

**AN INTIMATE MIX OF HIGHLY OXIDIZING AND HIGHLY REDUCING ENVIRONMENTS: RELICT SPINEL DETERMINED BY XANES IN A PARTIALLY MELTED ALLENDE CA-AL-RICH INCLUSION.** J. M. Paque<sup>1,3</sup>, S. R. Sutton<sup>2</sup>, D. S. Burnett<sup>1</sup>, J. R. Beckett<sup>1</sup> and S. B. Simon<sup>2</sup>, <sup>1</sup>California Institute of Technology, M. C. 100-23, Pasadena, CA 91125, <sup>2</sup>Dept. Geophy. Sci., 5734 S Ellis Ave., Univ. of Chicago, Chicago, IL 60637, <sup>3</sup>julie@paque.com.

**Introduction:** Spinel is often the liquidus phase in Ca-Al-rich inclusion (CAI)-like melts, and one of the last minerals to melt during a reheating event. Spinel potentially record earlier igneous events, or even environments, providing insights into the evolution of CAIs and conditions in the early history of the solar nebula. We used X-ray absorption near edge spectroscopy (XANES) to determine the Ti and V valence in spinels from a previously characterized Type B1 CAI [1, 2]. We also analyzed spinel in an experimental sample of CAI composition run under reducing conditions.

**Analytical methods:** Spinel from the Allende Type B1 CAI, TS-34, and an experimental sample (1316.4-5) were analyzed by XANES at the Advanced Photon Source (APS) at Argonne National Laboratory (beamline 13-1D, GEOCARs). The 1316 bulk composition is taken from CAI-2 glass of [3] and was run under the C-CO buffer (graphite capsule with a flowing CO gas). The sample was initially held at 1390°C for 24 hr, followed by cooling at 5°C/hr to 1270°C, for a soak of 18 hours, followed by quench. The sample contained glass, spinel and melilite (mel).

The excitation volume for analysis is narrow (~2 μm) but deep (~10 μm) so inclusion of signal from the host material must be considered, particularly near surfaces of spinel included in clinopyroxene (cpx), which is generally Ti-rich. Contamination of analyses by mel doesn't significantly affect the valence ratios for Ti or V in spinel because of the low bulk Ti-V, but cpx, which often decorate the spinel [4-7], may. Ti and V were monitored to gauge the extent of interference.

**Results:** 1316.4-5. The two spinel analyses from 1316 have Ti valence of  $3.0 \pm 0.05$  and  $3.05 \pm 0.05$  (i.e., essentially all of the Ti is  $Ti^{3+}$ ). The sample was V-free.

**TS-34 spinel in clinopyroxene.** A XANES linescan was taken across spinel B3 in TS-34, an inclusion in cpx (Fig. 1). Fig. 2 shows Ti and V valence vs. distance across the spinel into the host cpx. The central portion of the spinel is  $Ti^{4+}$ -rich, whereas the host cpx contains mostly  $Ti^{3+}$ . Note also that as the traverse approaches the grain edges the mean Ti valence approaches a 50:50 mix of  $Ti^{3+}$  and  $Ti^{4+}$ . V valence ratios in spinel B3 are uniform within the 1σ error but  $V^{3+}/V^{2+}$  may be lower in the spinel than in the host cpx. Cpx has been found to have spikes in Ti valence, with uniform V valence [5]. B3 is zoned with respect to Ti, with wt. %  $TiO_2=0.74$  in the core increasing to 0.77 at the edge, typical of spinel inclusions in cpx. Concentration profiles of  $Ti^{3+}$  and  $Ti^{4+}$  can be calculated (Fig. 3, spinel analyses only).  $Ti^{4+}$  decreases towards the edge of the spinel and  $Ti^{3+}$  increases.

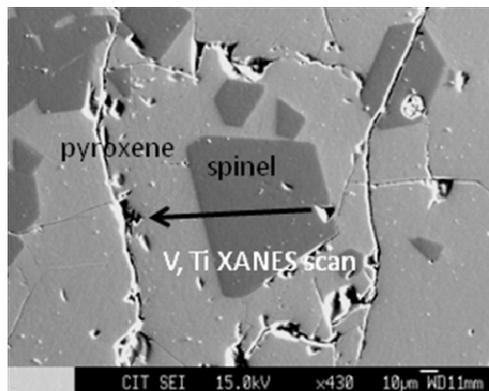


Figure 1. Spinel B3 from TS-34. Host phase is pyroxene. The arrow indicates location and direction plotted in Fig. 3.

