Radiation-induced oxidation of Fe in hydrous basalt glasses

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Mantle oxygen fugacity (fO_2) has a first-order effect on the geochemical evolution of Earth's crust and mantle. Many studies have used iron K-edge X-ray absorption near-edge structure (XANES) to determine the $Fe^{3+}/\Sigma Fe$ ratios of silicate glasses as a proxy for fO_2. With data obtained at Advanced Photon Source 13-ID-E, we show that synchrotron radiation causes oxidative beam damage to the Fe absorption spectrum in hydrous glasses [1]. Such damage increases as a function of radiation dose and the molar ratio of molecular water to ferric iron (XH_2O/XFe^{3+}). Damage can be extreme. For example, a hydrous 4.9 wt.% H_2O glass with $Fe^{3+}/\Sigma Fe = 0.19$ from its Mössbauer spectrum may appear to have a $Fe^{3+}/\Sigma Fe \geq 0.35$ if analysed at a synchrotron with an insertion device and a focused beam ($\sim 2 \bullet 10^9$ photons/s/μm^2). This would overestimate fO_2 by ~ 2 orders of magnitude.

For glasses with $XH_2O/XFe^{3+} > 1.0$, we detect oxidative beam damage down to the lowest photon densities for which high quality spectra could be obtained ($3 \bullet 10^6$ photons/s/μm^2). At these low flux densities, however, the calibration between centroid and Mossbauer-derived $Fe^{3+}/\Sigma Fe$ ratios for hydrous glasses is not distinguishable from the anhydrous calibration curve [1] given the accuracy of Mössbauer and potential for inter-laboratory bias. We verified this with additional data collected at NSLS X26A, a bending magnet beamline with photon flux $\sim 9 \bullet 10^7$ photons/s/μm^2. Thus $Fe^{3+}/\Sigma Fe$ ratios from reduced, hydrous glasses obtained at typical bending magnet sources may be accurate within measurement error.

The oxidation mechanism is unknown but is consistent with radiation-induced hydrolysis of water and associated H migration and oxidation of Fe^{2+} to Fe^{3+}. This is consistent with the observation that anhydrous glasses show no damage under any beam conditions and that the damage is at least partially reversible on rapid timescales of <24 hours at ambient conditions.

[1] Botcharnikov et al., GCA. (2005) [2] Cottrell et al., Chem. Geol. (2009)