

## THE EFFECTS OF $fO_2$ ON MINERAL COMPOSITIONS IN ANGRITES: NEW INSIGHTS FROM ANGRITE CRYSTALLIZATION EXPERIMENTS

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**Introduction:** Angrites are achondritic meteorites that represent some of the oldest basaltic rocks in the Solar System, with ages as early as  $4564.18 \pm 0.14$  Ma [1]. They are silica under-saturated, enriched in refractory elements such as Ca and Ti, depleted in alkali elements such as Na and K, and vary in texture and modal mineralogy. While it's accepted that angrites originated from a differentiated angrite parent body, the  $fO_2$  of angrite magmas or its effects on the liquid line of descent and mineral chemistry is still debated. To shed new light on these petrologic relationships, we have performed a suite of angrite crystallization experiments to investigate the impact of  $fO_2$  on phase equilibria, equilibrium mineral compositions, and the valence partitioning behavior of Fe in plagioclase and pyroxene. Results of these experiments, along with chemical trends observed in real angrites, will be used to evaluate existing models of angrite petrogenesis. One of these models is the oxidized chondrite partial melting hypothesis. This hypothesis invokes low-degree partial melting of CV-like precursor material at oxidizing conditions ( $\Delta IW+2$ ) to generate silica undersaturated, CaO- and FeO-enriched, angritic liquids [2], however this hypothesis has yet to be critically evaluated.

**Methods:** A suite of angrite crystallization experiments was performed in a vertical Deltech tube furnace equipped with a programmable Eurotherm controller. Mixtures of CO-CO<sub>2</sub> were used to control the  $fO_2$  of individual experiments, which were conducted using a synthetic oxide powder mixture modeled on the Sahara 99555 bulk composition. The series was performed across a range of  $fO_2$ , from  $\Delta IW-0.57$  to  $\Delta IW+2.88$ . EMPA and  $\mu$ -XANES were then conducted for all experiments. Spot analyses included points on both the silicate phases and surrounding quenched liquid.

**Results:** Experimental charges contain varying amounts of olvine, clinopyroxene, anorthite, and spinel (and Fe metal in the  $\Delta IW-0.57$  experiment). Olivine occurs as large (100-400  $\mu$ m in the maximum dimension) crystals, Fe-Mg zoned, skeletal phenocrysts as well as small un-zoned crystals that are intergrown with anorthite. Anorthite occurs with a tabular euhedral texture in all experiments. Spinel occurs as both euhedral Cr-rich inclusions in the clinopyroxene and anhedral Fe-Ti spinel with the anorthite and surrounding glass. Cpx occurs as large (100-300  $\mu$ m in the maximum dimension) euhedral crystals.

**Pyroxene Chemistry.** EMP data revealed compositional trends in non-quad components (e.g. Al, Ti). Notably, the Fe and Al content of clinopyroxene varies as functions of  $fO_2$ . Cpx crystallized at oxidizing conditions are notably more enriched in FeO<sub>total</sub> and have elevated  $Fe^{3+}/\Sigma Fe$  (calculated from charge balance) compared to those crystallized at reduced conditions. Cpx grown under oxidizing conditions also contain more Al in the tetrahedral site than those in the reduced experiment. We interpret this increase in tetrahedral Al and  $Fe^{3+}$  content as formation of an  $Fe^{3+}$ - $Al^{3+}$  charge couple (a ferri-tschermak component). A comparison of EMP data from pyroxenes in angrite meteorites such as Sahara 99555 and D'Orbigny with the observed Al-Fe relationship may provide useful constraints on the oxidation state of the meteorites.

**Plagioclase-Liquid Partitioning of Fe.** Plagioclase-liquid partition coefficients for Fe, calculated from EMP data, suggest that  $fO_2$  exerts influence on FeO<sub>total</sub> concentration of anorthite, where experimental anorthite grown at higher  $fO_2$  are slightly more enriched in FeO<sub>total</sub> than those grown at lower  $fO_2$ . To compare experimental anorthite with real angrites such as D'Orbigny, we utilized published D values for plagioclase and  $Fe^{3+}/\Sigma Fe$  predicted by Kress and Carmichael to model predicted FeO concentrations in plagioclase as a function of  $fO_2$  [4][5]. D'Orbigny's reported concentration of 0.5-0.8 wt% FeO most resembles the experiments produced from  $\Delta IW-0.57$  to  $\Delta IW+1.43$ , and we expect to see a similar relationship in other diabasic angrites [6].

**Future Work:** Additional experiments are currently in progress which will expand the investigated temperature conditions to span from the liquidus to near solidus. Additional experiments will also be conducted using a modified bulk composition that is more Mg-rich in order to crystallize zoned olivine that closely resembles those observed in angrites NWA 7812 and NWA 12774. These experiments will be analyzed via EMPA and incorporated into a larger synchrotron  $\mu$ -XANES study of Cr (olivine) and Fe valence (plagioclase, and cpx) in a suite of meteorites.

**References:** [1] Keil, K. (2012) *Chemie der Erde* 72:191-218. [2] Jurewicz, A. J. G. et al. (1993) *Geochimica et Cosmochimica Acta*, 57:2123-2139. [3] Steenstra, E.S. et al. (2017) *Geochimica et Cosmochimica Acta*, 212:62-83. [4] Lundgaard, K.L., and Tegner, C. (2004) *Contributions to Mineralogy and Petrology*, 147:470-483. [5] Kress, V.C. and Carmichael, I.S.E. (1991) *Contributions to Mineralogy and Petrology*, 108:82-92. [6] Mittlefehldt, D.W. et al. (2002) *Meteoritics & Planetary Science*, 37:345-369.