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Fe Kα XANES, Fe Kβ HERFD XANES and EPMA flank method determinations of the oxidation state of Fe in garnet

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Knowledge of iron oxidation states in garnet provides geochemical information about the conditions of crystallization in Earth's crust and mantle. However, techniques with a high analytical and spatial resolution are necessary to distinguish differences in garnet $Fe^{3+}/\sum Fe$ ratios at the percent level and to accurately measure garnets that are zoned or contain inclusions. We acquired conventional Fe Kα and high-resolution energy fluorescence detection (HERFD) Fe Kβ X-ray absorption near edge structure (XANES) spectra on a suite of 27 peridotitic and eclogitic garnets with $Fe^{3+}/\sum Fe$ ratios previously determined by Mössbauer spectroscopy to evaluate the precision of each technique [1]. We examined variations in the energy and intensity of three XANES spectral features as a function of $Fe^{3+}/\sum Fe$ ratios: 1) the intensity ratio of two-post edge features (I-ratio; Fe Kα only); 2) the energy of the Fe edge at 90% normalized intensity ($E_{0.9}$; Fe Kα only) and 3) the pre-edge centroid energy (Fe Kα and HERFD Fe Kβ). In accordance with previous work, we find the energies of garnet pre-edge centroids are relatively insensitive to $Fe^{3+}/\sum Fe$ ratios, while I-ratio garnet XANES calibrations are composition-specific. The $E_{0.9}$ feature is independent of garnet major element composition in spectra that have been corrected for the effects of self-absorption. Our XANES calibrations based on the $E_{0.9}$ feature may be used to characterize the $Fe^{3+}/\Sigma Fe$ ratios of garnet unknowns with an uncertainty of ±0.02 $Fe^{3+}/\Sigma Fe$; the high precision of our calibration is critical for accurate measurement of peridotitic and eclogitic garnets with low $Fe^{3+}/\Sigma Fe$ ratios. We compare XANES measurements of garnet $Fe^{3+}/\sum Fe$ ratios with those calculated from the flank method for electron microprobe for garnets in the same sample suite. The standard error of the mean $Fe^{3+}/\sum Fe$ ratio calculated from the flank method approaches the Mössbauer-determined $Fe^{3+}/\sum Fe$ ratio within estimated error (3%) after three analyses; however, the precision of the flank method does not approach the precision of XANES under any microprobe analytical condition tested here. Garnet reference materials measured here are available for loan from the Smithsonian Institution as NMNH Catalogs #118530 and #118540.

[1] Holycross et al. (2024) *Chem Geol* 647, 121937