**DO ANGRITE METEORITES RECORD PROCESSES FROM A DIFFERENTIATED PARENT BODY OR DUST-RICH REGIONS OF THE PROTO-PLANETARY DISC?** P. L. King<sup>1</sup> and R. W. Henley<sup>1</sup>, <sup>1</sup> Research School of Earth Sciences, The Australian National University, Canberra ACT 2601, Australia.

**Introduction:** In the first ~5 Ma of the Solar Sytem, the proto-solar nebula collapsed to a protoplanetary disc of gas and dust, and discrete planetary or asteroidal bodies began to form. These events are recorded by refractory calcium-aluminosilicate inclusions (CAIs), chondrules, iron meteorites, and some igneous achondrites – most notably the angrites [1].

The attributes of angrites were recently summarized by Keil [2]. Angrites have "magmatic" textures and glass indicating that they were partially or wholly melted prior to crystallization. They are alkali-depleted (very low Na, K, Li, Rb, Cs, Mn and Ga), but enriched in Ca and Ti relative to the average solar composition. Within the angrites, there are meteorites with finegrained  $\pm$  vesicular textures that cooled relatively quickly (e.g., D'Orbigny, Sahara 99555 and LEW 87051) and those with more coarse-grained/porphyritic  $\pm$  metamorphic -textured textures that are inferred to have a 'plutonic' origin (e.g., Angra dos Reis, Lewis Cliff 86010 and NWA 2999). The finer-grained angrites such as D'Orbigny are relatively pristine; lacking shock, brecciation, and parent-body weathering textures and preserve evidence of melting at 1000 -1100 °C.

In D'Orbigny [2, 3], four petrographic domains are proposed: (a) Ca-Al-Mg pyroxene, anorthite, and Mgrich olivine; (b) mesostasis with kirschsteinite (Caolivine), ilmenite, troilite, Ca- and/or silico-phosphates, rhönite, and other accessory phases including glass; (c) vesicles (<~2 vol. %) and cavities with protruding pyroxene and anorthite enclosing and coated in mesostasis, glass and Ca-(Mg)-carbonate; (d) glasses (~angrite composition) in vesicles, as inclusions and as beads; and (e) glass cross-cutting (a) and (b) domains. Domain (a) formed early because it is surrounded or cross-cut by all other domains; (b - d) have textural relations suggesting near-synchronous formation; and (e) formed after (a) and (b). Our analyses of the valence states of S and V [3] indicate that the earliest phases (a) formed at reduced conditions (0.7 log units below the ironwüstite buffer; IW-0.7  $\pm$  0.6 and CO/(CO+CO<sub>2</sub>)=~0.9) with slight oxidation to IW+0.5 recorded in protruding pyroxene (c) and the cross-cutting glasses (e) are more oxidized at IW+2.9  $\pm$  0.3 (CO/(CO+CO<sub>2</sub>)=~0.08).

Most workers subscribe to a model wherein angrites formed in a parent body of  $>\sim 100$  km radius. Melting is proposed to occur in either a magma ocean, via partial melting (with or without carbonate) on a differentiated planetary body, or through impact melting [review in 2]. Vesiculation may result from decompression and exsolution of a gas. However, these processes do not adequately explain the full complement of angrite geochemistry, petrography, and oxidation. Importantly, existing models do not fully account for disc processes occurring at the time of angrite formation. Studies of discs around YSOs show significant temporal and lateral variations in their physical properties and the distribution of solid and gas. YSO discs show a range of geometries and may have abrupt or smooth variations in density, heat and grain size (e.g., clumps of dust, gaps), and many show dynamic features (e.g., turbulence, shock fronts, spiral waves and gas/dust moving at different velocities).

Methods: We examine the hypothesis that all of these features of angrites can be explained by a model that better incorporates realistic physiochemical dynamics in the early Solar System disc. To test this idea, we undertook Gibbs Free Energy minimization calculations with a solar nebular composition [4; excluding Mn and Cr], stellar gases and early solar system minerals - i.e., those abundant in angrites, ironnickel metal, CAIs, presolar grains and salts. Pressure was fixed at 0.001 bars and a range of temperatures were examined. Our approach differs from many similar calculations because we include salts and gases like TiO that are found in young stellar objects (YSOs). Activity coefficients were assumed to be unity. Because the composition of many angrites glasses is similar to their bulk composition, we assume that the activity of components in the melt are equivalent to those in the sum of endmember minerals rather than explicitly modeling melt. We also made calculations with lower O to simulate a more reduced composition (i.e., higher  $CO/(CO + CO_2)$ ,  $H_2$  etc.).

