

RAPIDLY CHANGING OXYGEN FUGACITY IN THE EARLY SOLAR NEBULA RECORDED BY CAI RIMS. K. A. Dyl¹, J. I. Simon¹, S. S. Russell², and E. D. Young^{1,3}, ¹Department of Earth and Space Sciences, UCLA (kdyl@ess.ucla.edu, jis@ess.ucla.edu, eyoung@ess.ucla.edu), ²Department of Mineralogy, the Natural History Museum, London (sarr@nhm.ac.uk) ³Institute of Geophysics and Planetary Physics, UCLA,

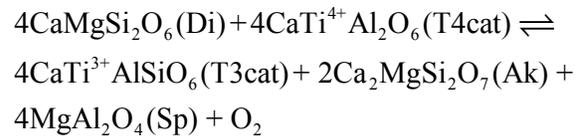
Introduction: Most rocky objects in the solar system formed at oxygen fugacities within several log units of the Iron-Wüstite (IW) f_{O_2} buffer. Calcium aluminum-rich inclusions (CAIs), on the other hand, apparently formed at f_{O_2} values ~ 6 to 7 log units lower just below those defined by a solar gas [1]. We present estimates of Ti^{3+}/Ti^{4+} in Al-Ti-rich diopsides showing that Wark-Lovering (WL) rims on CAIs record this shift from nearly solar f_{O_2} during initial CAI crystallization to “chondritic” f_{O_2} (\sim IW) during condensation that formed the rims. In combination with phase equilibria models for WL rim formation and new initial $^{26}Al/^{27}Al$ measurements for the rims, these results show that CAIs experienced a shift from \sim solar to \sim chondritic f_{O_2} in less than 300,000 years.

Sample: We performed electron microprobe analyses of Al-Ti-rich diopsides (fassaite) from the interior and WL rim of the compact type A CAI 144A from the Leoville CV3 meteorite in order to estimate the Ti^{3+}/Ti^{4+} in the fassaite. The sample was chosen because of its well-developed WL rim (Fig. 1). The present measurements compliment a number of other studies of this inclusion. Previous work showed that 144A is typical in its oxygen isotopic composition with most data points lying close to the CCAM line. Studies of its Mg isotope systematics show that it exhibits supra-canonical initial $^{26}Al/^{27}Al$ of at least 6×10^{-5} while its WL rim, together with points from WL rims from other CAIs, define an initial $^{26}Al/^{27}Al$ of 5.2×10^{-5} . We interpret these data to indicate that the rims formed within 300,000 years of the core.

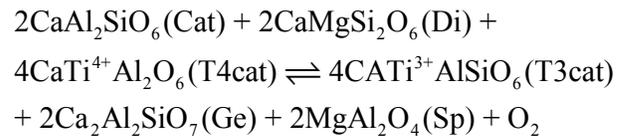
Origins of WL rim: The most likely origin for the WL rims on 144A and other CAIs is high-temperature condensation with partial pressures of Mg and SiO exceeding those attending original CAI formation. This is because: 1) $\delta^{25}Mg$ values for WL rims are chondritic or lower in all CAIs analyzed thus far while values for interiors of igneous CAIs are enriched in $\delta^{25}Mg$; and 2) monomineralic banding is a hallmark of large chemical potential gradients and these gradients would result from large increases in ambient P_{SiO} and P_{Mg} .

Titanium oxidation state as an oxybarometer: Previous studies have shown that estimates of Ti^{3+}/Ti^{4+} in Al-Ti-rich diopside (fassaite, fs) can serve as an oxygen barometer in CAIs [2, 3]. For fs in the interior

of the CAI we relied upon the two equilibria calibrated by Beckett and Grossman [3]. The first is

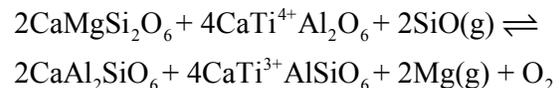


referred to as reaction (A) in [3]. The second, referred to as reaction (B) in [3], is



In both reactions Di, Cat, T4cat and T3cat refer to the indicated components in pyroxene, Ak and Ge to components in melilite, and so forth. Reactions (A) and (B) are appropriate for the CAI interiors where melilite is abundant.

In the WL rims melilite is scarce to absent. Here we used a reaction between pyroxene and gas:



The exchange character of this reaction, call it reaction (C), minimizes the influences of systematic uncertainties in the free energies of formation between the pyroxene Ti and Ti-free components. We assumed $P_{SiO} = P_{Mg}$ (a reasonable first approximation if evaporated dust was chondritic/solar) to arrive at the expression

$$\log f_{O_2} = \log f_{O_2}^{\circ} + 4\Delta\log \left(\frac{a_{T4cat}^{PX}}{a_{T3cat}^{PX}} \right) + 2\Delta\log \left(\frac{a_{Di}^{PX}}{a_{Cat}^{PX}} \right)$$

where $\log f_{O_2}^{\circ}$ refers to some initial condition (i.e., interiors). In Leoville 144A the ratio of Di to Cat activities changed little from interiors to WL rims, causing the last term to be negligible. This last

equation permits contouring of f_{O_2} -temperature space for Ti^{3+}/Ti^{4+} in fassaite even in the absence of melilite.

All three equilibria shown above were evaluated using ideal mixing-on-sites activity models. In evaluating reactions (A) and (B) we used a fixed mole fraction of Ak in melilite of 0.2 as indicated by electron microprobe analyses of melilites in the margin of 144A. The results are robust relative to changes in Ak content.

