

EFFECTS OF f_{O_2} ON PYROXENE AND PLAGIOCLASE COMPOSITIONS IN ANGRITE CRYSTALLIZATION EXPERIMENTS. Lydia A. Pinkham¹, Aaron S. Bell¹, and Charles Shearer^{2,3}, ¹Dept. of Geological Sciences, University of Colorado Boulder, Boulder, CO 80309 (lydia.pinkham@colorado.edu), aaron.bell@colorado.edu), ²Institute of Meteoritics and Dept. of Earth and Planetary Science, University of New Mexico, Albuquerque, NM 87131, ³Lunar Planetary Institute, Houston, TX 77058 (cshearer@unm.edu).

Introduction: Angrites are a group of achondritic meteorites that represent some of the oldest basaltic rocks in the Solar System, with ages dated to as early as 4564.18 ± 0.14 Ma [1]. They are classified as silica under-saturated, are relatively enriched in refractory elements such as Ca and Ti, depleted in alkali elements such as Na and K, and vary in textures and modal mineralogy. While it is generally accepted that the angrites originated from a differentiated parent body, likely greater than 100 km in radius and containing a metallic core, there is no single accepted model for their petrogenesis. Partial melting experiments conducted by Jurewicz et al. [2] led these authors to propose an oxidized chondrite partial melting hypothesis. This model advocates a scenario in which low-degree partial melting of CV-like precursor material at oxidizing conditions ($\Delta IW+2$) resulted in silica undersaturated, CaO- and FeO-enriched, angritic liquids [2]. However, the oxidized conditions from this study are at odds with the findings of Steenstra et al. (2017), which concluded that the core of the angrite parent body (APB) formed under reducing conditions at (roughly $\Delta IW-1.4$) [3]. This discrepancy may indicate an evolving oxygen fugacity (f_{O_2}) throughout the course of angrite formation, or possibly stratified f_{O_2} reservoirs within the APB. This evolution is also evidenced by the presence of both Fe-Ni alloy and ulvöspinel enriched in Fe^{3+} , indicating both reducing and oxidizing conditions, respectively. Therefore, a key to understanding angrite origins lies in the role of understanding the oxidation state of the angritic magmas, and if that oxidation state varied during crystallization or differentiation. As f_{O_2} critically influences the valence of Fe and Cr in angritic melts and crystallization products, we performed a suite of redox controlled angrite crystallization experiments to investigate the Fe valence partitioning behavior in plagioclase, as well as Fe and Cr valence partitioning in clinopyroxene. These experiments specifically address how changes in f_{O_2} may be manifested in the equilibrium compositions of anorthite and clinopyroxene. The valence partitioning behavior of Cr and Fe and systemic variations in anorthite and clinopyroxene compositions (as a function of f_{O_2}) has the potential to provide useful insights into the f_{O_2} conditions experienced by volcanic angrites such as Sahara 99555 and D'Orbigny.

Methods: A suite of angrite crystallization experiments has been performed at the gas mixing laboratory at the University of New Mexico. The lab houses a vertical Deltech tube furnace equipped with a programmable Eurotherm controller. Mixtures of CO-CO₂ were employed to control f_{O_2} . All experiments were conducted using a single composition (a synthetic oxide powder mixture modeled on the Sahara 99555 bulk composition) and target temperature of 1115°C. The series was performed across a range of f_{O_2} , from $\Delta IW-0.57$ to $\Delta IW+2.88$. The samples were returned to the University of Colorado Boulder where they were examined using electron microprobe analysis (EMPA) with the JEOL 8230 Electron Microprobe. Phase assemblages were identified via energy dispersive analysis (EDS) and backscattered electron (BSE) images, and compositions of olivine, anorthite, pyroxene, and glass were measured via wavelength dispersive analysis (WDS).

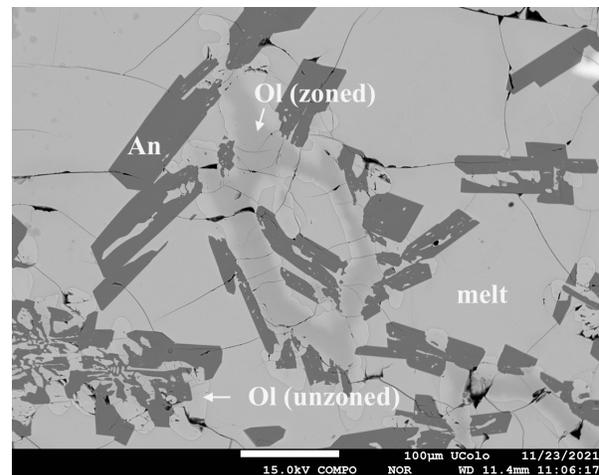


Figure 1 shows a BSE image of a synthesized angrite sample, containing phase assemblages of zoned skeletal and unzoned olivine, anorthite, and surrounding melt.

Results: The experimental charges all contain olivine, clinopyroxene, anorthite, and spinel. The olivine occurs as large Fe-Mg zoned skeletal phenocrysts as well as small un-zoned crystals that are intergrown with anorthite. Anorthite occurs with a tabular, euhedral texture (as shown in Figures 1 and 2), and frequently is intergrown with olivine. Spinel occurs as euhedral Cr-rich inclusions in the clinopyroxene but

also with an anhedral texture intergrown with the anorthite and surrounding melt (Figure 2). Three of the experiments contain exposed high-Ca clinopyroxene.

