

Comment

Comment on “Valence state of titanium in the Wark–Lovering rim of a Leoville CAI as a record of progressive oxidation in the early Solar Nebula” by K.A. Dyl, J.I. Simon and E.D. Young

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Abstract

Dyl et al. (2011) state that their results confirm the conclusion of J. Simon et al. (2005) that the pyroxene in Wark–Lovering rims (Wark and Lovering, 1977) found on Ca-, Al-rich refractory inclusions has lower $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ ratios than the primary pyroxene in the interiors of inclusions. While true, the claim is misleading because J. Simon et al. (2005) concluded that there was no Ti^{3+} in the rims, whereas Dyl et al. (2011) found Ti^{3+} in 41 of 42 new rim analyses. In addition, J. Simon et al. (2005) concluded that rims formed under much more oxidizing conditions, $\log f\text{O}_2 \geq \text{IW}-1$, or $\geq 6-7$ log units higher, than inclusion interiors. The conclusions of J. Simon et al. (2005) were disputed by S. Simon et al. (2007) and are not supported by the new data of Dyl et al. (2011). The present work is intended for clarification of this and other issues.

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1. INTRODUCTION

The oxygen fugacity ($f\text{O}_2$) of a gas of solar composition is so low, ~ 6.8 log units below the iron–wüstite buffer ($\log f\text{O}_2 = \text{IW}-6.8$), that trivalent Ti can occur in phases that have equilibrated with it. This makes the Ti-bearing pyroxene found in CAIs and in their rims important recorders of the $f\text{O}_2$ of their formation. The $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratios of pyroxene in Types A and B refractory inclusions have been shown experimentally to be consistent with formation in a gas at least as reducing as a solar gas (Grossman et al., 2008). There has been some controversy, however, about the $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratios of pyroxene in the rims on CAIs, termed Wark–Lovering rims (Wark and Lovering, 1977). J. Simon et al. (2005) analyzed pyroxene in the rim of Leoville inclusion L144A by electron probe, concluded that it had no detectable Ti^{3+} , and assigned a lower limit to its $\log f\text{O}_2$ of formation of $\text{IW}-1$. S. Simon et al. (2007)

analyzed the same rim by X-ray absorption near edge structure (XANES) spectroscopy, and found an average $\text{Ti}^{3+}/(\text{Ti}^{3+} + \text{Ti}^{4+})$ ratio, henceforth $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$, of 0.41 ± 0.14 . From this significant proportion of Ti^{3+} , and from the observation of rim pyroxenes with $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ and $\text{V}^{2+}/\text{V}^{\text{tot}}$ ratios typical of interior pyroxenes, S. Simon et al. (2007) concluded that the rims could have formed under reducing conditions, possibly in a solar gas. S. Simon et al. (2007) also pointed out a possible analytical problem with some of the J. Simon et al. (2005) data.

Dyl et al. (2011) have revisited the situation. They collected additional electron microprobe analyses of rim pyroxene, not with the goal of determining who is correct, but “to verify our previous assertion that WL rim Ti^{3+} values were distinct and lower than those found in CAI interiors.” While the new Dyl et al. (2011) results do show that rim pyroxene tends to have lower Ti^{3+} proportions than are found in interior pyroxene, their measurements are actually similar to those of S. Simon et al. (2007) and do not support the conclusion of J. Simon et al. (2005) that rim pyroxenes have no Ti^{3+} .

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2. DISCUSSION

2.1. Data analysis

In electron probe analyses, if the cations present in a Ti^{3+} -bearing pyroxene are calculated assuming all the Ti is $4+$, too much oxygen is assigned to Ti and a low cation total results upon normalization to a fixed number of oxygen anions. The $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ ratios of such analyses can be calculated from electron probe data by normalizing them to exactly four cations per six oxygens. This is best done for analyses with ≥ 4 wt.% Ti as TiO_2 , because at lower Ti contents poor counting statistics cause the error on Ti to become too large for a reliable calculation (S. Simon et al., 1991). In contrast, the XANES technique does not require assumptions about stoichiometry, and its use is not restricted to Ti-rich phases. It yields a direct measure of Ti valence from the systematic variation of pre-edge peak energy and intensity with Ti valence and coordination (Waychunas, 1987; Farges et al., 1997).

Of the 26 electron probe analyses of L144A rim pyroxene used in J. Simon et al. (2005), 22 have ≥ 4 wt.% Ti as TiO_2 . Of the latter, 15 have >4 cations per six oxygen anions and thus negative calculated Ti^{3+} . The authors attributed the high cation sums to analytical error and stated that those analyses were within their analytical uncertainty (of four total cations). The remaining seven analyses have an average $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ value of 0.31 ± 0.15 . This is within error of the average of the L144A measurements by XANES of 0.41 ± 0.14 (S. Simon et al., 2007). In the interpretation of their results, however, J. Simon et al. (2005) included the Ti^{3+} contents of *all* of their measurements, treating the fictive (i. e., not real), negative Ti^{3+} components as actual values. This yielded an average of -0.03 ± 0.02 cations per six oxygens, leading to the erroneous conclusion that pyroxene in the rim of the inclusion they analyzed did not contain Ti^{3+} .

