THE VALENCE OF TITANIUM IN REFRACTORY FORSTERITE. S. B. Simon[1], S. R. Sutton[1,2] and L. Grossman[3]. [1]Dept. Geophysical Sci., 5734 S. Ellis Ave.; [2]Consortium for Advanced Radiation Sources; [3]Enrico Fermi Institute, 5640 S. Ellis Ave., The University of Chicago, Chicago, IL 60637, USA (sbs8@midway.uchicago.edu).

Introduction: One of the more intriguing components of unequilibrated chondrites is the population of relatively Ca-, Al-rich, Fe-poor isolated olivine grains known as "refractory forsterite" [1, 2, 3]. Some workers [e.g. 4, 5] have concluded that these grains formed in and were released from chondrules. Other workers [6], noting that these grains occur in all major types of unequilibrated chondrites yet have many features in common, favor a single, pre-chondrule source from which the grains were distributed into their present hosts. Thought by some [e.g. 1, 2, 7] to be condensates, refractory forsterite (RF) grains have been found in chondrules, but their high CaO contents and trends of decreasing CaO contents from core to rim are inconsistent with closed-system fractional crystallization, so those grains must be relict.

Previous workers [8] calculated the compositions of melts parental to RF from the minor and trace element contents of RF grains and known olivine/liquid partition coefficients. Results indicated that melts in equilibrium with RF would have been uniformly enriched in refractory lithophile elements by ~20×CI, as is observed in many refractory inclusions [9]. Two exceptions are V, for which enrichments <20×CI were derived, and Ti, for which enrichments of 50-65×CI were obtained. For V, the depletion was attributed to its enhanced volatility under reducing conditions. The inferred Ti content is higher than observed in refractory inclusions. This rather unreasonable result was obtained using the olivine/liquid partition coefficient for Ti^{4+} (D_{Ti4+}). A higher D for Ti would allow lower Ti contents in parental melts, and [8] noted that the larger ionic radius of Ti^{3+} relative to that of Ti^{4+} could yield a D_{Ti3+} that is a factor of ~50 greater than D_{Ti4+}.

The presence of significant proportions of Ti^{3+} in RF would provide important evidence of reducing conditions where the grains formed, support the model of [8] and rule out formation in typical, FeO-bearing chondrules. To test the prediction of [8], we have used X-ray absorption near-edge structure (XANES) analysis to determine the valence of Ti in two RF grains from the Tagish Lake carbonaceous chondrite.

Analytical methods: Grains were recovered from Tagish Lake by freeze-thaw disaggregation followed by density separation and hand-picking. Grains were mounted in epoxy, polished and analyzed by electron probe. Titanium K XANES spectra were collected using the GSECARS X-ray microprobe in fluorescence mode, with a 3 μm X-ray beam. Valences were determined following the results of [10]. That study demonstrated that Ti K-edge XANES spectra of Ti^{4+}-bearing minerals fall into distinct valence-coordination clusters on a plot of pre-edge peak intensity vs. energy. Those with tetrahedral coordination have high intensities and low energies whereas those with octahedral coordination have low intensities and high energies. Ti^{3+} in olivine is expected to be in octahedral coordination and have low intensity and low energy.

Samples: Two coarse olivine grains were selected for study. TL2-24 is a subhedral single crystal ~100 × 200μm. TL2-13 is anhedral and ~150 × 150 μm. It partially encloses a subhedral, 25 × 30 μm grain of Mg-Al spinel, a common inclusion in RF. The spinel has ~0.8 wt% Cr_2O_3 and 0.2-0.5 wt% FeO. Electron probe traverses show that both forsterite grains have cores that are enriched in Al_2O_3 and CaO relative to their rims. In 2-13 the core has 0.71-0.77 wt% CaO, 0.14-0.25 wt% Al_2O_3, and 0.02-0.08 wt% TiO_2, decreasing to 0.22, 0.07, and <0.01, respectively, at the edge of the grain. Grain 2-24 has 0.52-0.62 wt% CaO, 0.28-0.35 wt% Al_2O_3, and 0.03-0.07 wt% TiO_2 in the core, and 0.19, 0.05, and <0.01 wt% CaO, Al_2O_3 and TiO_2, respectively, at the rim. These values and trends are typical of RF [8, 12] and are not consistent with closed-system fractional crystallization, as these elements are not compatible in olivine.

Reference materials with known Ti^{3+}/Ti^{4+} ratios were also analyzed - endmember Ti^{3+}: synthetic $NaTi^{3+}Si_2O_6$, isostructural with acmite [11]; endmember Ti^{4+}: two synthetic forsterites produced in air (Ito and Allied), natural acmite, natural titanite, San Carlos olivine, and olivine from lunar basalt 15555; and with $Ti^{3+}/(Ti^{3+} + Ti^{4+}) = 0.6$: Allende fassaite [13].

