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Redox-sensitive trace element partitioning between apatite, biotite, and glass: Implications for oxygen barometry in evolved crustal rocks

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Apatite and biotite, ubiquitous minerals in the igneous crustal assemblages, can accommodate a variety of trace elements, including those whose valence state, and hence ionic radius and charge, can vary over the oxygen fugacity (fO_2) range of Earth's crust.

In this study, we empirically determine Nernst partition coefficients (D) between apatite (ap) and biotite (bt) in 5 suites of natural, mostly silicic rocks, comprising metaluminous to peraluminous compositions, and reduced to oxidized conditions (FMQ-2.8 to +4.3). Three vitrophyre suites enable glass (gl) measurements for mineral/glass D values. Elements considered include alkalis (Li, Rb, Cs), alkaline earths (Ba, Sr), rare earth elements (REE) and Y, transition metals (Sc, V, Mn, Co, Ni, Cu, Zn, Mo), metalloids (Ge, Ge, Cd, In, Sn, Pb, Bi) and high field-strength elements (Zr, Nb, Hf, Ta, W, Th, U), of which Eu, Ce, V, Sn, and W are expected to be heterovalent over the fO_2 range considered.

Here we present $D^{bt/gl}$ (29 elements), $D^{ap/gl}$ (39 elements), and $D^{ap/bt}$ values for the heterovalent elements. Results show that most of the heterovalent element partitioning relationships exhibit redox sensitivity. With increasing oxidation, $D^{bt/gl}$ for V decreases from ~500 to ~50 whereas $D^{ap/gl}$ increases from ~0.1 to ~4. Similarly, Sn becomes more compatible with both minerals as fO_2 increases (D = ~0.2 to ~1.0 for bt/gl and ~0.01 to ~0.4 for ap/gl). The ap/gl D for Eu increases with fO_2 (D = ~20 to 100) while values for bt/gl decrease (D_{Eu} = ~0.7 to 0.2). Bt/gl D values for W become progressively smaller with increasing fO_2 (D_W=~0.1 to 0.02), while values for apatite remain at ~0.2-0.3. Cerium becomes less compatible in biotite with oxidation (D_{Ce}=~0.02 to <0.001), however, D(Ce)ap/gl does not display redox-sensitivity.

Overall, the D for ap/bt partitioning of V varies from ~0.002 to ~0.5, in a positive correlation with the fO_2, suggesting a potential new oxybarometer. Application of the observed D_V-fO_2 relations to V partitioning systematics in the peraluminous South Mountain batholith, Nova Scotia (SMB) and Palabora carbonatite, South Africa yield relatively low fO_2 in the former (~FMQ-1) and high fO_2 in the latter (FMQ+4).