

MELILITE COMPOSITION TRENDS DURING CRYSTALLIZATION OF ALLENDE TYPE B1 REFRACTORY INCLUSION MELTS; Andrew M. Davis<sup>1</sup>, Steven B. Simon<sup>2</sup> and Lawrence Grossman<sup>1,2</sup>, <sup>1</sup>Enrico Fermi Institute, <sup>2</sup>Department of the Geophysical Sciences, University of Chicago, Chicago, IL 60637

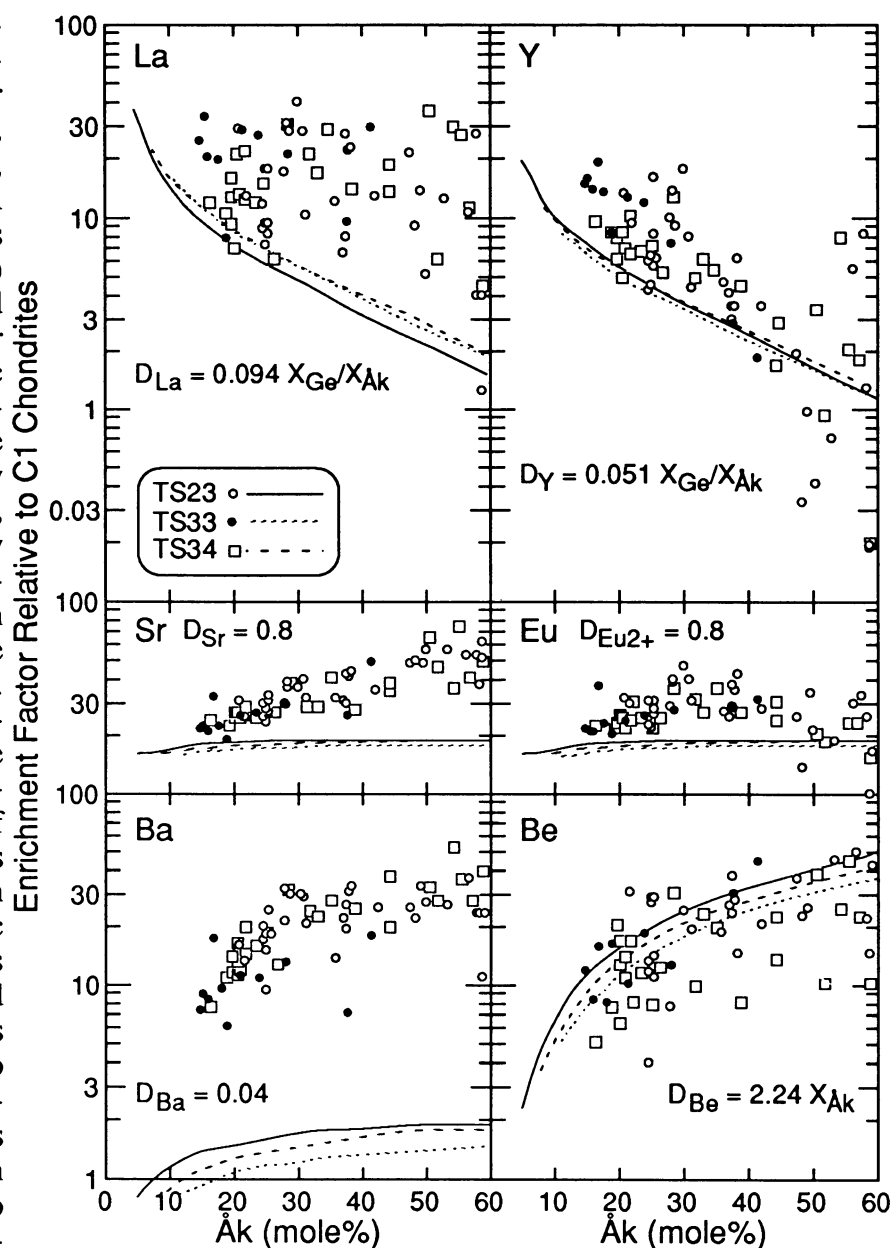
Type B1 refractory inclusions (CAI) in C3V chondrites are characterized by melilite-spinel mantles and melilite-fassaite-spinel-anorthite cores. These CAI are believed to have crystallized from melts, in which melilite crystals nucleated on the edges of the CAI and grew inward with falling temperature. Melilite/liquid partition coefficients ( $D^{\text{mel/liq}}$ ) for a variety of trace elements have been measured in bulk compositions appropriate for Type B1 crystallization [1,2]. We have measured major and trace element abundances in both core and mantle melilite from three Type B1 CAI from Allende by electron and ion microprobe, and compared the results to those calculated using literature  $D^{\text{mel/liq}}$  values in a simple fractional crystallization model.

