ORIGIN OF TRACE ELEMENTS IN SPINEL FROM Ca-Al-RICH INCLUSIONS: CONSTRAINTS FROM NanoSIMS ANALYSES OF SPINEL AND ENCLOSING MELILITE.

Introduction: Type B Ca-Al-rich Inclusions (CAIs) from Allende reflect a variety of processes including crystallization from a liquid and subsolidus diffusion, oxidation, sulfidization, and alteration of igneous phases [1]. Allende TS 34 has atypically large spinel grains making this CAI an attractive candidate for investigating the effects of different processes on this phase [2-5] and, thereby, constraining processes that affected CAIs. Previous work demonstrated that spinels in TS 34 are characterized by systematic zoning patterns for Fe, V and Ti [3]. Some features of the data (e.g., FeO enrichment) are easily explained by diffusion accompanying alteration, but the Ti distributions are more problematic. In this study, we analyzed the interface region between spinel and adjacent material by NanoSIMS to determine the relationship between the trace element content of the spinel and surrounding material, with the specific goal of testing for Ti gradients in melilitie which could support a diffusive origin for the spinel zoning.

Experimental: We used the same polished thin section of Allende TS 34 previously studied by [2-5], and chose ten spinel-melilitie interfaces from seven spinels whose V, Fe and Ti distribution had already been determined by high precision electron microprobe analyses [3, 5] conducted on a grid pattern covering the spinel and immediately adjacent area.

We analyzed \(^{26}\text{Mg}, ^{42}\text{Ca}, ^{47}\text{Ti}, ^{51}\text{V}, \) and \(^{56}\text{Fe}\) concentrations using the NanoSIMS 50 at Lawrence Livermore National Laboratory by simultaneous multi-collection at a mass resolving power of ~6000 A. A ~400 nA \(^{16}\text{O}\) primary ion beam focused to a ~1 \(\mu\text{m}\) diameter spot was rastered over a 10 \(\times\) 10 \(\mu\text{m}^2\) area. Eight to 25 scans of each area were summed to create a single 256 x 256 pixel image for each element. Data were normalized to \(^{42}\text{Ca}\) to reduce the dependence on melilitie composition. Data were summed parallel to spinel-melilitie interfaces to improve statistical precision.

Results: The \(^{26}\text{Mg}/^{42}\text{Ca}\) ratio in the melilitie is a direct measure of the åkermanite content. Of the ten profiles, five decreased, four increased and one was flat. No obvious connection between Mg in the melilitie and the trace element distribution in spinel was discerned, suggesting incorporation of spinel by crystallizing melilitie has little effect on either the trace element distribution in the spinel or on the chemistry of the host melilitie. Nor does there appear to be any significant post-crystallization reaction between the spinel and melilitie. The above observations on Åk variations might also be affected by better understanding of Ca\(^+\) intensity variations.

A decreasing Ti concentration in melilitie away from the spinel-melilitie interface would be expected for diffusion loss of Ti from spinel. We see no statistically significant variation in Ti\(^+\) intensity along the profiles. There are statistically significant variations in Ti/Ca, both increasing and decreasing away from the interface, but these all reflect variations in Ca\(^+\) intensity. More work is required to understand the Ca variations, but taking the Ti data at face value, we provisionally conclude that there are no Ti gradients in melilitie away from spinel interfaces.

\(^{51}\text{V}\) is so low in melilitie that no statistically significant profiles were obtained. \(^{56}\text{Fe}\) occasionally peaks near the spinel/melilitie boundary (perhaps due to alteration), but is generally uniform within the melilitie.

NanoSIMS analysis indicates that submicron phases are common along the spinel/melilitie boundary (Fig. 1), as well as included within the melilitie. The boundary phase shown in Fig. 1 is higher in both Mg and Fe than the adjacent spinel, perhaps an olivine or magnesiowustite crystal. The presence of ubiquitous boundary phases may affect the ability of spinel and melilitie to equilibrate. However, from the NanoSIMS images, there appears to be direct local spinel-melilitie contact, and these regions were selected for data processing.

Discussion: Further data processing is required, but there is no evidence in the NanoSIMS results to suggest that trace element zoning of the spinels has affected the composition of the melilitie, or vice versa.