**Results:** Select model results for the more oxidized bulk composition are shown in Figures 1 and 2. The calculations show that alkali-depletion in the angrites is consistent with partitioning of volatile elements like Na into a gas phase (Fig. 1), but also into soluble salts (NaCl and KCl) that may not be preserved in angrites delivered to Earth's surface because chlorides are highly soluble and/or lost during transit through the atmosphere. Ca is sequestered into anorthite and CAI components; although since the latter phases are not found in angrites they are likely components in the melt. At high temperatures, Ti is found in TiO(g) and CAIs, but is taken up by pyroxene/Ti-bearing oxides as the melt crystallizes. In both the oxidized and reduced models, the major angrite minerals (*a*) are most abundant at >1000 °C (Fig. 2); consistent with geothermometry. Kirschsteinite has generally decreasing stability from 1300-1400 °C in the oxidized model, whereas in the reduced model it is most abundant at 1200–1300 °C. The models indicate that abundant gas species co-exist with the solid phases over a range of temperatures, with H<sub>2</sub> dominating followed by CO, and either H<sub>2</sub>O (oxidized) or H<sub>2</sub>S (reduced).

**Discussion:** The most difficult aspects to explain in the D'Orbigny angrite – relevant to the angrite clan as a whole – are the cross-cutting glass, oxidation, and evidence for co-existing gas in a (partially) molten body. Below we examine scenarios for these processes in a differentiated body with a core versus a gas- and silicate-rich body in a dust clump in the disc.

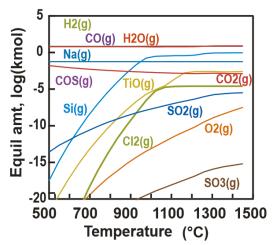
Formation of angrites in a differentiated planetary or asteroidal body. In this model, angrites form in the silicate- and gas-rich part of a differentiated body with an iron core. Cross-cutting glass and oxidation may be achieved through filter pressing, where gas (perhaps formed via exsolution) and melt moves through a preexisting crystal mush. Redox exchange between the gas and melt may result in oxidation. Impact into a partial molten or porous body may also produce these features without imparting shock or brecciation on the angrites.

Formation of angrites in the proto-polanetary disc. Angrites may form by (partially) melting a dust-rich region of a disc, in the presence of disc gases, without the requirement of a differentiated planet. In this scenario, iron separates from the silicates due to immiscibility and is concentrated elsewhere via 'smelting' [5]. Gases advect away from the solid-molten angrite parent 'clump' with faster cooling rates in the more permeable areas (e.g., the fine-grained angrites) relative to denser areas (e.g., the coarse-grained angrites). Gas removal or progressive gas reduction may occur over time as the disc evolves resulting in dust:gas gradients and pressure-temperature changes. Also, photochemical or photo-evaporation reactions, or gas shock would provide redox pairs to oxidize the angrites. The geochemical modeling supports reactions like:

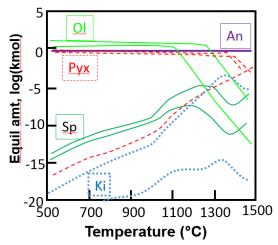
$$\label{eq:Fe2+} \begin{split} Fe^{2+}, &V^{3+ \ in \ melt} + (2H^+ \ dissolved \ in \ melt \ or \ in \ gases \\ like \ CH_4, \ H_2S \ or \ H_2O) = Fe^{3+}, \\ &V^{4+ \ in \ solid \ or \ melt} + H_2 \ gas \end{split}$$

and  $2\text{CO}_2^{\text{gas}} + \text{Ca}^{\text{in solid or melt}} = \text{CO}^{\text{gas}} + \text{Ca}\text{CO}_3^{\text{solid}}$ In a protoplanetary disc scenario, angrite compositions may be repeatedly produced in multiple parent 'clumps' that are likely small – allowing the body to avoid impact, brecciation and parent body weathering. This occurs in the inner disc where magnetic fields of ~ $10^{-2}$  Gauss (recorded in angrites) are found. Ongoing work aims to test the disc model in the context of other unique isotopic and geophysical features of the angrites.

**References:** [1] Amelin Y. and Ireland T. R. (2013) *Elements*, 9, 39–44. [2] Keil, K. (2012) *Chemie der Erde*, 72, 191–218. [3] King, P. L. et al. (2012) *LPSC*, 43, 2436. [4] Moynier, F. and Fegley Jr., B. (2015) Ch. 2 in *The Early Earth: Accretion and Differentiation* (eds J. Badro and M. Walter), John Wiley & Sons, Inc, doi: 10.1002/9781118860359.ch2 [6] Kirby, R. et al., (2016) *LPSC*, this conference.



**Figure 1:** Abundance of select calculated gas phases in a solar nebular composition (oxidized) as function of temperature.



**Figure 2:** Select solid phases observed in angrites, calculated for a solar nebular composition (oxidized). Ol – Mg and Fe olivine, An – anorthite, Pyx – clinopyroxene, Sp – spinel, Ki – kirschsteinite. In the cases of Ol, Ki and Sp phases, the more abundant phase is Mg-bearing and the less abundant is Fe-bearing. Pyroxene compositions are Ca-Mg, Ca-Fe and Ca-Al with decreasing abundance at 1100 °C.