Analytical details: Electron microprobe analyses were performed on 16 Ti-rich pyroxene spots in the WL rim of Leoville 144A. Titanium maps were used to identify local regions of pyroxene with Ti above detection limits. Spot size was on the order of several μm . Rim fassaite varied between 2 and 7% TiO_2 (total Ti as TiO_2) by weight, with relative uncertainties ranging from 1.2-2.5%. Twenty three analyses were obtained for 3 different fassaite inclusions located in the interior. Interior fs contained 17-19% TiO_2 with uncertainties of $\sim 0.7\%$. The Ti^{3+} contents were obtained using cation norms assuming no vacancies.

Results: Interior fassaite has average calculated Ti^{3+}/Ti^{4+} of 1.57 ± 0.14 1σ . Fassaite pyroxenes in the WL rim have a much lower average Ti^{3+}/Ti^{4+} of 0.05 ± 0.16 1σ with most points exhibiting no detectable cation deficiencies on the basis of total $Ti = Ti^{4+}$. These results signify a large shift in f_{O_2} between CAI formation and WL rim deposition.

Figure 2 shows the calculated f_{O_2} for average interior (reaction A and B) and WL rims (reaction C). Also shown are contours for the log of the activity ratio of T4cat to T3cat in 0.4 log unit intervals (red). The interior oxygen fugacity is several log units below solar while the WL rim value ($\log(aTi^{4+}/aTi^{3+}) = 1.7 \pm 0.4$) is about 1 log unit below the IW buffer curve.

Discussion: The moderately sub-solar f_{O_2} for the CAI interior is consistent with previous work [1]. The high f_{O_2} for the WL rim is, as far as we are aware, a new result. The coincidence between WL rims and many chondrite and bulk rocky planet f_{O_2} values suggests that condensation of WL rims may have taken place in a region enriched in chondritic dust. Support for this conclusion comes in the form of new Mg isotope ratio data showing that WL rims have $\delta^{25}Mg$ values virtually indistinguishable from carbonaceous and ordinary chondrite chondrules and matrix [4]. It appears that the WL rims formed from a reservoir of Mg isotopically identical to chondrules and matrix.

Conclusion: The simple explanation for these data is that WL rims are condensates formed when CAIs passed from low pressures of a solar-like gas into regions of chondritic dust enrichment. Both the lack of Mg isotope fractionation and the high f_{O_2} are explained

in this scenario. The initial $^{26}Al/^{27}Al$ of 5.2×10^{-5} for the rims [4] places temporal constraints on this movement from one reservoir to another if the initial for the solar system was uniform; the transition took no more than about 300,000 years if supra-canonical initial $^{26}Al/^{27}Al$ apply and less time if supra-canonical values do not apply. We suggest that such rapid transitions occurred during the same sorts of shock wave encounters invoked to explain chondrule formation.

References: [1] Krot A. N., *et al.* (2000) Protostars and Planets IV, 1019-1054. [2] Stolper E. M., *et al.* (1982) LPSC XIII, 772-773. [3] Beckett J. R. and Grossman L. (1986) LPSC XVII: 36-37. [4] Simon J.I. *et al.* (2005) LPSC XXXVI.

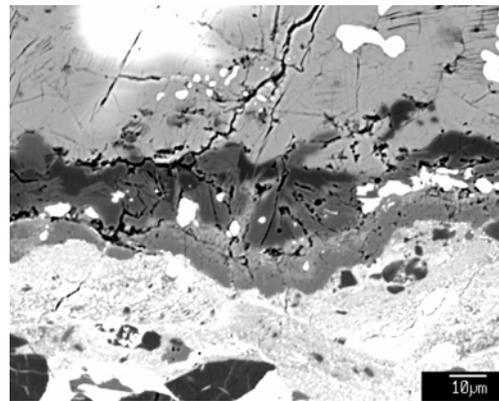


Figure 1. Back scattered electron image of the WL rim on Leoville 144A. Progression from top: interior mel; spinel+hibonite; +/- mel; Al-rich diopside; matrix.

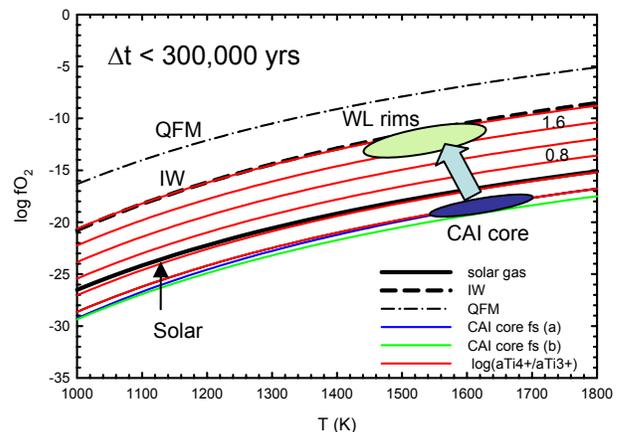


Figure 2. $\log f_{O_2}$ vs. temperature (T) plot showing CAI interior (blue ellipse, green and blue curves), the WL rim (pale green ellipse), solar gas and buffer curves. Red lines are contours of $\log(aTi^{4+}/aTi^{3+})$ activity ratios in pyroxene from equilibrium C.