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An experimental study of the oxidation state of vanadium in spinel and basaltic melt with implications for the origin of planetary basalt

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ABSTRACT

The distribution of V in magmatic rocks is controlled primarily by spinel stability. Extensive previous experimental work at oxidized conditions on doped (V-rich) compositions has led to the recognition of the importance of temperature, oxygen fugacity, and spinel composition, but also left ambiguity with respect to the relative importance of these variables in controlling $D_V^{\text{spinel/melt}}$. One major uncertainty has been the valence of V in the spinel and glass. Spinel-melt pairs were equilibrated at low and variable oxygen fugacities, with a range of V and Ti contents. XANES spectra were measured on the spinel and glass products, and pre-edge peaks measured and calibrated against valence with the use of glass and oxide standards. The valence of V is always greater in the glass than in the spinels. In spinel, V is dominantly 3+ at oxygen fugacities near the FMQ (fayalite magnetite quartz) buffer, but we find evidence for mixed 3+, 4+, and 5+ at oxidized conditions (FMQ to air), and 2+ and 3+ at very reduced conditions [FMQ to IW-1 (1 log f_{O_2} unit below the iron wüstite buffer)]. Increased V contents in spinels are correlated with increased $D_V^{\text{spinel-melt}}$, at constant temperature and oxygen fugacity. However, increased Ti content causes only a slight decrease in $D_V^{\text{spinel-melt}}$ and a shift to more reduced V (smaller pre-edge peak), which may be related to Fe-V exchange equilibria. Using the new partition coefficients, together with published results and valence information, expressions have been derived to predict $D_V^{\text{spinel/melt}}$ for basaltic systems. Application of these expressions to natural suites illustrate their utility and also the great range of $D_V^{\text{spinel/melt}}$ values relevant to natural systems. Calculation of V depletions in planetary mantles from basalt suites must take silicate, oxide, and metal fractionation into account, as is demonstrated using terrestrial, lunar, martian, and eucritic samples.

Keywords: Vanadium, oxygen fugacity, basalt, spinel