

FIRST Ti-XANES ANALYSES OF REFRACTORY INCLUSIONS FROM MURCHISON. S. B. Simon¹, S. R. Sutton¹ and L. Grossman^{1,2}, ¹Dept. of the Geophysical Sci., 5734 S. Ellis Ave., Univ. of Chicago, Chicago, IL 60637 (sbs8@uchicago.edu) ²The Enrico Fermi Institute, 5640 S. Ellis Ave., Univ. of Chicago, Chicago, IL 60637.

Introduction: A system of solar composition is so reducing that Ti^{3+} and Ti^{4+} can coexist, making the valence of Ti a valuable indicator of f_{O_2} conditions during formation of nebular materials. The Ti^{3+}/Ti^{4+} ratios observed in the Ti-rich phases fassaite and rhönite in coarse-grained refractory inclusions from CV3 chondrites have been shown [1,2] to be quantitatively consistent with formation in a gas of solar composition ($\log f_{O_2}=IW-6.8$), but these are the only objects in chondrites for which this is the case. Here, we report the valence of Ti in various phases in refractory inclusions from the Murchison CM2 chondrite.

The second-highest temperature, major-element-bearing phase predicted to condense from a gas of solar composition, hibonite (ideally $CaAl_{12}O_{19}$), can contain significant amounts of Ti, but the hibonite structure can have oxygen vacancies, so calculation of Ti valence from stoichiometry of electron probe analyses is not recommended for hibonite [3]. To date, the only reported measurement of Ti valence in meteoritic hibonite was done by electron spin resonance [3], on coarse crystals from a Murchison hibonite-perovskite-melilite inclusion [4]. Spinel and most of the pyroxene in CM inclusions contain too little Ti for derivation of Ti^{3+}/Ti^{4+} ratios from electron probe analyses.

X-ray absorption near edge spectroscopy (XANES), however, allows determination of Ti valence in relatively Ti-poor phases. In the present work, we apply synchrotron microXANES to a large hibonite grain from Murchison and to spinel-hibonite (sp-hib) and spinel-pyroxene (sp-pyx) inclusions from Murchison, refractory materials whose Ti^{3+}/Ti^{4+} ratios have not been previously measured. Analysis of these samples allows comparison of Ti valence of 1) pyroxene in sp-pyx inclusions with that of fassaite; 2) spinel in hibonite-bearing with that of hibonite-free inclusions; and 3) hibonite in sp-hib inclusions with that of large, single grains and the previously analyzed sample [3].

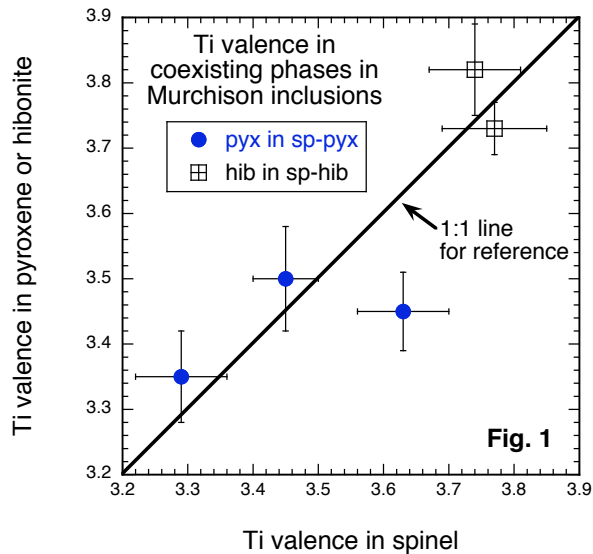
Analytical methods: Samples were documented with a scanning electron microscope and analyzed by electron probe. Ti K XANES spectra were collected using the GSECARS X-ray microprobe (fluorescence mode, 3 μm X-ray beam). Ti K-edge XANES spectra of pure Ti^{4+} -bearing minerals fall into three, distinct valence-coordination clusters on a plot of pre-edge peak intensity vs. energy [5]. Ti_{tet}^{4+} has high intensity and low energy, Ti_{oct}^{4+} has low intensity and high energy, and Ti^{4+} in five-fold coordination is intermediate to these two. Ti^{3+} is expected to be predominantly in

octahedral coordination in pyx and sp, yielding a fourth data cluster at relatively low intensity and low energy [6]. The relative amounts of Ti in different valence states were obtained by applying the lever rule to the " $Ti_{tet}^{4+} - Ti_{oct}^{4+} - Ti^{3+}$ " mixing triangle whose apices were determined from measurements of standards representing these three valence-coordination number end-members. Valences determined for hibonite in this way may be overestimated (i.e. Ti^{3+} underestimated) by up to 0.1 because in this phase Ti^{3+} mainly occupies a five-coordinated site [3].

