmelted nebular relict, rather than of igneous origin. However, strong textural evidence of an igneous origin exists for at least some aubritic oldhamite [2]. Despite this intense interest in oldhamite, few experimental studies have been conducted on oldhamite crystallization or REE partitioning [4,5]. We have previously reported results of experiments using a eucritic bulk composition [6] and early experiments using an aubritic composition [7], but which produced Ca-poor oldhamite. Here we report results for Ca-rich oldhamite that crystallized from an aubritic composition and discuss the implications for the genesis of aubritic oldhamite.

Experimental Method. We have conducted REE partitioning experiments between oldhamite and silicate melt using an aubritic bulk composition [7] at 1200 and 1300°C for 2 days and subsolidus annealing experiments at 800°C for 9 days. Calculated oxygen fugacities based on phase compositions are comparable to natural aubrites.

Petrography. All experiments produced crystalline oldhamite (as confirmed by XRD analysis; M. Zolensky, pers. comm., 1995), glass and Fe metal. The 1200°C experiments usually contained enstatite, SiO₂ and troilite. The 1300°C experiments largely lacked crystallized silicates. Opaque textures are complex, but oldhamite and troilite commonly occur together with a rounded boundary, suggesting the presence of immiscible Fe-rich and Ca,Mg-rich sulfide liquids, as reported by [5].

REE Partitioning. Our experiments allow us to examine how REE D_{CaS/silicate melt} varies with a number of parameters, including oldhamite composition, temperature, oxygen fugacity, and subsolidus annealing. *Oldhamite Composition.* Among these possible influences, oldhamite composition appears to be the strongest control. Partition coefficients of Nd, Sm, Gd and Yb are highly dependent on oldhamite composition. La, Ce and Eu show relatively small compositional dependences, particularly in the absolute value of the partition coefficient. This can be seen in Fig. 1 by comparing the 1200°C high- and low-Ca partition coefficients, which differ significantly. This compositional dependence tends to be minimal at oldhamite compositions above ~85% CaS. *Temperature.* REE partitioning also appears to be strongly temperature dependent, increasing with decreasing temperature. Fig. 1 illustrates this effect by comparing the 1200 and 1300°C partition coefficient patterns for Ca-poor oldhamite. *Oxygen Fugacity.* Partition coefficients appear independent of oxygen fugacity over the narrow range of fO₂ investigated in this work. *Subsolidus Annealing.* Subsolidus annealing experiments exhibit D_{Eu} uniformly elevated over the 1200°C experiments and D_{Gd} that scatter around the 1200°C data. The most marked enrichments are in oldhamites associated with troilite.

An important feature of our set of experiments is the general magnitude of the partition coefficients. Inferred oldhamite/silicate Ds in natural systems should be ~100-1000 [2], based on ion microprobe data of Norton County oldhamite and comparison with the bulk REE inventory. Our experiments, regardless of oldhamite composition, time or temperature, all yield REE partition coefficients < 20 and the vast majority are < 5. Actually, four data sets [4-7] using a variety of starting compositions and techniques all yield partition coefficients < 25 and most are < 5. Thus, we conclude that experimental partition coefficients, regardless of starting

OLDHAMITE REE PARTITIONING

T.L. Dickinson and T.J. McCoy

composition or technique, are less than partition coefficients inferred from natural samples [2]. This has been cited as evidence for the relict origin of some aubritic oldhamite [4].

Aubritic oldhamite genesis. We believe the REE enrichment and diversity of REE patterns in natural aubritic oldhamite could have been produced by a complex petrogenesis.

Chondritic Precursor. Aubrites likely formed from a precursor similar, but not identical to, enstatite chondrites [8, 9]. Enstatite chondrites typically contain oldhamite of nebular origin, associated with other sulfides and metal [10].

Metamorphism and Partial Melting. Initial heating prior to melting likely homogenized REE patterns [3]. Partial melting and removal of the Fe,Ni-FeS and basaltic partial melts between ~980-1100°C produced the depleted residues from which aubrites subsequently formed [11]. Removal of plagioclase from the basaltic partial melt fractionated the REE pattern of the residue, probably producing a negative Eu anomaly. Oldhamite did not melt during this phase.

Total Melting and Core Formation. Subsequent heating to ~1600°C (melting T of pure enstatite) caused near-total melting. Residual metal after partial melting largely drained away to a core. Total melting of silicates produced little further REE fractionation. Contrary to [4], oldhamite would melt at temperatures far below the melting point of pure CaS (2525°C). Oldhamite in contact with FeS (and other sulfides and metal) would experience melting point depression. A CaS-FeS eutectic of 1120°C has been reported [12]. Silicate-enclosed oldhamite may not melt until significant silicate melting allows chemical and/or physical contact between initially isolated sulfides and metal. The sulfide-metal melt would be immiscible in the silicate melt, but would probably reach diffusive REE equilibrium rapidly [4, this work].

Silicate Crystallization. Extensive silicate crystallization (~90% of the melt) would precede oldhamite crystallization, enriching the melt in REE by a factor of ≥ 10 , enriching the melt in Ca to allow CaS crystallization, possibly further fractionating the REEs of the melt by plagioclase crystallization, and isolating remaining melt pockets, allowing crystallization of oldhamite with a variety of REE patterns. Impact mixing of the crystallized oldhamite from these isolated melt pockets produces the diversity of REE patterns seen in a single aubrite [13].

Oldhamite Crystallization. Crystallization of oldhamite after silicate crystallization is supported by petrologic [2] and experimental [this work] evidence. Crystallized oldhamite can produce a variety of patterns dependent on the REE pattern of the melt and the composition of the crystallizing oldhamite. Experiments [4, this work] suggest that REE patterns with both Eu and Yb anomalies [3] can be produced by crystallization from a melt.

Equilibration and Exsolution. Subsolidus annealing can elevate partition coefficients. Together with the elevation of REE in the melt by silicate crystallization, this might explain the apparent contradiction between 1200°C partition coefficients and those inferred from natural systems [2]. Exsolution of Fe,Mg,Mn-rich phases (e.g., alabandite) from oldhamite [2] can also alter the REE pattern of natural oldhamite.

The diversity of aubritic oldhamite REE patterns probably reflects this complex history, rather than a nebular origin. This data suggests that REE patterns cannot discriminate a nebular vs. igneous origin for oldhamite; sulfur isotopic anomalies may provide such evidence [14].

- References:** [1] Watters and Prinz (1979) *Proc. LPSC 10*, 1073-1093. [2] Wheelock *et al.* (1994) *GCA* **58**, 449-458. [3] Floss and Crozaz (1993) *GCA* **57**, 4039-4057. [4] Lodders (1995) *20th Symp. Antarct. Met.*, NIPR. [5] Jones and Boynton (1983) *LPSC XIV*, 353-354. [6] Dickinson *et al.* (1990) *LPSC XXI*, 284-285. [7] Dickinson *et al.* (1991) *LPSC XXII*, 319-320. [8] Clayton *et al.* (1984) *Proc. LPSC 15*, C245-C249. [9] Brett and Keil (1986) *EPSL* **81**, 1-6. [10] Crozaz and Lundberg (1995) *GCA* **59**, 3817-3831. [11] Wilson and Keil (1991) *EPSL* **104**, 505-512. [12] Vogel and Heumann (1941) *Archiv Eisenhüttenw.* **15**, 195-199. [13] Floss *et al.* (1990) *GCA* **57**, 4039-4057. [14] Thiemens *et al.* (1994) *Meteoritics* **29**, 540-541.

