

**ZONING PATTERNS IN SPINEL FROM TYPE B CA-AL-RICH INCLUSIONS: CONSTRAINTS ON SUB-SOLIDUS THERMAL HISTORY.** D. S. Burnett, J. M. Paque and J. R. Beckett, Div. of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, burnett@gps.caltech.edu.

**Introduction:** Extensive study of Ca-Al-rich Inclusions (CAIs) has revealed a complex series of events subsequent to initial crystallization, including pervasive alteration. The alteration in Allende type B1 CAIs has produced obvious FeO enrichment in rim spinels, but also in interior spinels. Allende TS 34 has atypically large Fe-zoned spinel [1], opening the possibility of time-temperature constraints, as diffusion coefficients are known [2]. With our new extensive database, we have discovered systematic zoning patterns for Fe, V and Ti from in TS 34 spinels.

**Experimental:** This study utilized the same polished thin section of Allende TS 34 used by [3, 4]. The V, Fe and Ti distributions in 15 spinels (50-100 microns) have been analyzed by high precision electron microprobe analyses (200 nA beam current, 100 sec. count time, 15 kV accelerating voltage). The beam diameter was 2-3 microns, and the step size was generally 4 or 5 microns, done on a grid pattern to sample the spinel and the area immediately adjacent. Si was used as a discriminator for spinel vs. matrix or inclusions.

**Results:** The contour maps (100-300 data points each) display consistent behavior: No correlation between the two-dimensional distributions of Fe, Ti, and V; in all grains FeO concentrations are higher on at least one edge and decrease towards the center of the grains; for all spinel inclusions in melilite, Ti concentrations are peaked in the interiors of the grains; and when a spinel grain has a boundary with clinopyroxene, the Ti concentrations decrease with distance from the clinopyroxene. This is consistent with [1, 7] that there is subsolidus equilibration of Ti between spinel and clinopyroxene.

V distributions are complex. All grains show significant variability, although all but 2 grains have variations less than 10%. One grain (possibly two others) has a small (8%) core enrichment. Six other grains have V distributions that are higher on one edge or corner than for the rest of the grain (figures 1 and 2). The figures show SEM images and color-coded contour maps of the Fe, Ti, and V distributions for spinel B2 (melilite host) and sp14 (clinopyroxene host). In order to show the full range of variations, profiles of Fe, Ti and V were selected to go through the minimum and maximum concentrations for each element as determined by inspection from the two-dimensional data arrays.

The Fe contour map on Figure 1 shows two source regions on two corners of the grain, probably local spots of melilite alteration. In common with all melilite inclusions, the Ti contour map shows that Ti is concentrated in the interior of the grain relative to the edges. The V<sub>2</sub>O<sub>3</sub> contour map shows that V is enriched in one quadrant relative to the rest of the grain with the lowest concentrations on an adjacent edge. This type of edge/corner V enrichment is found in most, although not all, grains studied.

Although the general features discussed above are always present, most grains have some additional unique features, as illustrated for sp14 in Figure 2. Sp14 has a filled and an empty fracture (white points). Neither fracture appears to have any significant effect on the Fe distribution.

Instead, high Fe sources on the boundaries cause a systematic decrease of FeO towards the center of the grain and toward the corner where no source is observed. We interpret the FeO in the edge points as being incorporated from a thin film of alteration along the grain boundary (the surrounding clinopyroxene is FeO poor) and the decreasing FeO content towards the interior of the grain as a result of inward diffusion. The TiO<sub>2</sub> distribution illustrated for sp14 is very different from that for spinel B2, higher overall and higher on the edges than in the interior of the grain because of inward diffusion of Ti from the surrounding clinopyroxene. The V<sub>2</sub>O<sub>3</sub> contour map for sp14 is qualitatively similar to B2.

**Discussion:** The FeO profiles are well defined by exponentials (see figures). Evaluation of 27 FeO profiles from 15 grains yields an FeO diffusion length of 6 microns which, as an order of magnitude approximation, is equal to  $\sqrt{2Dt}$  where D is the FeO-MgO counterdiffusion coefficient and t is the duration of the alteration subsolidus heating. Our preliminary conclusions, using D from [2], are that (A) if the time of alteration is less than 1 my, then the temperature of alteration was greater than 450°C, (B) if the temperature of alteration can approach 1000°C, then the alteration time scale can be as short as 4 months.

The edge peaked Ti distributions in sp14 can be explained by subsolidus re-equilibration of Ti between spinel and clinopyroxene [1]. Our data show that the flow direction of Ti during re-equilibration was from clinopyroxene to spinel. The origin of Ti distributions for spinel inclusions in melilite (e.g., B2) is much more difficult to explain. If the center-peaked distributions represent changes in the liquid Ti concentration during spinel crystallization, a bulk partition coefficient for Ti >1 during this period is required. Ti is incompatible in spinel, melilite, and anorthite for all plausible oxygen fugacities, thus extensive co-crystallization of clinopyroxene along with the spinel is needed for the bulk partition coefficient to be >1. This is a problem because the texture of Type B1 CAIs (mantle of melilite of radially increasing Ak content) and experimental crystallization data [5, 6] indicate that clinopyroxene crystallization occurs much later than spinel. For spinel only, or spinel + melilite crystallization, core-depleted Ti profiles should have been observed. Re-melting models which have spinel and clinopyroxene co-crystallization do not adequately explain observations [1]. Alternative explanations to crystal-liquid processes are required. It may be that the center peaked Ti profiles represent partial diffusion loss of Ti from the spinel into the surrounding melilite. The Ti moves to match the equilibrium partitioning ratio between spinel and melilite at the subsolidus temperature. Relict phases [8] may also play a role.