Profiles were measured on 5 mantle melilites in TS23, 3 in TS33 and 2 in TS34. Each CAI has its own distinctive profile of  $\text{\AA k}$  vs. distance from the rim. Melilite grains in TS33 and TS34 both show a steady increase in  $\text{\AA k}$  with distance, consistent with normal fractional crystallization. Melilite in TS23 shows a curious premature reversal in zoning: the  $\text{\AA k}$  content rises from 5% at the rim to ~40% about 300  $\mu\text{m}$  in, drops to ~30% over the next 400  $\mu\text{m}$ , then rises to 60%. Mantle melilite in the three CAI is also zoned in FeO, with concentrations of 0.05–0.10 wt% at the edge of each CAI dropping to <0.01 wt% over the first 100–150  $\mu\text{m}$  inward. Mantle and core melilite in all three CAI shows remarkable zoning in Na. Virtually all melilite with  $\text{\AA k}_{<35}$  contains 10–100 ppm Na, melilite of  $\text{\AA k}_{35-45}$  contains 100–1000 ppm Na and all melilite with  $\text{\AA k}_{>45}$  contains ~1000 ppm Na. This zoning is seen in both mantle and core melilite. The Na zoning is not associated with alteration veins in melilite, nor is it related to distance from the edge of the CAI. This implies that Na, a volatile element, was present in the CAI melt prior to melilite crystallization, posing a problem for models of CAI formation requiring evaporation of large fractions of much more refractory elements such as Mg and Si from CAI melts, and opening up the possibility that other volatile elements, such as S in Fremdlinge, were present in CAI precursors prior to melting.

$\text{\AA k}$  and trace element contents can vary irregularly with distance in mantle melilite. The primary growth direction of melilite is along the  $c$ -axis. Since it is unlikely that the  $c$ -axes of any of the analyzed crystals are parallel to and lie along the plane of the section, irregularities in  $\text{\AA k}$  and trace element contents with distance are to be expected [3]. For this reason, we have plotted trace element contents versus  $\text{\AA k}$  content.

Predicted trace element crystallization trends for melilite were calculated in a manner similar to that of Beckett *et al.* [2]. Type B1 CAI were assumed to crystallize sp, sp+mel, sp+mel+fas, sp+mel+fas+an. Modal proportions of minerals in these three CAI were measured by Beckett [4]. For each CAI, we assumed that two-thirds of the spinel crystallized before melilite appeared and 80% of the melilite crystallized before fassaite appeared. The remaining one-third of the spinel was assumed to crystallize linearly with fraction crystallized. We assumed that melilite began crystallizing with the lowest  $\text{\AA k}$  content found in the mantle of each CAI ( $\text{\AA k}_5$ ,  $\text{\AA k}_{11}$  and  $\text{\AA k}_8$  for TS23, TS33 and TS34, respectively) and reached  $\text{\AA k}_{60}$  at the point when fassaite crystallized. The relationship between  $F$ , the fraction of liquid remaining, and melilite composition was assumed to take the form  $F = A + B/X_{\text{\AA k}}$  [2]. The values of  $A$  and  $B$  were calculated for each CAI. The literature  $D^{\text{mel/liq}}$  values used [1,2] are shown in the figure. All three CAI were assumed to have bulk compositions with 18×C1 chondritic enrichments in all refractory trace elements. The calculated trends cover a range from ~90% liquid at the onset of melilite crystallization to 40–50% liquid at the onset of fassaite crystallization.

Predicted crystallization trajectories are compared with melilite analyses for La (a representative LREE), Y (representative of HREE), Sr, Eu, Ba and Be (Fig). All data for large ion elements (REE, Y, Sr, Eu and Ba) plot above the calculated trajectories, whereas data for Be, which has a small ionic radius, scatter about the calculated trajectories. Since diffusion rates are generally slower for larger cations, this suggests that boundary layers enriched in incompatible elements developed in the liquids adjacent to the growing melilite crystals. Such enriched boundary layers increase the effective  $D_{\text{mel/liq}}$  during crystallization. This qualitative view of melilite crystallization is supported by the observation that  $\text{La}^{+3}$  has a larger ionic radius than  $\text{Y}^{+3}$  and deviates further from the calculated trajectory; similarly,  $\text{Ba}^{+2}$  is larger than  $\text{Sr}^{+2}$  and also plots further from the calculated trajectory. Eu follows Sr up to  $\text{Åk}_{40}$ , but then falls while Sr continues to rise. In order for Eu to behave differently from Sr in the latter stages of melilite crystallization,  $\text{Eu}^{+3}$  must be present. This is difficult to reconcile with the low oxygen fugacity required to stabilize  $\text{Ti}^{+3}$  that is observed in subsequently-crystallized fassaite.



Reversal of zoning in melilite at  $\text{Åk}_{60}$  caused by inhibition of anorthite nucleation [5] has been produced experimentally in Type B1 CAI melts at cooling rates of  $0.5\text{--}50^\circ\text{C/hr}$  [5,6]. The cooling rates used in the experiments used to derive  $D_{\text{mel/liq}}$  values [2] were  $1\text{--}2^\circ\text{C/hr}$ . Since the latter experiments do not seem to have been affected by boundary layer formation, this suggests that the Type B1 CAI studied cooled substantially faster than  $1\text{--}2^\circ\text{C/hr}$ .

References: [1] Kuehner S. M. *et al.* (1989) *GCA* **53**, 3115. [2] Beckett J. R. *et al.* (1990) *GCA* **54**, 1755. [3] MacPherson G. J. *et al.* (1989) *GCA* **53**, 2413. [4] Beckett J. R. (1986) Ph.D. Thesis, Univ. of Chicago. [5] MacPherson G. J. *et al.* (1984) *J. Geol.* **92**, 289. [6] Stolper E. & Paque J. M. (1986) *GCA* **50**, 1785.