Redox Model for Silicate Melts at Mantle Conditions

AARON S. WOLF[1], MARK S. GHIORSO[2], CHRISTY TILL[3], AND CAYMAN UNTERBORN[3]

[1]Univ of Michigan, Earth & Environ Sci, Ann Arbor MI, 48109, (aswolf@umich.edu)
[2]OFM Research, Seattle WA, 98115, (ghioros@ofm-research.org)
[3]Arizona State Univ, Earth & Space, Tempe AZ, 85287, (Christy.Till@asu.edu, Cayman.Unterborn@asu.edu)

Mantle redox is a key control on a wide variety of geologic processes including magmatic differentiation, core-formation, solubility & transport of volatiles, and volcanic outgassing. Quantitatively linking the oxidation state of iron in silicate melts to the oxygen fugacity (fO_2) is critical for interpreting both experimental and natural samples. In melting experiments, fO_2 conditions are imposed using a redox buffer, but the resulting iron redox state is rarely measured; for natural samples, conditions of formation in the mantle source region are inferred from measurements of Fe-redox state (e.g. using XANES). In either case, we rely on accurate models to link the ferric/ferrous ratio in silicate liquids to corresponding fO_2 conditions over a broad range of pressures, temperatures, and compositions (P-T-X).

Existing redox model for silicate liquids (reviewed in Putirka, 2016) use empirical equations fitted to 1-bar experiments on crustal rock compositions. When pressure-dependence is addressed, as in Kress & Carmichael (1991), calibration relies on 1-bar compressibility measurements. Despite widespread use, the empirical form proposed by Sack et al. (1980) limits accurate extrapolation in P-T-X space. Past calibrations have not included any mantle peridotites and compressibilities were assumed constant, even though liquid compressibilities rapidly trend toward solid-like values as pressure increases.

To address these shortcomings, we develop a new thermodynamically-based redox model for silicate liquids. We adopt a thermodynamic perturbation approach, which uses the MELTS code to predict non-linear composition-dependence, combined with a Bayesian method to avoid overfitting the empirical composition-correction terms. We expand beyond the original measurements of Kress and Carmichael (1991), including high-pressure data from the LEPR database (Hirschmann et al. 2008), using measured spinel-compositions as an accurate redox proxy for the liquid. The new resulting model is compared to the original and we discuss potential implications for magma evolution, core-formation, and volcanic outgassing.