XANES Results: As illustrated in Fig. 1, the intensity and position of the Ti K pre-edge peak vary with both valence and coordination of the Ti cations in a manner analogous to that observed by [10]. For Ti^{4+} in tetrahedral coordination, the peak is intense and at relatively low energy (synthetic forsterites, San Carlos olivine, and lunar olivine); for Ti^{4+} in an octahedral site, the peak is less intense and at higher energy (terrestrial titanite and acmite). The octahedral Ti^{3+} standard has low intensity and low energy as predicted. Similarly, both Tagish Lake samples have pre-edge peaks that are much less intense than those of the samples with tetrahedral Ti^{4+}, and at lower energies than

octahedral Ti^{4+} standards. Sample 2-24 plots within analytical uncertainty (1σ) of the octahedral Ti^{3+} standard, and 2-13 plots between that standard and the octahedral Ti^{4+} standard, near a measurement of Allende fassaite, indicating a mixed Ti^{3+}/Ti^{4+} state. A linear interpolation between the octahedral Ti^{3+} and Ti^{4+} standards indicates that the valence of 2-13 is consistent with 60% Ti^{3+}, the proportion inferred by [8]. Our calculations show that with this proportion of Ti^{3+}, D_{Ti3+} need be only ~4×D_{Ti4+} to yield a parental melt with a Ti content of 20×CI. These results indicate that a significant proportion of the Ti in both Tagish Lake samples is trivalent. The difference in the pre-edge peaks of the two Tagish Lake samples either reflects slightly different oxidation states, or possibly effects of different orientations of the crystals relative to the polarized X-ray beam. The latter will be investigated in future work.

Discussion: The measurements imply that the RF we analyzed formed under reducing conditions. The relationship between Ti^{3+}/Ti^{4+} ratios in olivine and oxygen fugacity has not been quantified, but similar Ti^{3+}/Ti^{4+} ratios in fassaite in Allende CAIs are consistent with equilibration with a solar gas [14]. If the Tagish Lake grains are representative of RF found in other meteorites, then, as suggested by [8], a significant proportion of the Ti in RF is trivalent and the argument for equilibration with parental melts enriched in refractory lithophiles by ~20×CI is strengthened. RF could have formed from condensate parental melts [6], such as the CMAS liquids which could have been stable at 10^{-3} atm and a dust/gas enrichment factor as low as 16 [15]. Glass inclusions in RF may also be condensates [2] but they would require higher pressures (0.3 atm) or dust/gas enrichments of ~70 [15], the latter implying non-solar f_{O2}s. The (solidified) sources of RF may have resembled forsterite-bearing refractory inclusions. The olivine in those inclusions is very CaO-rich [16] and would be likely to contain Ti^{3+}. In future work we plan to measure the Ti valence in olivine from a forsterite-bearing refractory inclusion.

The grains we analyzed came from a disaggregated meteorite sample. It is likely they were present as isolated grains, but we cannot be certain. In additional future work, we will determine Ti valence in RF found *in situ* in chondrules. If such grains contain Ti^{3+}, that would strengthen the link between isolated RF and those in chondrules, and would support the suggestion [6, 8] of a common, pre-chondrule history for RF.

References: [1] Grossman L. and Olsen E. (1974) *GCA, 38,* 173-187. [2] Olsen E. and Grossman L. (1978) *EPSL, 41,* 111-127. [3] Steele I. M. (1986) *GCA, 50,* 1379–1396. [4] McSween H. Y. Jr. (1977) *GCA, 41,* 411–418. [5] Jones R. (1992) *GCA, 56,* 467-482. [6] Pack A. et al. (2004) *GCA, 68,* 1135-1157. [7] Weinbruch S. et al. (2000) *Meteoritics & Planet. Sci., 35,* 161-171. [8] Pack A. et al. (2005) *GCA, 69,* 3159-3182. [9] Grossman L. (1980) *Ann. Rev. EPS, 8,* 559-608. [10] Farges F. et al. (1997) *Phys. Rev. B, 56,* 1809-1819. [11] Prewitt C. (1972) *Contrib. Min. Pet., 35,* 77-82. [12] Steele I. (1989) *GCA, 53,* 2069-2079. [13] Simon S. et al. (2007) *GCA,* submitted. [14] Grossman L. et al. (2007) *RIMG,* in press. [15] Yoneda S. and Grossman L. (1995) *GCA, 59,* 3413-3444. [16] Clayton R. et al. (1984) *GCA, 48,* 535-548.

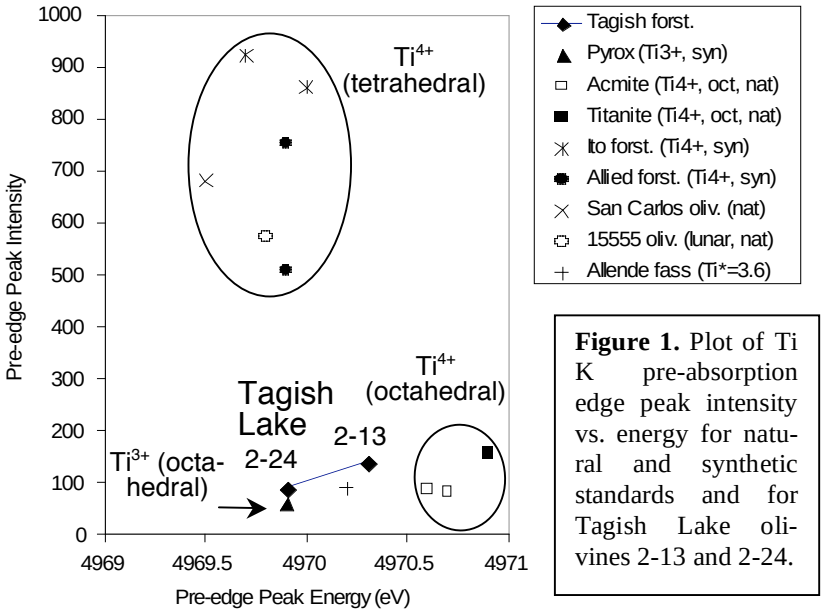

Figure 1. Plot of Ti K pre-absorption edge peak intensity vs. energy for natural and synthetic standards and for Tagish Lake olivines 2-13 and 2-24.