

REDOX HISTORY OF EARLY SOLAR SYSTEM PLANETISIMALS RECORDED IN THE D'ORBIGNY ANGRITE. P. L. King^{1,2}, S. R. Sutton^{3,4}, M. N. Spilde¹, S. Wirick⁵, A. Lanzirotti⁴, and C.B. Agee¹, ¹Inst. Meteoritics, Univ. New Mexico, Albuquerque NM 87131, ²Res. School of Earth Sci., Aust. Nat. Univ., Acton ACT 0200, Australia, ³Dept. Geophys. Sci., Univ. Chicago, Chicago, Illinois 60637, ⁴Cen. Adv. Radiation Sources, Univ. Chicago, Chicago, Illinois 60637, ⁵Nat. Synchrotron Light Source, Brookhaven Nat. Lab., Upton NY 11973.

Introduction: Angrites are ancient basaltic meteorites (~4.56 Ga) that preserve evidence of some of the solar system's earliest melting events [e.g., 1]. The volcanic-textured angrites such as D'Orbigny were rapidly crystallized and are relatively pristine; lacking shock, brecciation, and parent-body weathering textures. Thus, these angrites provide a unique "window" into the petrogenesis of planetary bodies in the early solar system. Angrites may be formed by partial melting of CV chondrites under relatively oxidized sources compared to the eucrites [2], and therefore may document variations in fO_2 conditions on carbonaceous chondrite parent bodies. Thus, understanding the intrinsic fO_2 conditions of the angrites is needed to determine how different early Solar System basalts form, to model separation of the core, mantle and crust, and to understand magnetic fields on planetary bodies.

The D'Orbigny angrite contains a range of textures [3-5]: *a.* crystalline texture containing interlocking crystals of fassaite (pyroxene) with Ti-rich rims, anorthite, and Mg-olivine with Fe-rich rims (Fig. 1a); *b.* cavities with protruding needle-like pyroxene and anorthite dusted by Ca-(Mg)-carbonate (Fig. 1c); *c.* mesostasis with kirschsteinite, ilmenite, troilite, phosphates (e.g., merrillite, whitlockite and Ca-silicophosphate), rhönite and minor glass (Fig. 1b); *d.* glasses (~angrite composition) in vesicles, as inclusions and as beads [4], and also cross-cutting crystal-rich portions of the rock (Fig. 1d); *e.* vesicles (e.g., ~1.4 vol. %, 0.0219-87.7 mm³; [6]).

Analysis of the textures [5] and Fe^{3+}/Fe_{total} of the cavity pyroxene [7] suggests that the oxygen fugacity (fO_2) increased in the D'Orbigny angrite perhaps due to introduction of a gas phase [7]. Here we examine the detailed fO_2 history using micro-analyses that allow us to avoid inclusions that may cause spurious results. We present analyses of both S- and V- oxidation states to complement other work using Fe-oxidation state [7] and to avoid problems related to measuring low concentrations of Fe^{3+} and propagating errors when calculating fO_2 in samples with low Fe^{3+} concentrations.

Methods: We analyzed a sample acquired by the Institute of Meteoritics (IOM, ~66.5g) from E. Thompson, as well as thin sections from the IOM and the Southwest Meteorite Laboratory (K. and M. Killgore).

Electron microprobe – To determine S speciation in the glass, we modified the S K- α shift method [8], scanning with a 15kV, 10nA and 10 μ m diameter beam

over the S K- α peak using an LPET detector, a step size of 1.75×10^{-5} nm and dwell time of 1s. The sample was moved every 30s to limit electron bombardment and beam heating [e.g., 9]. Standards included jarosite, barite, troilite and pyrite, and troilite was analyzed before and after each glass. To determine calculated Fe^{3+} in rhönite, we used charge balance.

Synchrotron micro-XANES (*X-ray absorption near edge spectroscopy*) spectra for V valence state were collected of pyroxene and glasses. Measurements were made in fluorescence mode using X-ray microprobes at both Brookhaven National Laboratory X26A (~7 μ m beam diameter) and at the Advanced Photon Source GSECARS (~2 μ m beam diameter). To determine V-valence state we used the peak intensities of the pre-edge V peaks following [10]. For calibration, we used existing standards [10]. Spectra were edge-step normalized and fit by subtracting the background contribution from the main edge then fitting Lorentzian functions to individual pre-edge peaks.

Results: *Pyroxene in crystalline texture:* The pyroxene cores have an average V valence of 2.91 (12 spectra, $1\sigma = 0.09$) related to an average fO_2 at 1125 °C of an average fO_2 of IW-0.7 ($1\sigma = 0.6$). The pyroxene rims are slightly more oxidized with a V valence of 3.1 and fO_2 of IW+0.5 (2 spectra with considerable noise due to high Ti). The temperature uncertainty (1100 – 1150 °C) corresponds to an fO_2 uncertainty of ± 0.2 .

Pyroxene in cavities: We found that minerals in the cavities are commonly infilled with mesostasis and/or glass that extends into the cavity (Fig. 1c); these areas were avoided for micro-XANES analyses. Four spectra of cores of needle-like pyroxene from the cavities were measured at both BNL and APS. All eight spectra have average V valence of 2.91 ($1\sigma = 0.06$) producing an average fO_2 of IW-0.7 ($1\sigma = 0.4$).

