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A Mössbauer-based XANES calibration for hydrous basalt glasses reveals radiation-induced oxidation of Fe

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Abstract

Oxygen fugacity (f_{O_2}) exerts first-order control on the geochemical evolution of planetary interiors, and the $Fe^{3+}/\Sigma Fe$ ratios of silicate glasses provide a useful proxy for f_{O_2}. Fe *K*-edge micro-X-ray absorption near-edge structure (XANES) spectroscopy allows researchers to micro-analytically determine the $Fe^{3+}/\Sigma Fe$ ratios of silicate glasses with high precision. In this study we characterize hydrous and anhydrous basalt glass standards with Mössbauer and XANES spectroscopy and show that synchrotron radiation causes progressive changes to the XANES spectra of hydrous glasses as a function of radiation dose (here defined as total photons delivered per square micrometer), water concentration, and initial $Fe^{3+}/\Sigma Fe$ ratio.

We report experiments from eight different radiation dose conditions and show that Fe in hydrous silicate glasses can undergo rapid oxidation upon exposure to radiation. The rate and degree of oxidation correlates with radiation dose and the product of water concentration and ferrous/ferric iron oxide ratio on a molar basis ($\Phi = X_{HO_{0.5}} \cdot X_{FeO}/X_{FeO_{1.5}}$). For example, a basalt glass with 4.9 wt% dissolved H_2O and $Fe^{3+}/\Sigma Fe = 0.19$ from its Mössbauer spectrum may appear to have $Fe^{3+}/\Sigma Fe \geq 0.35$ when analyzed over several minutes at a nominal flux density of ~2×10^9 photons/s/μm^2. This radiation-induced increase in $Fe^{3+}/\Sigma Fe$ ratio would lead to overestimation of f_{O_2} by about two orders of magnitude, with dramatic consequences for the interpretation of geological processes.

The sample area exposed to radiation shows measureable hydrogen loss, consistent with radiation-induced breaking of O–H bonds, associated H migration and loss, and oxidation of Fe^{2+}. This mechanism is consistent with the observation that anhydrous glasses show no damage under any beam conditions. Cryogenic cooling does not mitigate, but rather accelerates, iron oxidation. The effects of beam damage appear to persist indefinitely.

We detect beam damage at the lowest photon flux densities tested (3×10^6 photons/s/μm^2); however, at flux densities ≤6×10^7 photons/s/μm^2, the hydrous glass calibration curve defined by the centroid (derived from XANES spectra) and $Fe^{3+}/\Sigma Fe$ ratios (derived from Mössbauer spectra) is indistinguishable from the anhydrous calibration curve within the accuracy achievable with Mössbauer spectroscopy. Thus, published $Fe^{3+}/\Sigma Fe$ ratios from hydrous glasses measured at low photon flux densities are likely to be accurate within measurement uncertainty with respect to what would have been measured by Mössbauer spectroscopy.

These new results demonstrate that to obtain accurate $Fe^{3+}/\Sigma Fe$ ratios from hydrous, mafic, silicate glasses, it is first necessary to carefully monitor changes in the XANES spectra as a function of incident dose (e.g., fixed-energy scan). Defocusing and attenuating the beam may prevent significant oxidation of Fe in mafic water-bearing glasses.

Keywords: XANES, Mössbauer, oxygen fugacity, oxidation state, iron, glass, synchrotron radiation, hydrous basalt; Invited Centennial Article