The origin of the edge/corner-peaked V distributions is even more difficult to explain. One possibility is that the V distributions in spinel were uniform prior to alteration, but a relatively small amount of V was introduced during the alteration and was preferentially picked up by spinel grains at one edge or corner.

**References:** [1] Connolly H. C. Jr. et al. (2003) *MAPS*, **38**, 19-224. [2] Liermann H.P. and Ganguly J. *GCA* **66**, 2903-2913. [3] Connolly H. C. Jr. and Burnett D. S. (2003) *GCA*, **67**, 4429-4434. [4] Connolly H. C. Jr. and Burnett D. S.

(1999) *MAPS*, **34**, 829-848. [5] Stolper E. (1982) *GCA*, **46**, 2159-2180. [6] Stolper E. and Paque J. M. (1986) *GCA*, **50**, 1785-1806. [7] Meeker G. P. et al. (1983) *GCA*, **47**, 707-721. [8] Greshake A. et al. *MAPS*, **33**, 75-87.

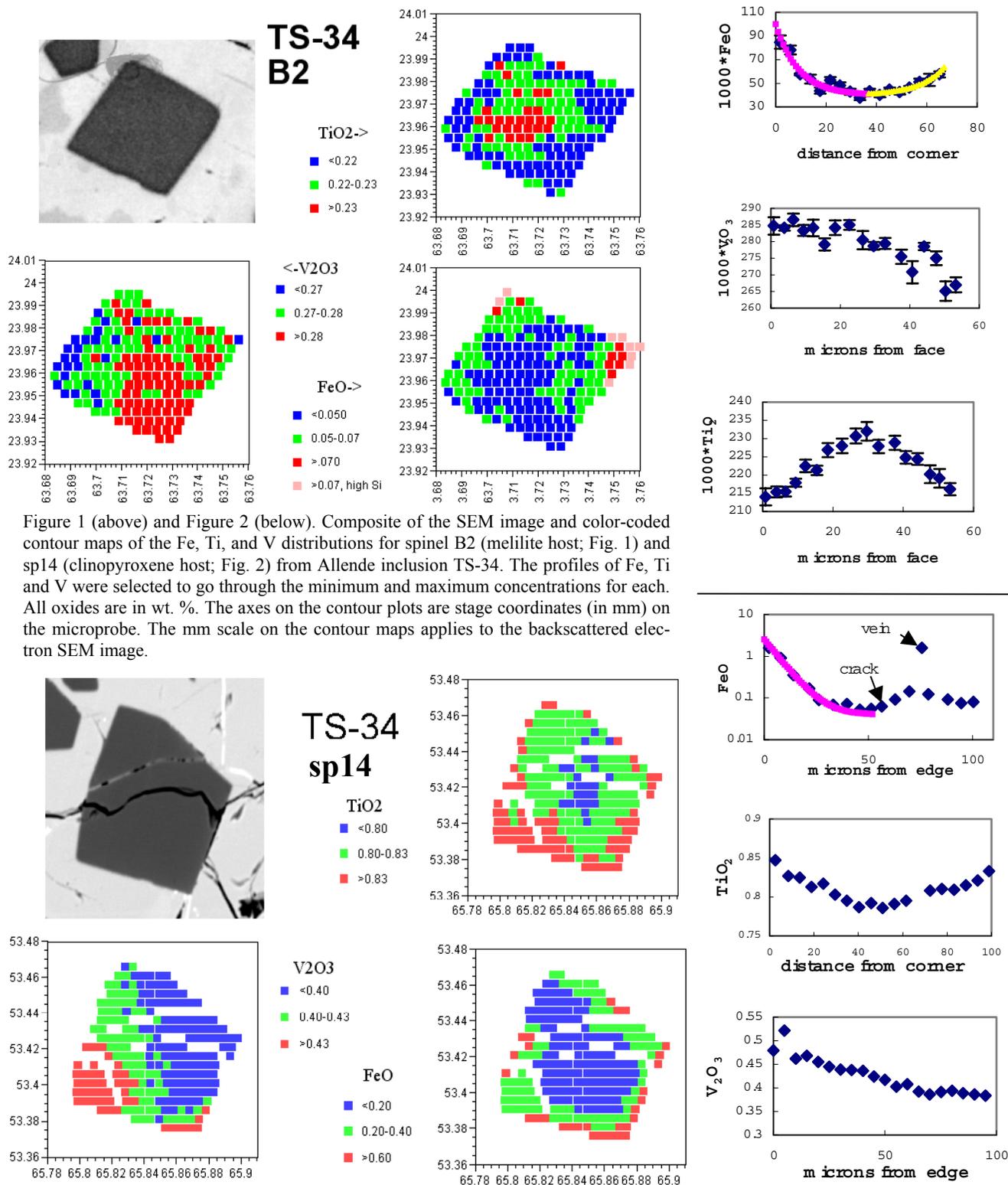


Figure 1 (above) and Figure 2 (below). Composite of the SEM image and color-coded contour maps of the Fe, Ti, and V distributions for spinel B2 (melilite host; Fig. 1) and sp14 (clinopyroxene host; Fig. 2) from Allende inclusion TS-34. The profiles of Fe, Ti and V were selected to go through the minimum and maximum concentrations for each. All oxides are in wt. %. The axes on the contour plots are stage coordinates (in mm) on the microprobe. The mm scale on the contour maps applies to the backscattered electron SEM image.