

MEASUREMENT OF $\text{Ti}^{3+}/\text{Ti}^{4+}$ RATIOS IN PYROXENE IN WARK-LOVERING RIMS: EVIDENCE FOR FORMATION IN A REDUCING SOLAR NEBULA. S. B. Simon¹, S. R. Sutton^{1,2} and L. Grossman^{1,3}. ¹Dept. Geophysical Sci., 5734 S. Ellis Ave.; ²Consortium for Advanced Radiation Sources; ³Enrico Fermi Institute, 5640 S. Ellis Ave., The University of Chicago, Chicago, IL 60637, USA (sbs8@midway.uchicago.edu).

Introduction: Ti-bearing clinopyroxene, known as fassaite, is a major phase in the interiors of coarse-grained, Ca-, Al-rich refractory inclusions (CAIs). Electron microprobe (EMP) analyses of such pyroxene yield low cation sums when normalized to six oxygen anions if it is assumed that all Ti is present as Ti^{4+} . Instead, we can assume that there is one Ca cation [1] and two tetrahedral cations present per six oxygens, and can then calculate a $\text{Ti}^{3+}/(\text{Ti}^{3+} + \text{Ti}^{4+})$, or $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$, ratio that gives exactly one cation in the remaining site and a total of exactly four cations per six oxygens. Additional evidence for the presence of Ti in multiple valence states includes: pleochroism in Ti-rich crystals with negligible amounts of other multivalent elements; results from measurements of optical spectra [2]; and X-ray absorption near-edge structure (XANES) analysis [3]. Calculation of accurate $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ ratios from EMP analyses is generally limited to analyses with >4 wt% $\text{TiO}_2^{\text{tot}}$ (all Ti as TiO_2), because at low Ti contents the analytical uncertainties approach the magnitude of the cation deficit caused by assuming all Ti is Ti^{4+} .

Many refractory inclusions are enclosed in sequences of mineralogically distinct layers, first described by [4], that must have formed after the host inclusions did. In most cases, from the CAI outward, the sequence consists of a layer of spinel±perovskite; voids, melilite, or alteration products; clinopyroxene; and hedenbergite. The pyroxene layer may be immediately adjacent to spinel and is commonly zoned from Ti-rich fassaite nearest the spinel layer to Ti-poor aluminous diopside over distances of ~ 10 μm [4]. A recent study of the pyroxene in the rims of one Allende and two Leoville inclusions [5] found that most points analyzed by electron probe had between 4 and 7 wt% $\text{TiO}_2^{\text{tot}}$ and 0.7-1.7 wt% FeO. Those authors also found < 1 Ca cation, but very close to 4 total cations, per 6 oxygen ions, and therefore little or no Ti^{3+} . They kindly loaned us one of their samples for analysis, and we also found low Ca contents, high FeO contents (~ 1 wt%) and undetectable to low Ti^{3+} contents compared to fassaite found in the interiors of CAIs. The low-Ca analyses would seem to reflect the presence of an enstatite component in addition to the standard fassaite components [1], but despite inclusion of such a component in our calculations we have not been able to satisfactorily resolve the analyses into pyroxene endmembers. This is a hint that pyroxene analysis spots are contaminated with another phase, a serious problem for stoichiometry-dependent calculation of $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ ratios. We need to know whether or not rim pyroxene contains Ti^{3+} because of its importance as a recorder of nebular

oxygen fugacity, but we are unsure of how to normalize EMP analyses in this case, so we cannot calculate $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ accurately. We therefore decided to measure the $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ of rim pyroxene directly, by XANES.

We have conducted a detailed study of pyroxene in the rim on TS24, a fluffy Type A inclusion from Allende. This inclusion is large and very irregularly shaped, giving it a relatively high surface area. It has a well-developed rim sequence, from the CAI outward, of spinel, clinopyroxene zoned from Ti-, Al-rich to nearly pure diopside over ~ 20 μm , and hedenbergite. The spinel-pyroxene and diopside-hedenbergite contacts are sharp.

Analytical methods: Suitable locations for study were documented optically and by scanning electron microscopy. Mineral compositions were determined by electron microprobe along 8 traverses across the rim in several locations, with ~ 1 μm between analysis points. $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ values were calculated by stoichiometry from the EMP analyses. Titanium K XANES spectra were collected in fluorescence mode (Ti $\text{K}\alpha$) using the GSECARS x-ray microprobe (Argonne Nat. Lab.) with a 3 μm X-ray beam along two of these traverses. The spatial registry between XANES and EMP analysis spots was estimated to be better than ~ 10 μm . Relative Ti abundances were determined from the Ti K fluorescence intensities. Valence determinations were made from the ratios of the intensities of pre-edge peaks at 4969 and 4971 eV, the intensity of the latter being most sensitive to valence variations [6], compared to spectra for endmember pyroxene standards: Ti^{3+} (synthetic $\text{NaTi}^{3+}\text{Si}_2\text{O}_6$ isostructural with acmite [7]) and Ti^{4+} (natural acmite, Norway). The validity of this calibration has been demonstrated in work on CAI fassaite crystals where good Ti valence agreement was found between EMP and XANES analyses [3].

