

FURTHER INVESTIGATIONS OF MINOR ELEMENT DISTRIBUTIONS IN SPINELS IN TYPE B CAIs.

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Introduction: Variations in minor element (Ti, V, Cr and Fe) concentrations within Mg-Al spinels in type B CAIs have provided insights into the early history of these objects, specifically the possibility that they may have experienced more than one episode of partial melting and recrystallization. Connolly and Burnett performed an extensive study on two Allende CAIs, TS-23 and TS-34, as well as a Leoville CAI 3537-2 [1,2], in which they found Ti vs. V trends that cannot be explained by a single-stage crystallization history. Here we report minor element concentrations in spinels from Efremovka E-44, a CAI that has been extensively studied for its record of short-lived radioactivity [3], and compare it to further analyses of TS-23. Our goals are to examine the spinels of type B CAIs in another CV chondrite which has been less effected by alteration (as is the case for Allende), or by post-crystallization shock events (as is the case for Leoville), to see if the same trends are apparent.

Experimental Technique: Following the technique of Connolly and Burnett [1], the CAIs were divided into three regions, Edge (corresponding to the mantle melilite area), Middle and Center (corresponding to the core area). We selected 3 areas from the edge of TS-23 (including spinels from the Wark-Lovering rim), 3 from the middle and 3 in the center; 9 areas were chosen for analysis in E-44 (4 edge, 3 middle and 2 center). All spinels chosen were at least 20 μm in diameter and spinels with obvious cracks were avoided. Spinel were categorized according to the enclosing host silicate phase. A single point was analyzed in each spinel grain, as close to its center as possible.

The JEOL JXA-8200 electron microprobe at UCLA was used to analyze the major (Mg and Al) and minor elements (V, Ti, Cr, Fe, Si and Mn) in each spinel by wavelength dispersive spectroscopy. Si was also analyzed to monitor for secondary x-ray fluorescence from the surrounding silicate phases. The major elements were analyzed at 15 kV, beam current 15 nA, counting times 10 sec, whereas minor elements were analyzed with beam currents of ~ 400 nA and counting times of 120 sec (255 sec for Cr). Interference from the $\text{TiK}\beta$ peak overlap on $\text{VK}\alpha$, as well as $\text{VK}\beta$ on $\text{CrK}\alpha$, were appropriately corrected for. Only analyses with less than 1000 ppm apparent SiO_2 are reported. Mn was found to be below detection limits in all cases.

Traverses across two 25 μm spinels, one enclosed in anorthite and the other in melilite, were performed to check for interference due to secondary x-ray fluo-

rescence as well as to check for possible zoning. No significant zoning was observed.

Results: As previously observed by Connolly and Burnett, Ti shows the greatest range in concentration within spinels in an individual CAI and there is a good correlation between Ti and V, which is apparent when one considers the host silicate phase. This correlation appears to possess the greatest potential for shedding light on possible remelting events, whereas Fe and Cr primarily provide evidence concerning post-crystallization alteration.

Efremovka E-44: Two separate positively correlated trends are seen for V vs. Ti (Fig. 1A): one for spinels enclosed in fassaite and the other for spinels enclosed in melilite and anorthite. The fassaite-enclosed spinels, which include edge, middle and center grains, are richer in Ti; the melilite and anorthite-enclosed spinels are richer in V. Both trends are anchored near the same low-Ti, low-V composition. The spinels enclosed in melilite form two separate groups, V-enriched edge grains and low-V center and middle grains. Ti ranges over a factor of 4, from ~ 990 ppm to 4000 ppm. V ranges from ~ 700 to 2400 ppm, a factor of 3.5. This positive correlation is similar to that found by Connolly and Burnett for both Allende TS-23 and Leoville 3537-2. Fig. 1B (Fe vs. Cr, log-linear plot) shows a large range in Fe concentration (~ 70 ppm to 6000 ppm, a factor of ~ 85), but is overall poorly correlated. The range in Cr (710 ppm to 2350 ppm) is ~ 3.3 , similar to the range in V but less than the range in Ti. Error bars on all plots are approximately the size of the symbols.

Allende TS-23: Our analyses of TS-23 also show a positive V-Ti correlation (Fig. 1C) with two separate trends, with a high-Ti fassaite branch better defined than in Efremovka E-44. The two trends are clearly divided into fassaite- and melilite-enclosed spinels, with anorthite-enclosed spinels only occupying a low-Ti, low-V field. This trend was not previously identified in Allende TS-23, and now brings to four the number of CAIs identified with Ti-enriched spinels enclosed in fassaite. In addition, TS-23 shows a separate population of high-V, high-Ti spinels similar to that found [1] in Leoville 3527-2. Ti ranges from $\sim 1100 - 4500$, a factor of ~ 4 . Again Fe and Cr are poorly correlated (Fig. 1D), although there is a well-defined group of high-Fe, low-Cr edge grains which is not seen in Efremovka or Leoville. The range of Fe concentration is large for Allende TS-23, a factor of ~ 170 .

Discussion: The appearance of the same positive Ti-V trend in fassaite-hosted spinels from CAIs in 3 different CV chondrites indicates that this is not sampling bias and lends further support to the hypothesis of Connolly and Burnett that such CAIs have recorded remelting events [1] or local subsolidus re-equilibration [2] in the minor element concentrations of their spinel grains. Because of the low compatibility of Ti in spinels, a range of not more than a factor of ~ 2 is expected from single stage fractional crystallization if spinels cease crystallizing early as is suggested by experimental studies [4].