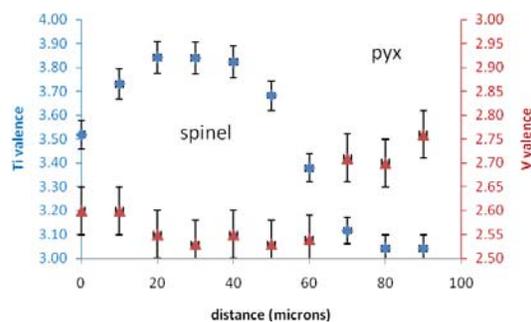


Figure 2. Results from XANES traverse across spinel B3. The Ti results are in blue (squares) and the V results are in red (triangles).

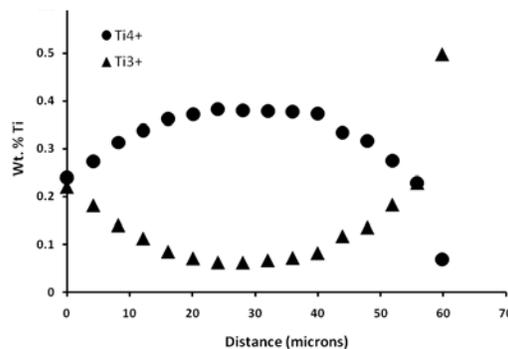


Figure 3. Wt. %  $Ti^{3+}$  and  $Ti^{4+}$  calculated from XANES Ti valence and electron probe concentration of Ti for spinel B3.

**TS-34 spinel in mantle melilite.** A traverse on spinel A9 in mantle mel (Fig. 4) is thematically similar to spinel B3 but the spinel core is virtually  $Ti^{3+}$ -free, with  $Ti^{3+}/Ti^{4+}$  increasing towards the edge. Based on Ti-counts acquired during analysis, the anomalous point at 84 μm contains contamination by boundary cpx [3-

6]. Melilite has very low concentrations of Ti but the valence is essentially pure  $Ti^{4+}$ . Our observation of  $Ti^{4+}$ -enriched cores in the spinel grains B3 and A9 is consistent with reconnaissance measurements of [8].

**Discussion:** Experiments [9] suggest that the Ti in cpx and spinel crystallizing in highly reducing gases should be largely trivalent. TS-34 cpx is consistent with this expectation but spinel B3, included in cpx, shows a core with  $Ti^{4+} \gg Ti^{3+}$ . This is completely inconsistent with co-crystallization from the same melt, closed system crystallization at different times along a shared liquid line of descent, or crystallization in a system open to a constant bulk composition gas. Spinel cores grew in a highly oxidized environment and cpx grew later in a highly reduced environment. It is difficult to quantify precisely what highly oxidizing means in this context as only data of [8] at CCO and in air are currently available but it seems unlikely that the virtually  $Ti^{3+}$ -free core of A9 grew in an environment much more reduced than the iron-wüstite buffer, which would have been several log units more oxidizing than plausible environments for crystallization of the cpx.

Although the cores of the spinels are  $Ti^{3+}$ -poor, the outer portions of the crystals are zoned to progressively higher  $Ti^{3+}/Ti^{4+}$  ratios. We envision a simple scenario in which a CAI containing spinel grains originally grown in a highly oxidizing environment was partially melted in a highly reducing environment. During heating, some of the original spinel dissolved but the peak temperature of the heating event was sufficiently low (or sufficiently brief) so that cores of the relict  $Ti^{4+}$ -enriched spinels were retained. Upon cooling, overgrowths grew on the spinel cores but since these would have been crystallizing from  $Ti^{3+}$ -enriched melts, the overgrowth also incorporated  $Ti^{3+}$ . Details of the as-crystallized zoning profiles in the overgrowths would have been dictated by a variety of factors including redox conditions, cooling rate, crystallization temperature, co-crystallization of cpx, and the rate of diffusive homogenization of melt produced by the previously dissolving spinels. (e.g., if the spinel grew into a melt incompletely homogenized with respect to Ti valence, then  $Ti^{3+}/Ti^{4+}$  in the melt from which the spinel was crystallizing would have varied as a function of time).