Alternatively, S. Simon et al. (2007) interpreted the Ti^{3+} -bearing analyses of J. Simon et al. as valid and the Ti^{3+} -free analyses as possibly contaminated by adjacent spinel, a phase with a higher cation/oxygen ratio than pyroxene. S. Simon et al. showed (their Fig. 14) that the data of J. Simon et al. with >4 cations per six oxygens plot on pyroxene-spinel mixing lines, with a positive correlation between Al and total cations and a negative correlation between Ca and total cations. The analyses with <4 cations per six oxygens do not show this relationship. If variations in Al and Ca were due to different proportions of pyroxene components, their abundances would not vary with total cations. Systematic relationships, like those seen for Al and Ca, are not expected for variations due to random analytical error. Note that (a) S. Simon et al. (2007) did not, as implied by Dyl et al. (2011), suggest that all of the J. Simon et al. (2005) data were affected; and (b) Dyl et al. (2011) found that the data (J. Simon et al., >4 cations per six oxygens) do not fall on pyroxene-spinel mixing lines for all components, but did not account for either the trends noted by S. Simon et al. (2007) or the occurrence of high cation totals of many of the analyses in J. Simon et al. (2005). Perhaps there are

multiple contaminants and multiple pyroxene starting compositions, obscuring the mixing relationships.

2.2. $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ ratios of interior and rim pyroxenes

In stark contrast with the results of J. Simon et al. (2005), all five new electron probe analyses of the L144A rim and 36 of 37 measurements of the rim on Efremovka inclusion Ef3 by Dyl et al. (2011) contain Ti^{3+} , yet Dyl et al. still claim that the previous results are supported. This claim is true only to the extent that $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ ratios of rim pyroxene are generally slightly lower than those of interior pyroxene, but not to the extent that Ti^{3+} is absent from the rims, nor that the rims formed at $f\text{O}_2 \geq 6$ –7 log units higher than did the host CAIs, nor perhaps that the rims formed at higher $f\text{O}_2$ s at all.

In describing their data set, Dyl et al. (2011) state that “we see no clear inconsistency between our electron microprobe data and the XANES data”. We therefore assume that the XANES data (S. Simon et al., 2007) are representative of the rim pyroxene analyses considered by Dyl et al. (2011), and the XANES data will be used here for comparison with interior pyroxene found in coarse-grained refractory inclusions. This is illustrated in Fig. 1, a histogram of $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ ratios in rim (XANES) and interior (electron probe) pyroxene. The data show much overlap, with the bulk of the rim analyses at lower values, ~ 0.3 – 0.6 , than that for the interior analyses, 0.45 – 0.7 . The average $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ ratio of the rim pyroxene is 0.41 ± 0.14 , and that of the interior pyroxene is 0.54 ± 0.15 .

The $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ ratios of pyroxene in inclusion interiors can be used to deduce the $f\text{O}_2$ at which they crystallized. For this purpose, however, it is not the mean ratio of pyroxene in an inclusion that is used. As seen in Grossman et al. (2008), the $f\text{O}_2$ is obtained not only from the $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ ratios of specific pyroxene grains but also from the activities of components in specific grains of other phases that can be inferred to be cogenetic with the selected pyroxene grains. In contrast to our understanding of CAI formation, the mode and temperature of formation of Wark–Lovering rims are obscure. The structures of the rim layers and complex textures within them (Zega et al., 2010) make it unclear as to which, if any, crystalline phases formed in equilibrium with the pyroxene grains of interest. This problem can be avoided by using equilibrium reaction [5] of J. Simon et al. (2005), which relates the activities of only the four pyroxene components, $f\text{O}_2$ and the $P_{\text{SiO}}/P_{\text{Mg}}$ ratio in a coexisting fluid of unknown origin. This procedure is more uncertain than that for interior pyroxenes, where compositions of all phases participating in the equilibrium are measured, and activities can be deduced because the equilibration temperature is known. J. Simon et al. (2005) used their measurements of the pyroxene composition to estimate an $f\text{O}_2$ by assuming a temperature of rim formation, assuming ideal mixing of pyroxene components, and assuming the $P_{\text{SiO}}/P_{\text{Mg}}$ ratio. If the temperature of rim formation were known, precise measurements of pyroxene composition could be converted to activities of pyroxene components and used to obtain $f\text{O}_2$ from this equilibrium reaction, but only by estimating the