Mesostasis: Some glass appears to be related to mesostasis and mesostasis appears to post-date the formation of the minerals in the cavities based on the infilling textures. The mesostasis is reported to host rare $FeNi_2$ [5] suggesting \leq IW conditions, but we have not yet observed this phase. In the absence of other oxybarometers, we used rhönite [$Ca_2(Fe^{2+}, Ti, Al)_6(Si, Al, Fe^{3+})_6O_{20}$] to calculate $Fe^{3+} < 0.17$ afu with an average of 0.06 ± 0.06 . The D'Orbigny rhönites contain slightly more Fe^{3+} than lunar rhönite [11] that have $Fe^{3+} = 0$, which is consistent with the D'Orbigny pyrox-

ene results indicating that it may be slightly more oxidizing than the Moon (IW-1 to IW-2).

Glasses: The V in the glasses (5 fragments, 20 spectra) has an average valence of 3.7 (standard deviation 0.06) corresponding to fO_2 (1200 °C) of -9.0 which is IW+2.9 (± 0.3 with temperature uncertainty of $\pm 50^\circ\text{C}$). The S in the glass has peak positions within error of troilite indicating that it is essentially all S^{2-} constraining fO_2 to $< \sim \text{QFM}$ [12] or $< \text{IW}+3.5$, which is consistent with the V data.

Discussion: Pyroxenes: The value of $\sim \text{IW}-0.7$ for the pyroxene cores in crystalline parts of D'Orbigny is essentially the same as the pyroxene in rims and the cavities (Fig. 2). IW-0.7 is slightly lower than fO_2 estimates for other angrites [IW to IW+1.2;13-15].

Cavity pyroxene: Our fO_2 value for the cavity pyroxene (IW-0.7) is lower than an estimate using a bulk sample with measured $\text{Fe}^{3+}/\text{Fe}_{\text{total}} = 9$ wt% to calculate an $fO_2 = \sim \text{IW}+3.7$ [7] although their 'modeled' $\text{Fe}^{3+}/\text{Fe}_{\text{total}} = 0$ wt% allowed much lower fO_2 . There are likely large errors in Mössbauer analysis at low Fe^{3+} contents and the model to convert $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ to calculated fO_2 is poorly calibrated at such reduced values.

Mesostasis: The calculated Fe^{3+} from the rhönite supports the low fO_2 from the pyroxene micro-XANES work. New studies are needed to measure the multivalent elements in rhönite produced at known fO_2 because inaccuracies in calculating Fe^{3+} are well known.

Glass: The micro-XANES results show that the glass is oxidized, in contrast to bulk Mössbauer analysis suggesting that no Fe^{3+} is present [16]. We suspect that the non-unique nature of fitting Mössbauer spectra in glasses contributes to error in the Mössbauer results. We further note that the fitting parameters used in [16] differ greatly from those used for basaltic glasses with a large range Fe^{3+} contents [17]. Thus, we conclude that the V results are robust, although further analyses will be conducted to confirm them.

The unusual nature of the glass contact and its near angrite bulk composition suggests that it was injected into the crystallized part of the (more reduced) crystalline angrite. Possible scenarios include impact into a partially molten parent body (leaving little record of impact in the remaining angrites) or filter-pressing from the parent body's interior to the near-surface. Thus, oxidation of the glass (based on the V data) relative to the crystalline rock may involve redox reactions that are not related to crystallization of the more reduced portions of D'Orbigny with fO_2 (IW-0.7) similar to other angrites. We are actively investigating the roles of gas, fluids and ice in oxidizing the glass with the discovery that the angrite glasses contain CO_2 -bearing fluid inclusions with possible SO_4^{2-} and NO_3^- species present (Fig. 1d). We hypothesize that loss of

H_2 from the angrite melt or removal of early solar system gases rich in H_2 , resulted in oxidation of the glass following:



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Acknowledgements: PLK gratefully acknowledges NASA Cosmochemistry grant NNX11AG65G and Whitney McCutcheon's help with sample preparation.

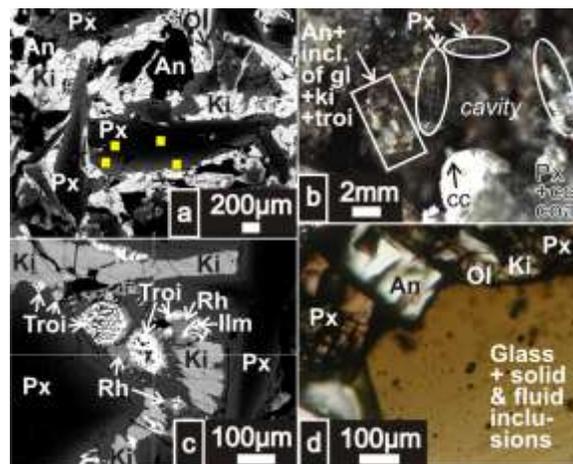


Fig. 1: Textures found in D'Orbigny. a) Crystalline texture with yellow micro-XANES analysis locations. Px=pyroxene, An=anorthite, Ki=kirschsteinite, Ol=olivine, Gl=glass, Troi=troilite, Rh=rhönite. b) Cavity texture with Cc=calcite. c) Mesostasis with Ilm=ilmenite. d) Cross-cutting glass.

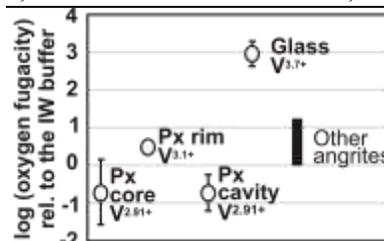


Fig. 2: $\log(fO_2)$ relative to the IW buffer for the phases measured in the D'Orbigny meteorite relative to the fO_2 for other angrites [13-15].