

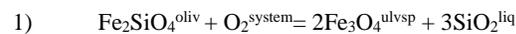
Thermodynamic and Phase Equilibria Constraints on the Late-Stage Magmatic fO_2 and Petrogenesis of the Angrite Sahara 99555

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Introduction: At present there is a significant dearth of high-quality, quantitative fO_2 estimates for the angrite suite meteorites [1-5]. This paucity stems not from lack of effort, but rather from the fact that most angrites lack phase assemblages amenable to the application of “classical” oxybarometers which utilize experimentally calibrated mineral redox equilibria (e.g., the ol-opx-spinel and magnetite-ilmenite equilibria). Constraints on the magmatic oxidation of angrite suite meteorites are an important cornerstone on which our understanding their petrogenesis rests. The most widely accepted hypothesis for the origin of angritic magmas postulates that the angrites are the product of melting “oxidized” CV chondrite-like precursor material at fO_2 conditions outside the stability field of Fe-enriched metallic alloys (i.e., $\sim\Delta IW+1.5$). However, it is difficult to reconcile this hypothesis with the observation that many angrites contain metallic Fe-Ni alloys as a part of their phase assemblage, as well as evidence indicating the angrite parent body (APB) contains a small Fe-S-Ni core [6]. Recent modeling of HSE partitioning behavior and oxygen isotope data suggest that the core formed by the segregation of metallic alloys from a “global” magma ocean (i.e., isotopically homogenized) at redox conditions of $\sim\Delta IW-1.5$ [6]. The conditions of magma ocean-core equilibration contrast sharply, at least on the surface, with the growing number of diabasic and porphyritic angrites (e.g., Sah99555, D’Orbigny, NWA 1296, NWA 12774, LEW87051, and Asuka881371) in which magnetite-bearing ulvöspinel has been identified as a constituent the magmatic phase assemblage. Additionally, there are several notable occurrences of angrites that contain both Fe³⁺-enriched ulvöspinel and Fe-Ni alloy (e.g., NWA 12774). The juxtaposition of ferric iron-bearing spinel in meteorites derived from source regions that ostensibly equilibrated with metallic Fe-rich alloys suggests that many angrites may have experienced a continuum of redox conditions or perhaps a discrete oxidation event during or prior to their crystallization. Isotopic evidence in the form of ¹⁸²Hf–¹⁸²W systematics also suggests the APB experienced a complex differentiation history, perhaps involving several distinct core formation events and inefficient mixing of geochemical reservoirs within the bulk silicate portion of the APB interior [7]. The complexity suggested by the ¹⁸²Hf–¹⁸²W systematics may point to a heterogenous accretion and core formation scenario that involves the partial mixing of oxidized and reduced planetesimal feedstock.

Using the Olivine-Spinel and Anorthite-Ca-Tschermak Equilibria to Calculate fO_2 in Sah99555:

In an effort to generate new insights into the oxidation state of angrite liquids saturated with Fe³⁺-bearing ulvöspinel, we have developed a new approach to extracting fO_2 values from the unique phase assemblages present in angrites. The phase assemblage of olivine-magnetite-silicate liquid defines the fO_2 of the system via:



Oxygen fugacity values can be calculated from the ol-mag-liq equilibrium if one can reliably calculate the silica activity of the system. The equilibrium between the Ca-Tschermak (CaTs) component of the clinopyroxene and anorthite component of the plagioclase conveniently defines the a_{SiO_2} of angritic liquids via:



This silica activity buffer is uniquely suited to the fassaitic pyroxene in the angrites, as these pyroxenes are notably enriched in Al. Assuming an anorthite activity of unity (the plagioclase in angrites is essentially Na-free) these equilibria can be combined to yield an expression for fO_2 as follows:

$$3) \quad \ln fO_2 = 2\ln a_{Fe_3O_4^{ulvsp}} - 3\ln a_{Fe_2SiO_4^{oliv}} - 3\ln a_{CaAl^{[VI]}Al^{[IV]}SiO_6^{cpx}} - \Delta_r G_{(T-1bar)}/-RT$$

Low pressure phase equilibrium experiments on Sah99555-like bulk compositions suggest that the pyroxene, and Fe-enriched olivine (i.e., subcalcic kirschsteinite), and ulvöspinel crystallize from late-stage liquids at $\sim 1100^\circ C \pm 20^\circ C$ [8]. With this temperature constraint, we have calculated the $\Delta_r G_{(T-1bar)}$ for the relevant reactions using the SUPCRTBL software package. The activities fayalite, magnetite, and CaTs activities were calculated from a new set of EMP spot analyses targeted to constrain the compositions olivine, pyroxene, and ulvöspinel crystals in physical contact with one another (See Fig. 1). Charge balance calculations indicate that the ulvöspinel in Sah99555 contains ~ 0.59 Fe³⁺ cations per formula unit. The activity of the magnetite component of the ulvöspinel was calculated with the solution models endemic to the MELTS supplemental calculator. The activity of the CaTs component of the clinopyroxene rims in contact

with the ulvöspinel was calculated using an ideal on-site mixing model, and the fayalite activity in the olivine was calculated using the experimentally determined Margules parameters for fayalite-kirschsteinite solutions from [9].

