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Radiation-induced changes in vanadium speciation in basaltic glasses: Implications for oxybarometry measurements using vanadium *K*-edge X-ray absorption spectroscopy

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Abstract

Magmatic oxygen fugacity (f_{O_2}) exerts a primary control on the discrete vanadium (V) valence states that will exist in quenched melts. Vanadium valence proxies for f_{O_2}, measured using X-ray absorption near-edge spectroscopy (XANES), can provide highly sensitive determinations of the redox conditions in basaltic melts. However, X-ray beam-induced changes in V speciation will introduce uncertainty in the calculated average V valence (V*) that must be properly evaluated to make meaningful interpretations of the igneous evolution of the system. The study presented here showed that beam-induced modifications in V speciation are observed in silicate glasses that are dependent on the radiation dose rate used during analysis. Changes in V speciation are observed to be most pronounced at the highest flux density tested, 9.25×10^{11} ph/s/μm^2 (photons per second per square micrometer), with rapid changes occurring in the first 200 s of analysis. The high-dose rate conditions result in changes in calculated V* ~0.3 valence unit for the most oxidized glass analyzed (V* = 4.94), which can correspond to ~0.5 log unit reduction in calculated f_{O_2}. However, at flux densities $\leq 1.13 \times 10^9$ ph/s/μm^2, measured changes in V* were found to be <0.03 for all standard glasses analyzed. The degree of reduction observed during analysis is also found to be progressively smaller as the initial V* of the glass decreases, such that magmatic glasses with V* values ≤3.7 show no statistically significant change in calculated valence during analysis at any flux density tested. For most terrestrial magmatic glasses, where V* is found to be <4, beam-induced changes in V* can be effectively minimized (<0.04), within analytical uncertainty of the XAFS analysis, by limiting flux densities to be $\leq 1 \times 10^9$ ph/s/μm^2.

Keywords: XANES, vanadium, spectroscopy, oxybarometry, X-ray, synchrotron, XAFS