EMPA was conducted for all experiments. These spot analyses included points on both the silicate phases and surrounding quenched liquid.

Plagioclase-Liquid Partitioning of Fe. We calculated plagioclase-liquid partition coefficients for Fe from the experimental EMP data. These partitioning data suggest that fO_2 exerts an influence on the Fe total concentration of anorthite, where anorthite from higher fO_2 ($\Delta IW+2.38$ and $\Delta IW+2.88$) are slightly more enriched in total FeO than those produced under lower fO_2 . As plagioclase typically prefers Fe^{3+} over Fe^{2+} , this relationship was expected [4]. EMPA of plagioclase in D'Orbigny conducted by Mittlefehldt et al. [5] and Kurat et al. [6] reported 0.65-0.76 wt% FeO, which most closely resembles the compositions of plagioclase generated under intermediate fO_2 ($\Delta IW+0.44$ and $\Delta IW+1.43$).

Pyroxene Chemistry as a Function of fO_2 . EMP data revealed compositional trends in Fe partitioning and Al_2O_3 and Cr_2O_3 concentrations within high-Ca clinopyroxene which vary as a function of fO_2 . The clinopyroxene crystallized at oxidizing conditions are notably more enriched in FeO, ranging from 12.4-13.6 wt% FeO, compared to a range of 11.1-11.7 wt% FeO measured in clinopyroxene from reduced conditions. Charge balance calculations were also performed for each clinopyroxene grain comparing core and interface compositions. While the clinopyroxenes do not appear to be zoned, the experiment conducted in oxidized conditions ($\Delta IW+2.88$) indicates the presence of Fe^{3+} , while the experiment conducted in reduced conditions ($\Delta IW-0.57$) does not. The clinopyroxenes also contain more Al_2O_3 in the cores crystallized under more oxidized conditions, ranging from 7.2-9.5 wt% Al_2O_3 compared to just 6.1-7.1 wt% Al_2O_3 in the reduced experiments, likely due to the presence of Fe^{3+} and its displacement of Al^{3+} in the M1 site.

Crystal liquid partition coefficients for Cr in clinopyroxene also show a relationship with fO_2 . The experiment conducted under reduced conditions ($\Delta IW-0.57$) resulted in DCr values ranging from 7.3-15.3, while that under oxidized conditions ($\Delta IW+2.38$) resulted in DCr values ranging from 38.1-54.3. Clinopyroxene from the $\Delta IW+2.88$ experiment contained no measurable Cr_2O_3 (below EMP detection limit of approximately 170 ppm Cr_2O_3), therefore no DCr values were calculated. The $\Delta IW+2.88$ experiments also notably contain Cr-spinel inclusions in pyroxene. We interpret the low Cr concentration in the $\Delta IW+2.88$ experiment as a consequence of the appearance of a Cr-spinel on the liquidus before the

pyroxene. The crystallization of Cr-spinel before pyroxene may effectively sequester most of the Cr from the melt and produce Cr-depleted clinopyroxene. This differs from clinopyroxenes in D'Orbigny (which contain 0.27-0.54 wt% Cr_2O_3) [5]. This Cr depletion suggests that the angritic pyroxenes could not have crystallized in oxidizing conditions greater than approximately $\Delta IW+2.88$.

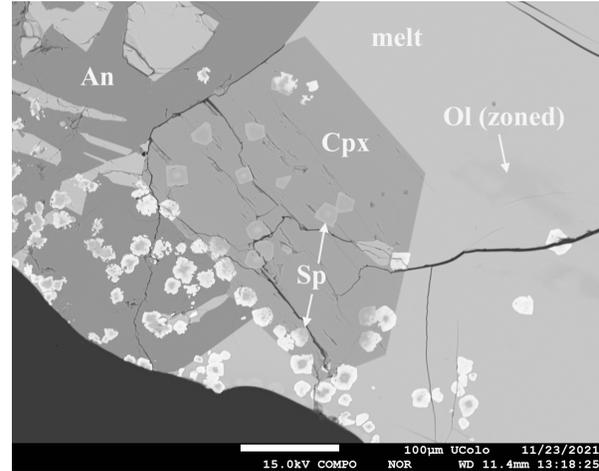


Figure 2 shows a BSE image of a synthesized angrite sample, containing phase assemblages of zoned olivine, anorthite, clinopyroxene, spinel, and surrounding melt. Spinel occurs as darker, euhedral Cr-rich inclusions in the clinopyroxene, but also as brighter, anhedral Fe-Ti spinel with the anorthite and melt.

Future Work: Continued investigations will consist of additional experiments in the gas mixing laboratory, to include series with a similar range of fO_2 but at both higher and lower temperatures, to represent crystallization conditions ranging from liquidus to near solidus. These experiments will be an integral part of a synchrotron μ -XANES study of Cr and Fe valence systematics at the Advanced Photon Source at Argonne National Laboratory to characterize Cr and Fe valence in the synthesized angrites and determine both $Fe^{3+}/\Sigma Fe$ and $Cr^{2+}/\Sigma Cr$, and subsequently compared to D'Orbigny and Sahara 99555 to constrain angrite magma fO_2 conditions and evolution.

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] Phinney, W.C. (1992) *Geochimica et Cosmochimica Acta*, 56, 1885-1895. [5] Mittlefehldt, D.W. et al. (2002) *Meteoritics & Planet. Sci.*, 37, 345-369. [6] Kurat, G., et al. (2004) *Geochimica et Cosmochimica Acta*, 68, 1901-1921.