Modeling $Cr^{2+}/\Sigma Cr$ in Crystallizing Basaltic Liquids: Applications to the Cr-Valence in Olivine Oxybarometer

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The $Cr^{2+}/\Sigma Cr$ ratios preserved in silicate minerals that appear as early liquidus phenocrysts in mafic magma systems, such as olivine, are well suited to serve as recorders of the primitive fO_2 their parental liquids. Harvesting quantitative fO_2 information from μ-XANES measurements of $Cr^{2+}/\Sigma Cr$ in olivine phenocrysts requires robust thermodynamic or empirical models that can accurately predict $Cr^{2+}/\Sigma Cr$ in basaltic liquids as a function of fO_2, temperature, and liquid chemistry. A combined experimental-XANES study was conducted to illuminate how evolving liquid chemistry and decreasing temperature influence the equilibrium $Cr^{2+}/\Sigma Cr$ ratios in crystallizing basaltic liquids. The $Cr^{2+}/\Sigma Cr$ dataset produced from these experiments was fit with a symmetric regular solution model; this fitting produced a predictive model for $Cr^{2+}/\Sigma Cr$ systematics in tholeiitic basaltic liquids. Using MELTS in conjunction with the newly calibrated Cr valence model, the equilibrium $Cr^{2+}/\Sigma Cr$ values of a tholeiitic liquid undergoing isobaric equilibrium crystallization at buffered fO_2 conditions were calculated at 5°C intervals. These model calculations indicate that primitive tholeiitic liquids crystallizing along or parallel to an oxygen fugacity buffer curve will experience a 15-20% decrease equilibrium $Cr^{2+}/\Sigma Cr$ values. At ΔFMQ-0.5, the $Cr^{2+}/\Sigma Cr$ of the modeled liquids falls from 0.26 at 1225°C to 0.11 at 1125°C. This modeling demonstrates that the accurate translation of $Cr^{2+}/\Sigma Cr$ values from olivine phenocrysts into magmatic fO_2 values requires special attention to the thermal and chemical context under which the phenocryst of interest grew, as $Cr^{2+}/\Sigma Cr$ values may be partially decoupled from magmatic fO_2 values.