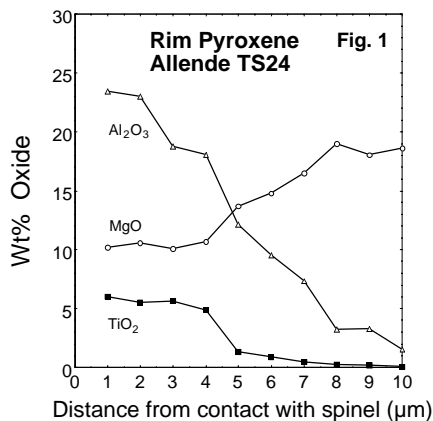
Results. Data from a representative electron probe traverse across the pyroxene rim layer of TS24 are illustrated in Fig. 1. Note the sharp decreases in $\text{TiO}_2^{\text{tot}}$ and Al_2O_3 with distance from the CAI. In most traverses the $\text{TiO}_2^{\text{tot}}$ contents drop below 4 wt% within 6 μm of the contact with spinel. We found that V_2O_5 contents also decrease with distance from spinel. Fig. 2 shows the $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ ratios calculated for the EMP analyses plotted in Fig. 1. The first four points all have ≥ 5 wt% $\text{TiO}_2^{\text{tot}}$. The first two points appear to contain no Ti^{3+} whether or not the analyses are normalized to one Ca per 6 oxygen. These two analysis points also have low Ca contents relative to pyroxene farther from the spinel layer, as shown in Fig. 3. They therefore have several features in

common with data of [5]. The next two points have $Ti^{3+}/Ti^{tot} \sim 0.5$ and nearly 1.00 Ca per 6 oxygens. The calculated values then become meaningless as TiO_2 drops to ~ 1 wt% and less (Fig. 1).

The XANES data (Fig. 4) tell quite a different story. The measured Ti^{3+}/Ti^{tot} ratios are uniform regardless of Ti content, and average 0.49 ± 0.09 (2σ). No evidence of Ti-rich pyroxene with low Ti^{3+}/Ti^{tot} was found; the XANES data do, however, agree with the Ti^{3+}/Ti^{tot} ratios calculated for the third and fourth points in the EMP traverse. In the other XANES traverse, Ti^{3+}/Ti^{tot} decreases slightly, from 0.58 ± 0.03 nearest spinel to 0.45 ± 0.18 furthest away. The traverse mean is 0.56 ± 0.07 . The analyses thus show that Ti^{3+}/Ti^{tot} is fairly constant across the pyroxene layer, neither increasing nor decreasing strongly with distance or Ti abundance, at values well within the range of pyroxenes in inclusion interiors [1, 3, 5].

Discussion. The results indicate that there is a fundamental problem with many of the EMP analyses used for the determination of Ti^{3+}/Ti^{tot} ratios in rims. We believe it is likely that many analyses of Ti-rich rim pyroxene reflect minor contributions from the adjacent spinel layer. A 5% spinel component would decrease the Ca cations by that amount (~ 0.05 per 6 ox) while increasing the cation total, decreasing the apparent Ti^{3+}/Ti^{tot} relative to a “pure”, Ti^{3+} -bearing analysis. It would also explain the difficulty in resolving the analyses into pyroxene components.

The work of [5] reached the conclusions that a) rims are $1-3 \times 10^5$ yr younger than their host inclusions; b) the pyroxene in the rims does not contain Ti^{3+} ; and c) the oxygen fugacity of the solar nebula therefore increased by five orders of magnitude within the time scale of rim formation. In contrast, we find uniform Ti^{3+}/Ti^{tot} values across a rim at levels within the range typical of fassaite in CAI interiors. The present results are strong evidence for formation of rims at an oxygen fugacity very close to that of a solar gas, and they argue against large-scale changes in nebular oxygen fugacity either during rim formation or in the time between formation of refractory inclusions and their rims.



References: [1] Beckett J. (1986) Ph. D. dissert. Univ. Chicago. [2] Dowty E. and Clark J. (1973) *Am. Min.* 58, 230. [3] Simon S. et al. (2005) *Wkshp. Oxygen Earliest Solar System*, 35. [4] Wark D. and Lovering J. (1977) *PLSC 8th*, 95. [5] Simon J. et al. (2005) *EPSL* 238, 272. [6] Waychunas G. (1987) *Am. Min.* 72, 89-101. [7] Prewitt C. et al. (1972) *Contrib. Min. Pet.* 35, 77-82.