After spinel growth ceased and the grain was incorporated into a host phase, diffusive interactions between the spinel and host may have further modified the zoning. Where no significant reservoir of Ti existed (e.g., mel) only partial diffusive homogenization of  $Ti^{3+}$  would have been supported. In the presence of an exchangeable host such as cpx, concentrations of both  $Ti^{4+}$  (leaving) and  $Ti^{3+}$  (entering) may have been modified.

The mean valence for V is quite low in both spinel grains,  $\sim 2.5$ , lower than in coexisting cpx ( $\sim 2.7$ ) and essentially constant, suggesting complete equilibration between spinel and cpx and a relative preference for  $V^{2+}$  in the spinel relative to cpx. The highly zoned nature of the Ti valence profiles suggests that diffusion

of V in the spinel may be significantly faster than Ti.

**Summary:** The  $Ti^{4+}$  cores of spinels in TS-34 are relict and not in equilibrium with the host mineral. The V and Ti valence profiles in the center of spinel in both the mantle melilite and core pyroxene are similar.

**References:** [1] Paque J. M. et al. (2007) *MAPS*, 42, 899-912. [2] Burnett D. S. et al. (2004) *LPS XXXV*, Abstract #1253. [3] Stolper E. (1982) *GCA* 46, 2159-2180. [4] MacPherson et al. (1984) *GCA* 57, 231-243. [5] Kuehner S. M. et al. (1989) *Geoph. Res. Lett.* 16, 775-778. [6] Simon S. B. et al. (1991) *GCA* 55, 2635-2655. [7] Paque J. M. et al. (2009) *MAPS* 44, 665-687. [8] Simon S. B., per. comm. [9] Connolly H. C. and Burnett D. S. (2003) *GCA* 67, 4429-4434.

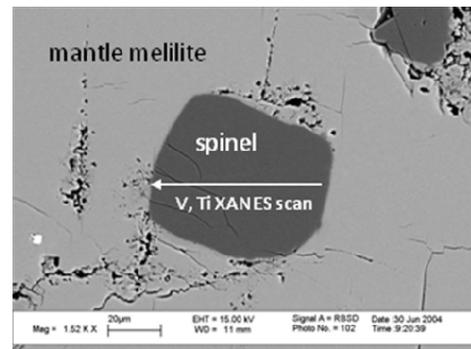


Figure 4. Spinel A9 from TS-34. Host phase is mantle melilite. The arrow indicates location and direction of line plotted in Figure 5.

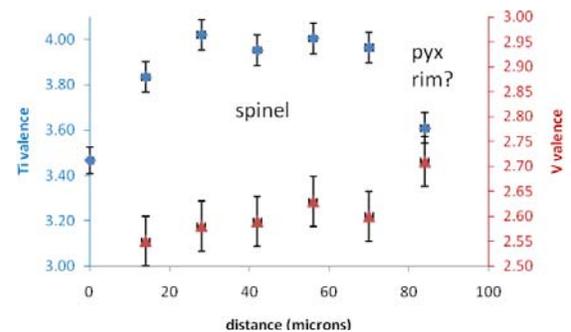


Figure 5. Results from XANES traverse across spinel A9. The Ti results are in blue (squares) and the V results are in red (triangles).

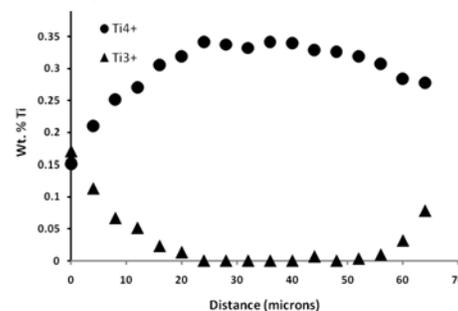


Figure 6. Wt. %  $Ti^{3+}$  and  $Ti^{4+}$  calculated from XANES Ti valence and electron probe concentration of Ti for spinel A9, spinel analyses only.