Sample Details: We analyzed six typical samples from Murchison [e.g. 7-9], all ~150 – 200 μm across, recovered by freeze-thaw disaggregation: two spinel-hibonite (M98L4, M98L5) and three spinel-pyroxene (M98L1, M98L10, M98L12) inclusions and a coarse (250 x 65 μm) hibonite grain (M98L6) with fine perovskite inclusions. M98L4, shown in Fig. 1h of [9], also contains fine perovskite blebs, and melilite. M98L5 has relatively coarse perovskite (~15 μm) and trace melilite. Hibonite TiO_2 contents average 5.9 wt% in M98L4, 5.2 wt% in M98L5, and 2.2 wt% in M98L6.

M98L1 and M98L12 are spherule fragments with spinel-rich cores and diopside rims. The interior of M98L1 has trace amounts of perovskite and pyroxene but the interior of M98L12 has a significant pyroxene content. In M98L10, pyroxene fills a large embayment in spinel; this sample is likely a fragment of an OC, a convoluted sp-pyx inclusion [7].

Results: The hibonite, pyroxene and spinel all contain Ti^{3+} ; perovskite does not. Results are summarized in Table 1 and in Fig. 1, which shows a good correlation of average Ti valence in spinel with that of coexisting pyroxene or hibonite. Four of the five samples, including both sp-hib inclusions, plot within 1σ uncertainty of the 1:1 correlation line; only M98L1 does not. The sp-hib inclusions have higher average valences (lower Ti^{3+}/Ti^{4+} ratios) than the sp-pyx inclusions and the large, single hibonite grain, whose average valence is 3.43 ± 0.16 (not plotted). Traverses across hibonite in M98L5, spinel in M98L12, and pyroxene rims in M98L1 and M98L12 show uniform valence, except for the two outermost analyses of the M98L12 rim, which are slightly more oxidized than the inner analyses (~3.60 vs. 3.45). This traverse is plotted in Fig. 2, which otherwise illustrates the minor degree of variability typically seen in the traverses. There is no discontinuity in valence across the spinel-pyroxene contact in this traverse.



Discussion: The pyroxene in the present inclusions, unlike fassaite in coarse-grained CAIs from CV3 chondrites, has very low Ti, Sc and V contents, indicating formation from a different source, yet it has Ti^{3+}/Ti^{4+} ratios within the range of fassaite. If the f_{O_2} - Ti^{3+}/Ti^{4+} relationship for the pyroxene compositions in these sp-pyx assemblages is similar to that derived for fassaite [1], then this is consistent with formation in a solar nebular environment.

Spinel occurring with pyroxene has higher Ti^{3+}/Ti^{4+} ratios than that occurring with hibonite (Fig. 1) and the coarse, single grain of hibonite has a higher Ti^{3+}/Ti^{4+} ratio than hibonite occurring with spinel. The wide ranges of Ti^{3+}/Ti^{4+} ratios seen in the latter phases suggest that, unlike perovskite, in which virtually all Ti is Ti^{4+} , neither spinel nor hibonite have a strong preference for Ti^{3+} or Ti^{4+} . The similarity of valences of spinel and either coexisting hibonite or coexisting pyroxene (in two of three inclusions) also indicates that these phases do not strongly fractionate Ti^{3+} from Ti^{4+} during formation; otherwise, displacements from the 1:1 line should be observed for coexisting phases. In spinel, pyroxene and hibonite, the Ti^{3+}/Ti^{4+} ratio is therefore most likely largely determined by the f_{O_2} of the formation environment. The Ti^{3+}/Ti^{4+} ratios in these assemblages are not calibrated with respect to f_{O_2} , but it seems likely that sp-hib inclusions formed at higher f_{O_2} s than sp-pyx inclusions or the coarse, isolated grains of hibonite found in CMs.

