

A NOVEL THERMODYNAMIC-PHASE EQUILIBRIUM APPROACH FOR CALCULATING MAGMATIC fO_2 VALUES OF FE-RICH DIABASIC ANGRITES. DO WE NEED A NEW MODEL FOR ANGRITE PETROGENESIS?

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Introduction: Constraints on the magmatic oxidation state of the angrite suite meteorites are an important cornerstone on which our understanding of their petrogenesis rests. One hypothesis postulates that the angrites are the partial melts of modestly oxidized (i.e., $fO_2 = \Delta IW + 1.5$) chondritic precursor material [1]. One of the enduring problems in angrite petrogenesis is how to reconcile the extraordinarily Fe-rich compositions of some angritic liquids – which seemingly require primordial melting at fO_2 conditions that fall outside the stability field of Fe-rich alloys – with the geochemical evidence that the angrite parent body contains a small metallic Fe-Ni-S core [2,3]. One of the major impediments to resolving this contradiction stems from a notable lack of rigorous fO_2 data for angritic meteorites. To begin addressing this issue, we have developed a novel approach for calculating magmatic fO_2 values directly from the late-stage magmatic phase assemblages present in Fe-rich diabasic angrites, and we have applied this method to Sahara 99555, D’Orbigny and NWA 12004.

Using the Ulvöspinel-Olivine- $a_{SiO_2}^{melt}$ Equilibrium as a Magmatic Oxybarometer: Most Fe-rich angrites contain small euhedral to skeletal Fe³⁺ bearing ulvöspinel. Ulvöspinel phenocrysts, along with troilite ± rhönite ± silicoapatite, are typically set in matrix of texturally complex Ca-rich fayalite and sub-calcic kirschsteinite intergrowths. We interpret these textures as the crystallization products of a late-stage interstitial silicate liquids. In phase assemblages that contain olivine, Fe³⁺ bearing spinel, and silicate liquid, the oxidation state of the magmatic system may be defined using the peritectic reaction:



which can be recast in standard thermodynamic notation as:

$$Eq.1 \quad \log_{10} fO_2 = \frac{-\Delta G^{\circ}_{T,P}}{\ln(10)RT} + 3\log a_{SiO_2}^{liq} + 2\log a_{Fe_3O_4}^{usp} - 3\log a_{Fe_2SiO_4}^{ol}$$

Values of $a_{SiO_2}^{melt}$ for use in Eq.1 were obtained from 1) purpose designed experiments in which olivine saturated angritic liquids were equilibrated with Fe-Ni alloys, and 2) Ca-Tschermak (in cpx)-anorthite- $a_{SiO_2}^{melt}$ equilibrium calculations which utilized the EMP measured compositions of the Al-rich clinopyroxene and plagioclase phenocrysts enclosing the mesostasis phases. The $a_{SiO_2}^{melt}$ values generated from these independent approaches are in excellent agreement, thus lending confidence to the fO_2 values obtained from Eq.1. The crystallization temperatures for the late-stage phase assemblage were estimated using sub-solvus compositions of co-existing fayalite and sub-calcic kirschsteinite. The sub-solvus conjugate olivine compositions and constraints from angrite crystallization experiments [6] indicate that ulvöspinel and the olivine intergrowths crystallized between 1060°C and 1040°C. The solution models for Ca-rich olivine [4] and ulvöspinel-magnetite [5] were employed to calculate the values of $a_{Fe_2SiO_4}^{ol}$ and $a_{Fe_3O_4}^{usp}$. The $\Delta G^{\circ}_{(T,P)}$ values for the temperature conditions of interest were calculated with the SUPCRTBL software package. We calculate remarkably consistent fO_2 values of $\Delta IW - 0.10$ (± 0.20) for the olivine-ulvöspinel pairs from all three of the investigated meteorites.

Implications for Proposed Models of Angrite Petrogenesis: The mildly reducing fO_2 values obtained from our analysis are inconsistent with the redox conditions required by the oxidized melting hypothesis. A degree of caution is warranted in extrapolating these late-stage magmatic fO_2 values to higher temperatures. However, it is perhaps more likely that at higher temperatures angrite liquids are even more reducing, as fractionated silicate liquids typically become more oxidized with increasing extent of crystallization by a mechanism of auto-oxidation (i.e., the accumulation of incompatible ferric iron in the residual liquid). Thus, we suspect that the late stage magmatic fO_2 values from our calculations represent the most oxidized conditions along the angrite liquid line of descent. We suggest that a new model for angrite petrogenesis is required, which must incorporate a mechanism for generating critically silica undersaturated liquid compositions and which does not require the wholesale oxidation of the metallic phases present in a presumably undifferentiated chondritic precursor material. We propose that Fe-rich diabasic angrites may represent fractionated residual liquids derived from MgO-enriched, silica undersaturated parental liquids that had a_{FeO}^{melt} values low enough to be consistent with Fe-metal saturation at the proposed redox conditions ($\sim \Delta IW - 1.0$) of core formation.

References: [1] Jurewicz, et al., (1993) GCA, 57, 2123-2139. [2] Steenstra et al. (2017) GCA, 212, 62-83. [3] Kleine, et al. (2012) GCA, 84, 186-203. [4] Mukhopadhyay and Lindsley (1983) Am.Min., 68, 1089-1094. [5] Woodland and Wood (1994) E.J. Min., 6, 23-27. [6] McKibben and O’Neill (2018) MAPS, 53, 206-325.