Ferric iron partitoning between pyroxene and melt during partial melting of the Earth's upper mantle

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Mantle redox state influences melt production, volatile behavior, partitioning of key trace elements and possible saturation of metallic alloy at depth [1]. The redox state of the sub-oceanic mantle is known from study of MORB and abyssal peridotite with the two reservoirs giving conflicting constraints, perhaps owing to the effects of melt extraction. Mantle f_{O2} derived from Fe^{3+}/Fe^T ratios of MORBs are comparatively oxidizing (QFM or above) and occur in a narrow range (chiefly <1 log unit) [2,3]. In contrast, abyssal peridotites extend to more reduced conditions (typically QFM-1) and show 3 log units f_{O2} variation [4]. Quantification of the relationship between basalt and source Fe^{3+}/Fe^T, oxygen fugacity, and degree of melting requires constraints on Fe^{3+} partitioning between melt and mantle minerals and in particular with the principal Fe^{3+} host in solid peridotite, pyroxene. We are conducting 100 kPa and high pressure (1.5-2 GPa) controlled f_{O2} experiments between ΔQFM = 2.5 to -1.5 to grow pyroxenes of variable tetrahedral and octahedral cationic population from mafic melts of varying Mg#, alumina and alkali content. Oxygen fugacity is fixed by CO-CO_2 gas mixing and metal-metal oxide buffers in ambient and high-pressure experiments respectively. A dynamic crystallization technique facilitates growth of pyroxene crystals (100-200 μm) that EPMA analyses show to be compositionally homogeneous and in equilibrium with the melt. Synthetic pyroxenes have been analyzed by XAFS spectroscopy at the APS synchrotron, which in principle can constrain Fe^{3+}/Fe^T, given appropriate calibration. To provide such calibration and to quantify the x-ray anisotropy, we collected Fe K-edge XAFS spectra of 14 oriented natural single crystal pyroxenes of a wide range of compositions whose Fe^{3+}/Fe^T we have determined by Mössbauer spectroscopy. For each standard, six spectra in multiple orientations have been collected followed by normalization and averaging. A preliminary calibration based on the the pre-edge centroid energy shows a good correlation (r^2=0.92) with Fe^{3+}/Fe^T, but additional constraints from EXAFS structure are needed to account for the combined crystal chemical influences of valence, coordination and orientation. In the near future, the resulting XAFS standardization for pyroxene will be used to determine Fe^{3+}/Fe^T of experimental pyroxenes crystallized at controlled thermodynamic conditions.

[1] Frost and McCammon, 2008 Ann. Rev. EPS, 36:389-420. [2] Cottrell and Kelley, 2011 EPSL, 305:270-282. [3] Zhang et al. 2018, Chem. Geol. 479:166-175 [4] Bryndzia and Wood 1990 AJS, 290:1093-1116.