

**APATITE/MELT PARTITIONING EXPERIMENTS REVEAL REDOX SENSITIVITY TO CR, V, MN, NI, EU, W, TH, AND U.** K. Richter<sup>1</sup>, S. Yang<sup>2</sup> and M. Humayun<sup>2</sup>, <sup>1</sup>NASA Johnson Space Center, Mailcode XI2, 2101 NASA Parkway, Houston, TX 77058. [Kevin.richter-1@nasa.gov](mailto:Kevin.richter-1@nasa.gov). <sup>2</sup>National 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  $fO_2$  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  $BaCO_3$  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 ( $fO_2$  controlled to near FMQ-2) for 5.5 hrs. Experiment PhW-3 was done in a Mo capsule ( $fO_2$  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  $\mu m$  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  $fO_2$ . 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  $fO_2$ . On the other hand, U and Th change from weakly compatible / incompatible to strongly compatible at high  $fO_2$ . Finally, Eu exhibits a positive Eu anomaly (relative to other REE) at low  $fO_2$  and a negative anomaly at high  $fO_2$ .

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  $fO_2$  [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  $fO_2$ , consistent with the observations of [3]. We also see higher  $D(Ni)$ ,  $D(Cr)$ , and  $D(V)$  at low  $fO_2$ . Although Ni does not experience a valence change across these  $fO_2$ , Cr and V do, and the enhanced compatibility may be related to stability of  $Cr^{2+}$  and  $V^{2+}$  at these lower conditions [10,11]. The compatibility of Ni may be related to crustal chemical differences between the low and high  $fO_2$  apatites. Apatite is a key phase for U-Pb geochronology and dating, and the incompatibility of Pb in apatite at all  $fO_2$  is essential to the utility of this system.

$D(W)$  apatite/melt in our experiments is ~1.5 at low  $fO_2$ , 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 un-noticed previously. Even though there are anomalies in Eu for partitioning, the absolute values of  $D(Eu)$  are  $\gg 1$  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:** [1] Hughes, J.M. and Rakovan, J.F. (2015) *Elements* 11, 165-170. [2] Shirai, N. and Humayun, M. (2010) LPS 41, #2642. [3] Miles, A.J. et al. (2014) GCA 132, 101–119. [4] Prowatke, S. and Klemme, S. (2006) GCA 70, 4513–4527. [5] Righter, K. and Rosas-Elguera, J. (2001) J Pet. 42, 2333-2361. [6] Yang, S. et al. (2015) MaPS 50, 691-714. [7] LaTourrette, T. et al. (1995) EPSL 135, 13-30. [8] Benjamin, T.M. et al. (1983) GCA 47, 1695-1705. [9] McKay, G.A. et al. (1994) GCA 58, 2911-2919. [10] Sutton, S.R. et al. (2005) GCA 69, 2333-2348. [11] Berry, A.J. and O'Neill, H.St.C. (2004) Amer. Min. 89, 790-798. [12] Danielson, L.R. et al. (2008) LPS 39, #2075. [13] Dickinson, J.E. and P.C. Hess (1983) LPS 14, 158-159.

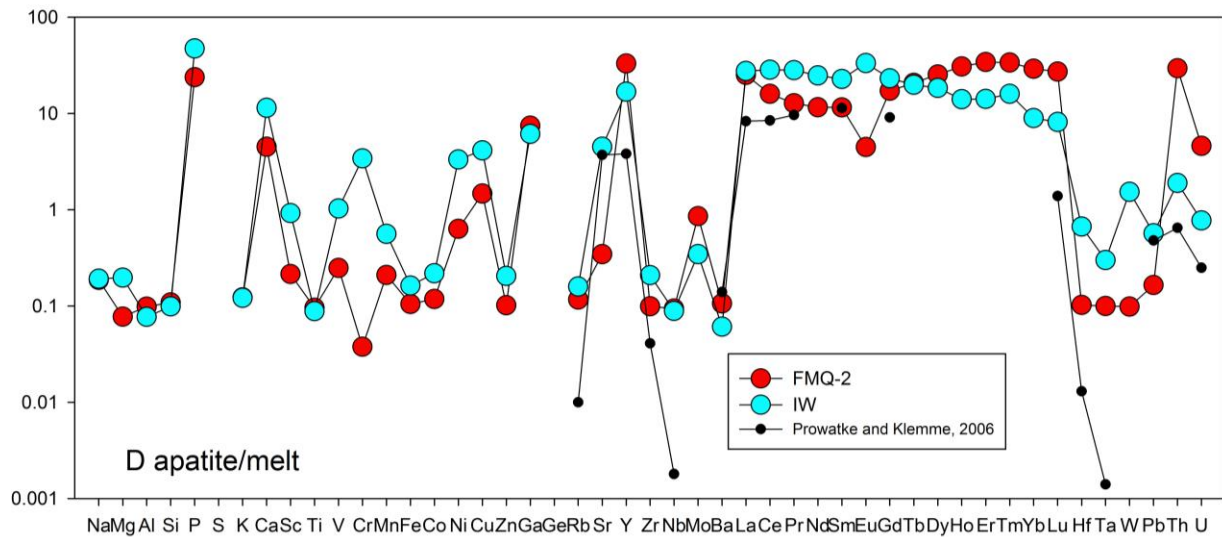


Figure 1: Comparison of apatite/melt  $D$ s from experiments PhW-2 (FMQ-2) and PhW-3 (IW) and exp# 78 from [4].

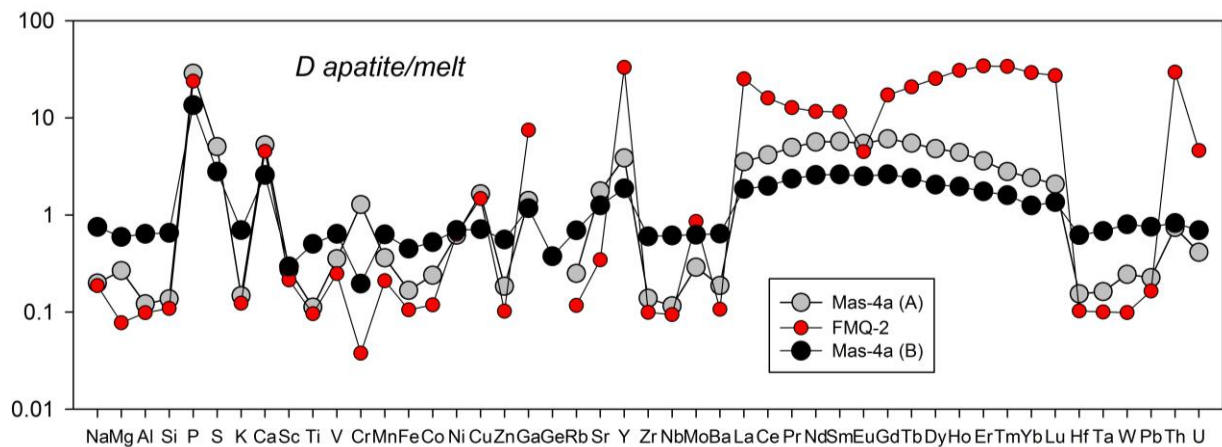


Figure 2: Comparison of apatite/melt  $D$ s from experiments PhW-2 (FMQ-2) and Mas-4a matrix/melt measurements.