

**REASSESSING TITANIUM VALENCE STATE IN THE WARK-LOVERING RIM OF A LEOVILLE CAI: FURTHER EVIDENCE FOR AN OXIDIZING NEBULAR ENVIRONMENT FOR WARK-LOVERING RIM FORMATION.** K. A. Dyl<sup>1</sup>, E. D. Young<sup>1,2</sup>, and J.A. Simon<sup>3</sup>. <sup>1</sup>Department of Earth and Space Sciences, UCLA, Los Angeles, CA 90095 ([kdyl@ucla.edu](mailto:kdyl@ucla.edu), [eyoung@ess.ucla.edu](mailto:eyoung@ess.ucla.edu)), <sup>2</sup>Institute of Geophysics and Planetary Physics, UCLA, Los Angeles, CA 90095, <sup>3</sup>BGC Berkeley Geochronology Center, Berkeley, CA 904709.

**Introduction:** In 2005 J. Simon et al. reported low  $Ti^{3+}/Ti^{4+}$  values in Al-Ti pyroxenes in the Wark-Lovering rim (WL) of Leoville 144A as compared to the interior of the inclusion [1,2]. These electron microprobe analyses were interpreted as evidence for lower oxygen fugacity during rim formation. Low  $Ti^{3+}$  abundances, Mg isotopic compositions, and activity-activity diagrams depicting rim growth in a nebular chemical environment all consistently support a time-evolution of CAIs towards higher  $f(O_2)$ , or higher [O]. The growth of the Wark-Lovering rim was determined to be the manifestation of this evolution to a more oxidizing environment.

Further work by S. Simon et al. called into question the electron microprobe estimates of  $Ti^{3+}/Ti^{4+}$  in the rim of Leoville 144A [3]. They used XANES analyses to argue for higher  $Ti^{3+}$  abundances and interpreted the data of J. Simon et al. [1] as the result of x-ray contamination by neighboring phases. Specifically, the higher Al content and Ca <1.00 pfu were used as evidence for spinel mixing in the analyses. Alteration was also included as a possible explanation for spurious results.

To investigate these claims, we re-analyzed Leoville 144A to obtain a more complete data set of  $Ti^{3+}/Ti^{4+}$  values in the Wark-Lovering rims. Furthermore, we conducted experiments on spinel-mixing to determine whether this was a plausible explanation for our data. While we found a wider range of  $Ti^{3+}/Ti^{4+}$  in these WL rims than before, we find that the original conclusion that rims are lower in  $Ti^{3+}/Ti^{4+}$  than interiors is valid. We conclusively rule out spinel mixing as an explanation for our data. We maintain that the WL rim pyroxenes are compositionally distinct from those in the interior, and are evidence of a more oxidizing environment during WL rim formation.

**Methods:** Two sets of experiments were run on the compact type A CAI Leoville 144A. To quantify the effects of spinel-fassaite mixing, eight traverses were run from spinel into fassaite in the interior of the object. Starting at a spinel-fassaite interface, we obtained an analysis every 0.5  $\mu m$  along a line perpendicular to the phase boundary. The electron beam activation spot size is on the order of 2  $\mu m$  as determined from our traverses.

Five additional analyses were run on fassaite present in the WL Rim. The weight percent  $TiO_2$  ranged

from 5-8%; this is within the range of the more Ti-rich fassaite previously analyzed. Data reduction techniques were previously described [1,2]. The Ca pfu of these pyroxenes ranged from 0.93-0.96. These ratios are consistent with previous analyses.

**Results:** The spinel-fassaite traverses illustrate that phase contamination is only a concern at distances less than 1.5  $\mu m$  from the phase boundary. The traverses, the theoretical spinel-fassaite mixing line, CAI interior fassaite analyses, and WL rim analyses were all plotted in terms of multiple elements. S. Simon et al. [3] used Ca-Al space to argue for phase contamination, showing that the WL rim pyroxenes plotted along the theoretical mixing line. If correct, fassaite-spinel mixing should be evident in all relevant composition spaces.

Figure 1 illustrates that this is not the case. While the theoretical mixing line and representative traverse show the same trend in Mg-Si space (different initial composition, but same slope of mixing), the WL rim pyroxenes behave in a wholly different manner. Analogous plots for other elements give similar deviations of the CAI rim data from fassaite-spinel mixing trends.

Our new electron microprobe study of Leoville 144A show more spots with greater  $Ti^{3+}/Ti^{4+}$  than found in our original study. However, it is important to emphasize that these data are still distinctly different from the interior pyroxenes. The distinction between rim and interior for this CAI is clear in a probability density plot of all collected data as shown in Figure 2.