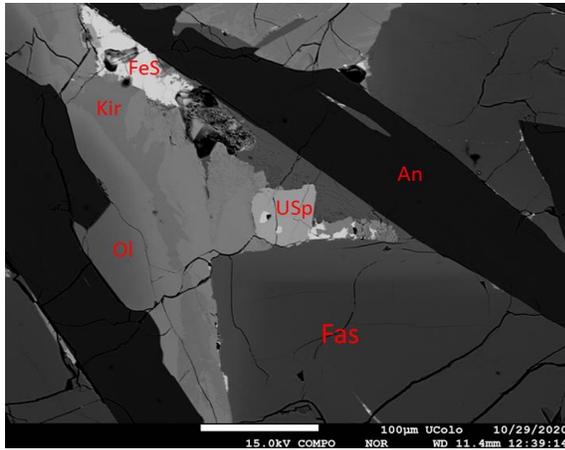


Figure 1 shows a backscattered electron image depicting the textural relationships among the late-stage magmatic phase assemblage utilized in the fO_2 calculations. EMP spot analyses used to calculate activity values targeted locations where all three phases of interest were in direct contact.

Results: The silica activity values calculated from the CaTs-An equilibrium were broadly consistent the $aSiO_2$ values generated by the MELTS supplemental calculator, which lends credibility to our approach to evaluating $aSiO_2$. Our preliminary calculations indicate that the fO_2 values recorded by this phase assemblage center around $\sim\Delta IW+0.10$ (± 0.30). A quick sensitivity analysis suggests that minor changes in the $aSiO_2$ value of the liquid - perhaps induced by errors in assessing the activity of the CaTs component of the clinopyroxene - have a relatively insignificant impact on the resultant fO_2 values, shifting them at most 0.30 log units in either the oxidizing or reducing direction.

Conclusions: The fO_2 value calculated from our analysis of Sah99555 curiously falls in between the fO_2 values required by the oxidized melting hypothesis and the fO_2 of the APB mantle/magma ocean inferred from HSE partitioning constraints. Unfortunately, our calculations only constrain the fO_2 of the system after it became ulvöspinel saturated, which occurs relatively late in the crystallization sequence. It is not entirely clear how the fO_2 obtained from our analysis relate to the oxidation state of the less evolved Sah99555 liquid that crystallized the Fe_{60} cores of the zoned olivine phenocrysts, let alone how this fO_2 relates the source regions in the APB interior from which Sah99555 was derived. It should be stressed that the olivine and pyroxene compositions utilized in our fO_2 calculations contain < 1.0 wt. % MgO, thus it is difficult to establish

a direct link to the more “primitive” redox conditions of more magnesian Sah99555 liquids. The fO_2 values calculated from our analysis are consistent with neither the values predicted by the oxidized melting hypothesis nor those inferred for the APB from core formation constraints. One possible explanation for the intermediate fO_2 values produced by our calculations is that angrites such as Sah99555 represent the mixing product of a highly oxidized, and FeO-enriched liquid with more primitive, reduced, and metal/sulfide saturated, eucrite-like liquid. Such a scenario may result in “hybridized” fO_2 values. We also speculate that kinetic effects associated with the mixing of oxidized and reduced magmas on short time scales could perhaps generate some of the more the unusual textural features of the diabasic angrites (e.g., the patchy intergrowths of olivine and subcalcic kirschsteinite and the strange sulfide-oxide-olivine symplectites). The core-rim Cr valence zoning profiles observed in the preliminary Cr-XANES study of olivine xenocrysts of LEW 87051 [10] also hint at the presence of both reduced and oxidized fO_2 signatures in some angrites. These data suggest that the xenocrystic ($>F_{080}$) olivines preserve a record of early reducing fO_2 conditions which may have been overprinted by later oxidizing conditions. Alternatively, the fO_2 values from our calculations may suggest that a “conventionally” oxidized Sah99555 parental liquid experienced progressive reduction during its crystallization, however, the redox reactions or mechanism driving this late-stage reduction are not readily apparent. Finally, we note that the presence of magnetite bearing ulvöspinel is a bit of a red herring with respect to qualitatively interpreting the magmatic fO_2 of angrites. Despite the low $Fe^{3+}/\Sigma Fe$ liquids implied by our fO_2 calculations, the highly Fe-enriched mesostasis liquids ($\sim 25-30$ wt.% FeO^{tot}) may still contain a sufficient quantity of Fe^{3+} (perhaps on the order of ~ 0.50 to 1.0 wt. % $FeO_{1.5}$) to support the crystallization Fe^{3+} -bearing accessory phases such as ulvöspinel, rhönite, and ferric-silicoapatite.

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