The (pyroxene) rim of M98L1, however, is more reduced than the (spinel) interior, suggesting that the rim may have formed at a lower f_{O_2} than the spinel. In the sp-pyx inclusions in which the coexisting phases have equal valence (M98L10 and M98L12), spinel and pyroxene are intergrown in the interiors, whereas the interior of M98L1 is nearly pyroxene-free. The textures and XANES results are consistent with formation

of the intergrown spinel and pyroxene in M98L10 and M98L12 in the same event, under similar redox conditions. The M98L1 rim probably formed under different conditions than the interior and was deposited upon it.

In the sample analyzed by [3], 15-28% of the Ti is trivalent. This corresponds to an average Ti valence of 3.85-3.72, indistinguishable from our results for hibonite-bearing inclusions and contrasting with our result for coarse hibonite M98L6. Compared to large, single hibonite crystals, hibonite-bearing inclusions have lower Ti^{3+}/Ti^{4+} ratios, finer grain sizes and, in general, much greater excesses of ^{26}Mg [8]. The difference in Ti valence supports previous suggestions [8,10] based on differences in grain size, composition and initial $^{26}Al/^{27}Al$ ratio that there were multiple hibonite-formation events that recorded varying physico-chemical conditions in the early solar nebula.

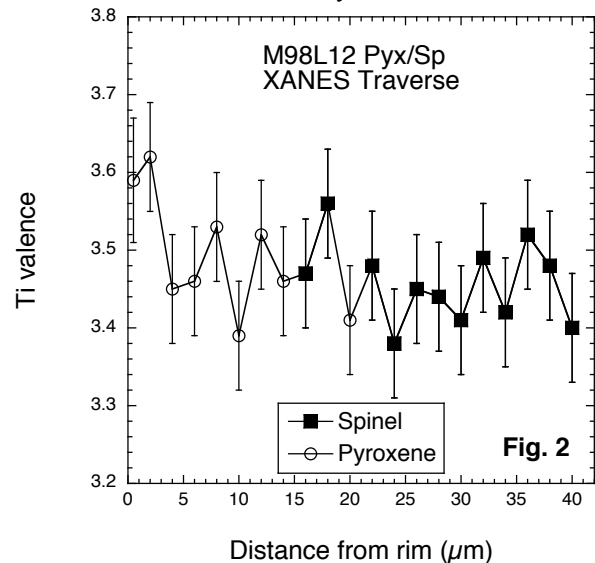


Table 1. Ti valence by XANES. Sp: spinel; Px: pyroxene; Hb: hibonite; Pv: perovskite; Mel: melilite.

Sample	Mineral.	Spinel	Pyroxene	Hibonite
M98L1	Sp-Pv-Px	3.63±0.07	3.45±0.06	-
M98L4	Hb-Sp-Pv-Mel	3.74±0.07	-	3.82±0.07
M98L5	Hb-Sp-Pv	3.77±0.08	-	3.73±0.04
M98L6	Hibonite	-	-	3.43±0.16
M98L10	Sp-Px	3.35±0.07	3.27±0.07	-
M98L12	Sp-Px	3.45±0.05	3.50±0.08	-

References: [1] Grossman L. et al. (2008) *RiMG*, 68, 93-140. [2] Beckett J. et al. (1986) *Meteoritics*, 21, 332-333. [3] Beckett J. et al. (1988) *GCA*, 52, 1479-1495. [4] Hashimoto A. et al. (1986) *LPS XVII*, 317-318. [5] Farges F. et al. (1997) *Phys. Rev. B*, 56, 1809-1819. [6] Simon S. et al. (2007) *LPS XXXVIII*, Abstract #1892. [7] MacPherson G. et al. (1983) *GCA*, 47, 823-839. [8] Ireland T. (1988) *GCA*, 52, 2827-2839. [9] Simon S. et al. (2006) *Am. Min.*, 91, 1675-1687. [10] Simon S. et al. (1997) *MAPS*, 32, 259-269.