Relict grains: Connolly and Burnett suggested that V-rich edge grains may be candidates for relict spinels. (defined as either nebular condensates or having crystallized in an earlier generation of CAIs). Although E-44 does contain V-rich edge grains, the group is not as clearly defined as in Leoville 3537-2[1] and TS-23.

Re-melting event: A difference between E-44 and the other CAIs studied is that in the former a steeply sloping Ti-V trend is seen in both melilite and anorthite, whereas in the Allende and Leoville CAIs the anorthite-enclosed spinels cluster around the low-Ti, low-V field. This is consistent with anorthite being the last phase to crystallize. The remelting event proposed

by Connolly and Burnett [2], where fassaite + anorthite + high Åk melilite remelted, leaving the low Åk melilite intact, cannot explain this trend. In E-44 the spinels enclosed in anorthite follow the same trend as the non-remelted spinels enclosed in melilite.

Secondary alteration/W-L rims: The high Fe spinels seen in E-44 and TS-23 probably reflect secondary alteration. The larger range in found Allende than Efremovka is consistent with a greater degree of parent-body alteration. The lack of correlation between Fe and Cr suggests that the Cr range is not due to alteration. Interestingly, most of the high-Fe, low-Cr edge grains seen in Allende TS-23 are located within the Wark-Lovering rim. The high-V edge grains in the W-L rims may also be related to rim formation if V were less volatile than Cr. Since the high-V and low-Cr group includes spinels both in the W-L rim and the mantle melilite, the effects of W-L rim formation may have reached to a fairly great depth within the inclusion, as suggested by Connolly and Burnett [1].

References: [1] Connolly and Burnett (1999) *MAPS* **34**, 829-848. [2] Connolly et al. (2003) *MAPS* **38**, 197-224. [3] Srinivasan et al. (1996), *GCA* **60**: 1823-1835. [4] Stolper and Paque, (1986) *GCA* **50**, 1785-1806.

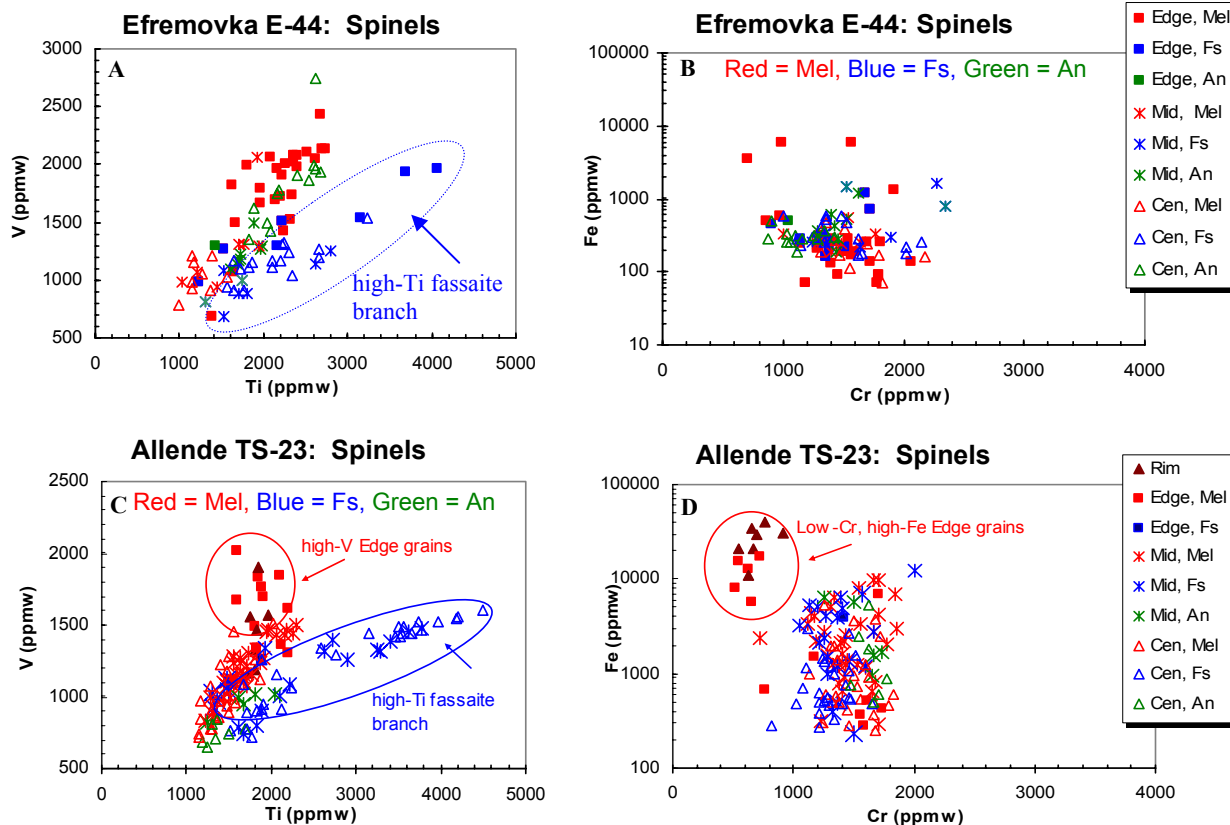


Fig. 1. Spinel minor element correlation plots for Efremovka E-44 and Allende TS-23. Left side is V vs. Ti. Right side is Fe vs. Cr. Data points are plotted according to host silicate phase and location in CAI; solid symbols are Edge, crossed symbols are Middle, open symbols are Center. The dark red triangles are in the W-L rim area.