**Discussion:** The results of this experiment eliminate the plausibility of spinel contamination as an explanation for our low  $Ti^{3+}/Ti^{4+}$  rim data. The traverses illustrate that spinel must be <1.5  $\mu m$  away to impact the pyroxene analyses. Since the nearest spinel is 8-9  $\mu m$  away from our analyses, we can conclusively determine there are no effects from this phase. In some cases, melilite and perovskite are nearby phases, but both of these would increase rather than decrease Ca pfu. Contamination from Al-diopside would have a negligible effect, and would only manifest itself as a lower Ti abundance. S. Simon et al. [3] refer to the possibility of unseen olivine contamination to explain the presence of Fe; we observe no evidence for proximal olivine.

Figure 1 illustrates that the addition of spinel results in a projection with a negative slope in Mg-Si

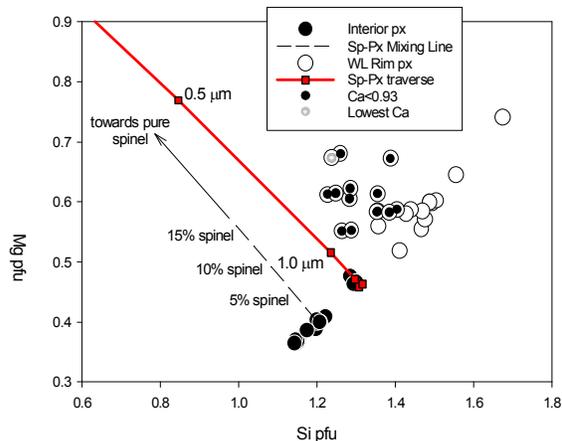
space (spinel increases Mg cations while decreasing Si). Analyses with  $\text{Ca} > 0.93$  pfu show no evidence of mixing with spinel, and in fact have increases in both Mg and Si. For  $\text{Ca} < 0.93$  pfu, similar to some rim pyroxenes, at much as 15% spinel contamination is required to explain their compositions. A much more plausible explanation for these elemental trends is crystallographic closure effects. Less Ca present results in augmented Si and Al cation totals in order to have 4 cations per 6 oxygen.

The comparison between our amended data set, the XANES data reported in [3], and the interior fassaite (interior fassaite  $\text{Ti}^{3+}/\text{Ti}^{4+}$  are not in dispute) reveals that there is a distinct difference between WL rim and interior pyroxenes using electron microprobe estimates and/or XANES. The differences that remain between the XANES results and the electron microprobe results for the rim can be attributed to the greater sampling volume of the former relative to the latter. Our additional data extends the original range of  $\text{Ti}^{3+}/\text{Ti}^{4+}$  because in the latest round of analyses, we searched for the most interior-like spots in the rim (i.e., highest Ti concentrations). The goal was to search for interior-like values. We do not yet claim to have a volumetrically representative data set for the rims.

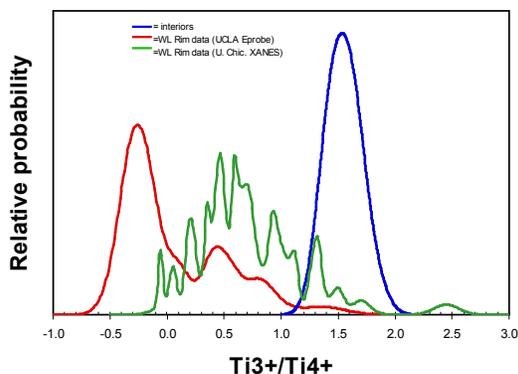
Alteration was offered as an alternative explanation for our data. We cannot eliminate this as a possibility; however, we have not found a plausible, balanced alteration reaction that would change the oxidation state of Ti and change the chemistry of the pyroxenes in the manner observed.

**Conclusion:** We reject contamination by spinel as an explanation for  $< 1.00$  Ca pfu in WL rim fassaite, as well as for the lower  $\text{Ti}^{3+}/\text{Ti}^{4+}$  in the rims. Mixing from other nearby phases is also ruled out. We maintain these analyses are of pure WL rim pyroxene. The pyroxene  $\text{Ti}^{3+}/\text{Ti}^{4+}$  in the Wark-Lovering rim of Leoville 144A still supports a more oxidizing environment for this feature of the CAI. We see no clear inconsistency between our electron microprobe data and the XANES data.

**References:** [1] J. Simon et al. (2005) *EPSL*, 238, 3-4, 272-284. [2] K. Dyl et al. *LPS XXXVII* Abstract #2060. [3] S. Simon et al. (2007) *GCA*, 71, 12, 3098-3118.



**Figure 1:** Mg-Si space for CAI pyroxenes and spinel-pyroxene mixtures. Theoretical addition of spinel (dashed black line) and the spinel-pyroxene traverse (red solid line) behave in the same manner. WL pyroxenes (various open circles) exhibit an entirely different trend.



**Figure 2:** Probability-density plot of  $\text{Ti}^{3+}/\text{Ti}^{4+}$  values in Leoville 144A. The blue peak corresponds to the interior fassaite, the red data are all UCLA electron microprobe data of the WL rim fassaite, and the green data represent XANES analyses of WL rim fassaite [3]. Note the overlap in rim data obtained by the two different methods.