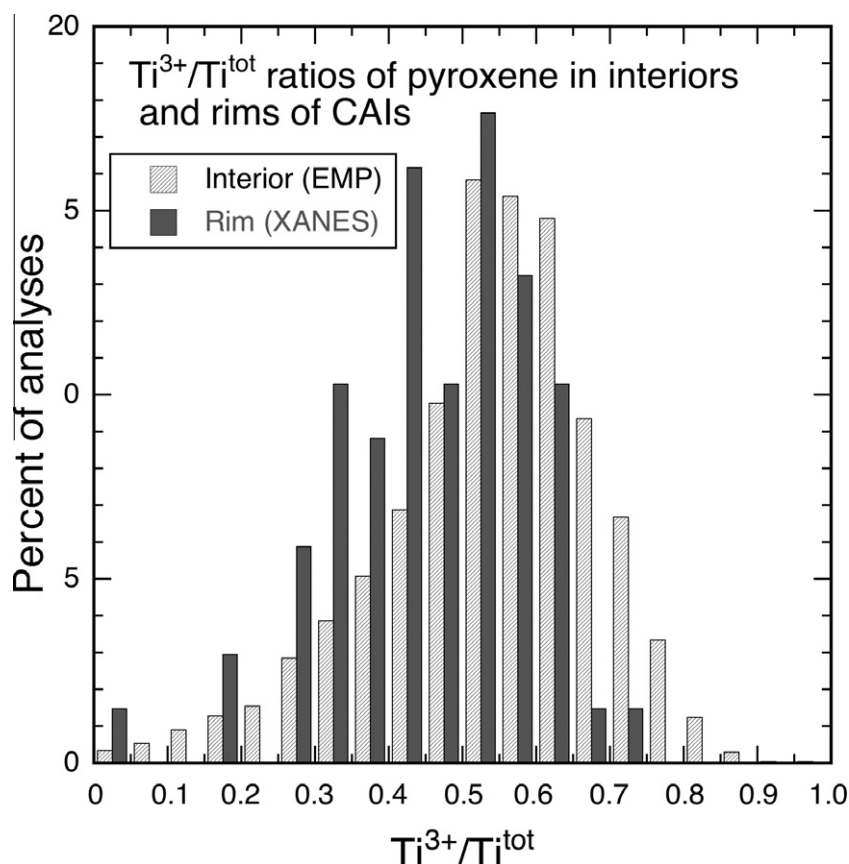


Fig. 1. Histogram of $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ ratios in 68 XANES analyses of rim pyroxene from two inclusions and in 2665 electron probe (EMP) analyses of Ti-pyroxene in the interiors of one Type A ($n = 96$) and six Type B ($n = 2569$) refractory inclusions. Both interior and rim analyses are divided into and plotted within bins that are 0.05 wide. The rim data are from S. Simon et al. (2007), and the interior data are from S. Simon and Grossman (2006) and S. Simon et al. (2008).

$\text{P}_{\text{SiO}}/\text{P}_{\text{Mg}}$ ratio. Alternatively, a normal $f\text{O}_2$ could be assumed and a value obtained for the $\text{P}_{\text{SiO}}/\text{P}_{\text{Mg}}$ ratio of the fluid phase. Until the temperature of rim formation and compositions of cogenetic phases are determined, it is premature to conclude that the slightly lower $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ ratios of Wark–Lovering rim pyroxenes imply that they formed at higher $f\text{O}_2$'s than pyroxene in inclusion interiors.

2.3. Effects of secondary alteration

For evidence that the rim on L144A experienced more oxidizing conditions than expected for a gas of solar composition, one need look no further than the FeO-bearing alteration products intimately intergrown with the very rim pyroxene grains analyzed by XANES and electron probe. Apparently these contribute several wt.% (up to 6%) FeO to electron probe analyses of L144A rim pyroxene. S. Simon et al. (2007) found that MgO is not anticorrelated with FeO in their data, suggesting that the presence of FeO is not due to the substitution of Fe for Mg in the pyroxene. S. Simon et al. (2007) used these observations to suggest that modification of $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ ratios in rim pyroxene during secondary alteration by oxidizing fluids could not be ruled out. These observations were downplayed by Dyl et al. (2011),

however, who cited the example of pyroxene with high $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ ratios that persist in inclusions in the Murchison CM2 chondrite (S. Simon et al., 2009), despite evidence of extensive alteration of this meteorite by aqueous fluids. Electron probe analyses of that pyroxene, however, yield FeO contents that are factors of 20–30 lower than found in pyroxene in the rim of L144A, implying, if anything, less intimate exposure of the Murchison pyroxene to oxidizing conditions.

3. CONCLUSIONS

In summary, we agree with Dyl et al. (2011) that rim pyroxene tends to have lower $\text{Ti}^{3+}/\text{Ti}^{\text{tot}}$ ratios than pyroxene in the interiors of coarse-grained refractory inclusions. The conclusions of J. Simon et al. (2005), that Ti^{3+} is absent from rim pyroxene and that this pyroxene formed at $f\text{O}_2$ s 6–7 log units higher than the interior pyroxene did, are supported by neither our work nor that of Dyl et al. (2011). Although one might intuitively conclude that the rims formed at slightly higher $f\text{O}_2$ s than the host inclusions, the conditions of rim formation have yet to be established, and it is possible that the rims formed from a gas of solar composition.

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