The presence of minerals along the boundary between spinel and melilitie is consistent with previous work [5]. Typically, these include blebs and rims of Ti-fassaite pyroxene, which were interpreted by [5] to be the product of crystallization from melt inclusions surrounding previously crystallized spinels. Experimental work by [6] found residual glass+pyroxene adjacent to spinel included in melilitie to be a common feature at slow cooling rates. However, in all cases analyzed there is an increase in Åk content of the melilitie adjacent to the glass. This increase was not seen for TS 34 when analyzed by microprobe or NanoSIMS. Recent work by A. Toppani and colleagues [pers. comm.], showing the presence of glass along the spinel-melilitie boundary in a Leoville inclusion, supports this hypothesis. We do not know whether TS 34 has glass along the spinel-melilitie boundary. Two options were presented by [5] to account for the observed zoning: (1) changes in the liquid Ti concentration or valence state distribution over the course of spinel crystallization; and (2) subsolidus diffusion of the Ti into the melilitie.

Subsolidus diffusion was attractive because a crystallization model with constant \(K_p\) and no valence state changes requires a bulk partition coefficient for Ti greater than 1 during spinel crystallization. Ti is an incompatible element in spinel, melilitie, and anorthite for all plausible oxygen fugacities (1). Thus, the only way for the bulk partition coefficient to be greater than 1 is for extensive co-crystallization of clinopyroxene along with the spinel.
The preliminary NanoSIMS data appear to rule out option (2) and we provisionally focus again on option (1).

Reservoir effects with constant \( K_D \) will drive concentrations of Ti up with progressive crystallization so that later crystallizing spinels have higher concentrations of Ti, not lower as observed. This was the essence of the argument against a single-stage crystallization model for producing the observed zoning pattern. This simple view is, however, misleading for spinel because of two complicating factors. (1) Ti\(^{3+} \) is so much more compatible in spinel than Ti\(^{4+} \) [2], that partitioning under reducing conditions is controlled by Ti\(^{3+} \) in the liquid, not total Ti (i.e., the appropriate \( K_D \) is vs. Ti\(^{3+} \)). (2) Ti\(^{3+}/Ti^{4+} \) in the liquid decreases with decreasing temperature along an oxygen buffer curve, by roughly a factor of ~2 over 200° based on [7] (i.e., the liquid appears more “oxidizing” as the temperature decreases). If a volatilization rind is formed [8], there may be additional variations in Ti\(^{3+}/Ti^{4+} \) as a function of distance from the surface of the cooling droplet due to bulk chemistry effects but data are not yet available to assess their magnitude. The basic supposition of this simple partitioning model is that decreasing Ti\(^{3+}/Ti^{4+} \) in the liquid, as temperature decreases, overwhelms reservoir effects; early, high temperature spinels have higher Ti and center peaked zoning profiles, as observed. Core spinels in this scenario, generally crystallized at lower temperatures than mantle spinels, neglecting possible liquid composition effects on Ti\(^{3+}/Ti^{4+} \). If profiles were not strongly modified by subsolidus diffusion, the center and rim compositions in a spinel are largely a measure of the temperature interval over which the grain crystallized.

There are many, less likely, scenarios to explain both the NanoSIMS data and trace element zoning patterns in the spinel. For example, the spinels could be relics and represent crystallization from a different bulk composition than is represented by the current inclusion, although the absence of Mg isotopic variation argues against this. Spinel co-crystallization with perovskite could cause sufficient changes in liquid Ti content to yield center-peaked zoning, but we have no evidence to suggest that a substantial fraction of TS 34’s Ti budget was ever tied up in this phase. Another possibility would be that spinel Ti was partitioned into an alteration fluid which was subsequently lost. This, however, seems unlikely because Ti solubilities are extremely low in hydrous alteration fluids, at least under the oxidizing conditions envisioned for the alteration process that affected Allende inclusions [1-9].

**Conclusion:** The NanoSIMS data did not reveal any evidence for diffusion of trace elements from the spinel to the melilite. Ti valence state changes during initial crystallization appear to be the most plausible alternative.

**References:**


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