APATITE/MELT PARTITIONING EXPERIMENTS REVEAL REDOX SENSITIVITY TO CR, V, MN, NI, EU, W, TH, AND U. K. Righter1, S. Yang2 and M. Humayun3. 1NASA Johnson Space Center, Mailcode XI2, 2101 NASA Parkway, Houston, TX 77058. Kevin.righter-1@nasa.gov, 2National High Magnetic Field Laboratory, Florida State Univ., Tallahassee, FL 32306.

Introduction: Apatite is a common mineral in terrestrial, planetary, and asteroidal materials. It is commonly used for geochronology (U-Pb), sensing volatiles (H, F, Cl, S), and can concentrate rare earth elements (REE) during magmatic fractionation and in general [1]. Some recent studies have shown that some kinds of phosphate may fractionate Hf and W [2] and that Mn may be redox sensitive [3]. Experimental studies have focused on REE and other lithophile elements and at simplified or not specified oxygen fugacities. There is a dearth of partitioning data for chalcophile, siderophile and other elements between apatite and melt. Here we carry out several experiments at variable fO2 to study the partitioning of a broad range of trace elements. We compare to existing data [4] and then focus on several elements that exhibit redox dependent partitioning behavior.

Experimental: Experiments were carried out in a non-end loaded piston cylinder apparatus at NASA-JSC, using a BaCO3 pressure medium, graphite furnaces, and W-Re Type C thermocouples. Starting materials consisted of augite minette (AY-506; [5]) powder that included a small amount of Durango apatite seeds to ensure apatite saturation. All experiments were carried out at 0.8 GPa and 1150 °C. Experiment PhW-2 was done in a graphite capsule (fO2 controlled to near FMQ-2) for 5.5 hrs. Experiment PhW-3 was done in a Mo capsule (fO2 controlled to ~IW buffer) for 6 hrs.

Natural samples: We also analyzed phenocryst-matrix pairs from several apatite-bearing volcanic rocks from the Mexican volcanic belt. Olivine minette scoria (Mas-4a) contain apatite, phlogopite, and olivine and glassy regions. Augite minette lava (AY-506) contain apatite and augite phenocrysts in a fine-grained groundmass. The apatite crystals are about 200 μm wide and can be ~1 mm long. These natural samples were analyzed to compare to the experimental results.

Analytical: LA-ICP-MS analyses were performed at FSU using an ESI New Wave UP193FX excimer laser ablation system coupled to a Thermo Element XR™ ICP-MS. The samples were imaged with BSE and reflected light microscope to avoid inclusions or other phases in selected spots or tracks. Spots were 25-microns in diameter, and lines were 15-micron wide, both ablated at 50 Hz. Ablation times of 5 seconds were used for spots, while lines were scanned at 5 microns/second. The abundances of the major elements and 36 other elements were determined using a multi-standard approach discussed elsewhere [6].

Results: Many lithophile elements (Sc, Co, Zn, Rb, Zr, Nb, Mo, Ba, Hf, Ta, and Pb) show incompatible behavior in apatite at both high and low fO2. REE, Th, Sr, Ga and Cu all exhibit compatible behavior in apatite, as expected from previous studies (Fig. 1). The most interesting results are that Mn, V, Cr, Ni and W change from incompatible to compatible at low fO2. On the other hand, U and Th change from weakly compatible / incompatible to strongly compatible at high fO2. Finally, Eu exhibits a positive Eu anomaly (relative to other REE) at low fO2 and a negative anomaly at high fO2.

Apatite – matrix measurements on the Mexican minettes reveal much of the same incompatibilities as the FMQ-2 experiment (PhW-2) such as Co, Ni, Zn, Rb, Zr, Nb, Mo, Ba, Hf, Ta, W, Pb, Th and U (Figure 2). The compatibility of W and Th and the positive Eu anomaly seen in the IW experiments (PhW-3) are not evident in the mineral/melt pair analyses. Results for phlogopite/matrix are largely similar to the literature data (Rb, K, Ba are compatible; [7]), but of extra interest is the compatibility of Ni, Co, Cr and Ta, and the positive Eu anomalies for both sets of measurements.

Discussion: Redox sensitivities of trace element partitioning and in particular for phosphates, have been reported previously. For example, Pu exhibits redox sensitive partitioning in whitlockite [8], Mn may exhibit enhanced solubility in apatite at lower fO2 [3], and we suspect W may be mildly compatible in angrites phosphates which equilibrated near the IW buffer [2,9]. Our data show a larger D(Mn) apatite/melt at low fO2, consistent with the observations of [3]. We also see higher D(Ni), D(Cr), and D(V) at low fO2. Although Ni does not experience a valence change across these fO2, Cr and V do, and the enhanced compatibility may be related to stability of Cr3+ and V3+ at these lower conditions [10,11]. The compatibility of Ni may be related to crustal chemical differences between the low and high fO2apatites. Apatite is a key phase for U-Pb geochronology and dating, and the incompatibility of Pb in apatite at all fO2 is essential to the utility of this system.

D(W) apatite/melt in our experiments is ~1.5 at low fO2, perhaps consistent with the angrite work. The angrites phosphates are silico-phosphates which may be an important compositional difference; the phosphates produced in our reduced experiment do not contain any more or less silica than the oxidized. Additional work on silico-phosphates may help to resolve this conundrum, but reduced conditions appear to favor W parti-
tioning in apatite, perhaps reflecting the change from \(W^{6+}\) to \(W^{4+}\) at lower \(fO_2\) [12].

Finally, the positive Eu anomaly in partition coefficients at low \(fO_2\) and the negative at high \(fO_2\) is notable. Previous studies have either included Sr as a proxy for Eu [13], or not included Eu among the REE studied [4]. Therefore, this behavior may have gone unnoticed previously. Even though there are anomalies in Eu for partitioning, the absolute values of \(D(Eu)\) are >>1 so Eu is still compatible regardless of the negative anomaly in the oxidized experiment.

**Conclusions:** In addition to offering constraints on chronology, volatile speciation, and REE distribution, apatite can also provide information on redox conditions and apatite/melt partitioning may be sensitive to \(fO_2\) variation. In future work, it will be important to decouple crystal chemical controls from \(fO_2\) controls.

**References:**


**Figure 1:** Comparison of apatite/melt \(D_s\) from experiments PhW-2 (FMQ-2) and PhW-3 (IW) and exp# 78 from [4].

**Figure 2:** Comparison of apatite/melt \(D\) from experiments PhW-2 (FMQ-2) and Mas-4a matrix/melt measurements.