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New Cr K-edge XANES and Phase Equilibrium Constraints on Primitive Magmatic Redox Conditions on the Angrite Parent Body and Implications for Core Formation

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We applied Cr K-edge XANES (X-ray Absorption Near Edge Spectroscopy) measurements in olivine phenocrysts as well as a thermodynamic analysis of the olivine-metal-melt assemblage present in the primitive (i.e., Mg-rich) porphyritic angrite NWA 12774 to constrain the prevailing magmatic oxygen fugacity of primitive angrite magmas and, by extension, their mantle source regions. We have applied MELTS modeling in conjunction with a new set of Fe-Ni alloy saturated phase equilibrium experiments to estimate the liquidus temperatures for olivine phenocrysts in NWA 12774 and to constrain the a_{SiO2} for primitive angritic magmas. Olivine liquidus temperatures from the experiments and the Al in olivine geothermometer indicate that the Fo_{83-82} phenocryst cores crystallized at 1360°C ± 20 °C. With these new temperature estimates and a_{SiO2} values, we performed a thermodynamic analysis of the olivine-metal-liquid assemblage in NWA 12774. Our thermodynamic assessment suggests that NWA 12774 olivine began crystalizing from a metal saturated melt at an oxygen fugacity of ΔIW-0.90 ± 0.20. In contrast, XANES measurements of Cr valence of olivine in NWA 12774 (calibrated against a $Cr^{2+}/\sum Cr$ curve determined from olivine grown in 1-bar gas mixing experiments) suggest that the olivine phenocrysts grew at ΔIW+0.10 - roughly one log unit higher than the estimates derived from the thermodynamic calculations. This difference perhaps suggests that the olivine-metal pairs and the inferred silicate liquid composition are not in fact an equilibrium assemblage, and thus are not a good analog for a magma derived from a mantle source in equilibrium with the APB core-forming alloy. Alternatively, this discrepancy could be interpreted as evidence that the olivine (and clinopyroxene) phenocrysts in NWA 12774 began crystallizing at pressures > 4 kbar, as increasing pressure has been experimentally shown to decrease equilibrium $Cr^{2+}/\sum Cr$ in silicate liquids (and by extension olivine phenocrysts grown from these liquids).