**VALENCE OF TITANIUM IN Ca-Al-RICH INCLUSIONS: EXPERIMENTAL SAMPLES AND RELEVANCE TO NATURAL CAIs**

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**Introduction:** Previous X-ray Absorption Near Edge Structure (XANES) Spectroscopy studies on spinels (sp) from Allende TS-34 [1, 2] have shown them to contain little $Ti^{3+}$, relative to $Ti^{4+}$, in spite of being hosted by $Ti^{3+}$-enriched clinopyroxene (cpx). This suggests that the spinels are products of a more oxidizing environment.

**Analytical Methods:** Sp and cpx from a suite of experimental samples [3] were analyzed by XANES at the Advanced Photon Source (APS) at Argonne National Laboratory (beamline 13-1D, GSECARS). The bulk composition represents an average Type B Ca-Al-rich inclusion (CAIB, [3]). Due to the narrow (~2 µm), but deep (~10 µm) excitation area, and the fine grained nature of the samples, it was difficult to ensure that only one phase was analyzed, particularly for sp. Ti counts and spectral shape were monitored to help distinguish sp from glass and cpx.

**Results:** Results are shown below for coexisting phases in experiments conducted in $H_2$-$CO_2$ gas mixtures, along with one dynamic crystallization experiment (1316.4-5) run under CCO [1]. There is a trend to increased $Ti^{3+}$ with decreasing $fO_2$, as expected. Valences for all glasses were dominated by $Ti^{4+}$ (>3.6) and showed no trend with $fO_2$.

| Sample | Phas | T (°C)/temp (hrs) | ΔIW | Ti valence | 1 σ |
|---|---|---|---|---|---|
| CAI-62 | Cpx | 1229°C/96.2 hrs | 0.0 | 3.98 | 0.0 |
| CAI-62 | Sp | 1229°C/96.2 hrs | 0.0 | 3.96 | 0.0 |
| CAI-63 | Cpx | 1226°C/120 hrs | -2.3 | 3.79 | 0.0 |
| CAI-63 | Sp | 1226°C/120 hrs | -2.3 | 3.64 | 0.0 |
| CAI-40 | Sp | 1407°C/5.7 hrs | -2.6 | 3.49 | 0.0 |
| CAI-64 | Cpx | 1227°C/74 hrs | -3.6 | 3.68 | 0.0 |
| CAI-64 | Sp | 1227°C/74 hrs | -3.6 | 3.42 | 0.0 |
| CAI-66 | Cpx | 1234°C/23 hrs | -5.1 | 3.22 | 0.0 |
| CAI-66 | Sp | 1234°C/23 hrs | -5.1 | 3.54 | 0.0 |
| CAI-65 | Cpx | 1227°C/29 hrs | -5.7 | 3.24 | 0.0 |
| CAI-65 | Sp | 1227°C/29 hrs | -5.7 | 3.30 | 0.0 |
| 1316.4-5 | Sp | See [1] | -6.4 to -5.7 | 3.05 | 0.0 |

**Discussion:** The experimental results indicate that sp co-crystallizing at equilibrium from a melt with $Ti^{3+}$-rich cpx will also be $Ti^{3+}$-rich. The fact that observed CAI sp hosted by $Ti^{3+}$-rich cpx is $Ti^{3+}$-poor is consistent with the idea that the CAI experienced oxidizing conditions prior to cpx crystallization. A late oxidizing metamorphic or alteration event, while improbable, could produce the observed Ti valence. However, the cpx blebs or rinds on the surface of sp [4-6] contain significant $Ti^{3+}$, which would not be expected if they formed during an oxidizing event, and the zoning to increased $Ti^{3+}$ at the edge of sp [1] is inconsistent with this theory.

**Conclusions**: Experimental results are consistent with the hypothesis that sp from CAIs are relict. The Ti valence in sp and cpx in TS-34 is one example that CAIs record multiple events.

**References:** [1] Paque J. M. et al. 2010. Abstract #1391. 41st Lunar & Planetary Science Conference. [2] Simon S. B. et al. 2010. Abstract #1459. 41st Lunar & Planetary Science Conference. [3] Stolper E. 1982. *Geochimica et Cosmochimica Acta* 46:2159-2180. [4] MacPherson G. J. et al. 1984. *J. Geology* 92:289-305. [5] Kuehner S. M. et al. 1989. *Geophysical Research Letters* 16:775-778. [6] Simon S. B. et al. 1991. *Geochimica et Cosmochimica Acta* 55:2635-2655. [7] Paque J. M. et al. 2009. *Meteoritics & Planetary Science* 44:665-687