

EXPERIMENTAL INVESTIGATION OF THE EFFECT OF COOLING RATE ON MELILITE/LIQUID DISTRIBUTION COEFFICIENTS FOR Sr, Ba, AND Ti IN TYPE B REFRACTORY INCLUSION MELTS; S.B. Simon¹, A.M. Davis², F.M. Richter¹, and L. Grossman^{1,2}.
¹Dept. of the Geophysical Sciences; ²Enrico Fermi Inst., University of Chicago, Chicago, IL 60637.

It is well established, from their textures, major element zoning within minerals, and phase equilibria, that Type B1 Ca-, Al-rich refractory inclusions (CAIs) were once at least partially molten. Although these inclusions represent closed magmatic systems and carefully determined melilite/liquid distribution coefficients (Ds) are available for many trace elements [1,2], attempts to model the trace element contents in melilite in CAIs have not met with much success. Davis et al. [3] showed that abundances of Sr and Ba in melilite in three Allende Type B1 inclusions were much higher than would be expected from equilibrium Ds; Kennedy et al. [4] made a similar observation, and both groups suggested that incompatible element-enriched boundary layers had formed in the melt, especially with respect to the trivalent cations [3,4] and Ba [3]. We note, however, that Sr abundances are also higher than predicted by the models even though its D of 0.8 is too close to 1 to give rise to sufficiently Sr-enriched boundary layers. It therefore seems that boundary layers cannot account for the observed enrichments. An alternative explanation, which we have now investigated, is that melilite/liquid Ds in inclusions truly are higher than the equilibrium values, which were determined in isothermal [1] or slowly cooled [2] experimental runs. CAIs, however, may have cooled at rates as fast as 50°C/hr [5]. We conducted a series of experiments on melts of Type B composition in order to determine the variation of $D^{\text{mel/liq}}$ with cooling rate for Ti, Sr and Ba, discussed here, and Y and nine REE, discussed in a companion abstract (Davis et al., this vol.), which could place important constraints on the crystallization histories of Type B1 CAIs.

Experimental methods. Melts of CAIB composition [6], doped with 10 ppm of each of La, Ce, Sm, Nd, Eu, Gd, Dy, Er, Lu and Y, ~ 200 ppm Sr and ~ 80 ppm Ba, were prepared from pure oxide and carbonate powders, and quenched. The starting material (glass + ~ 7 % spinel) was powdered, and aliquots were placed on platinum loops, held at 1430 °C (~ 100° below the liquidus and ~ 30° above melilite appearance [6]) for 3 hr, then cooled to 1200 °C at 2, 20, and 75°C/hr. Polished thin sections of the run products (spinel + melilite + glass) were studied optically and with the SEM, and several crystals from each run were analyzed along rim-to-rim traverses with the electron and ion probes.

Results. Runs cooled at 2°/hr contain coarse (500-1000 μm), euhedral melilite crystals with broad cores of uniform composition (Åk₂₅) and rims sharply zoned over the outer 250 μm to ~ Åk₆₀. Melilite grown at 20°/hr is blocky and euhedral (except for one hopper crystal) and is typically zoned from Åk₃₂ to Åk₅₂₋₅₆. As in the melilite from 2°/hr runs, rims are much more strongly zoned than the cores. The hopper crystal, with increasing Åk content both toward the outside of the crystal and toward the interior, glass-filled cavity, represents the first reported occurrence of this morphology in melilite, and might explain reverse zoning patterns observed in some melilite crystals found in compact Type A inclusions [7]. The runs cooled at 75°C/hr have blocky crystals that are smaller than those grown at slower cooling rates, but skeletal crystals up to 1500 μm long are also present. The latter grains exhibit much narrower compositional ranges, ~ 10 mole % Åk, than those in the more slowly cooled samples. The skeletal crystals are typically zoned from Åk₃₄₋₄₀ to Åk₄₅₋₅₀ with a sawtooth pattern of closely spaced increases and decreases in Åk superimposed on a general trend of a gradual increase in Åk content with continued crystallization. These variations of texture with cooling rate are consistent with the observations of Stolper and Paque [8].

Two melilite/liquid Ds were calculated for each element; one, at high Åk contents, from crystal rim/adjacent glass abundance ratios, and the other, at low Åk contents, from measured crystal core compositions and liquid compositions calculated assuming amounts of prior spinel crystallization inferred from equilibrium experiments [2,6]. The results for Sr are within the ranges of previously reported Ds of 0.62-0.72 [9] and 0.78-0.99 [1]: at 2°/hr and 20°/hr, $D^{\text{mel/liq}}$ for Sr is invariant with Åk, at 0.71 ± 0.02 . In the 75°/hr run, however, we calculate a low-Åk D of 0.80 and a high-Åk D of 0.63. These values are not well-constrained due to heterogeneities in the glass and crystals, and may not reflect true variations in the Ds. Note that their average is 0.72, however, similar to Ds obtained for the more slowly cooled runs. At 2°/hr, $D^{\text{mel/liq}}$ for Ba is constant at 0.025; at 20°/hr, it varies from 0.030 at Åk₃₀ to 0.022 at Åk₅₅; and, at 75°/hr, it appears to vary from 0.039

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($\text{\AA}k_{37}$) to 0.017 ($\text{\AA}k_{50}$). These values are lower than the published value of 0.04 [2]. Ds for Ti are also very low at all cooling rates: 0.020 at $2^\circ/\text{hr}$, 0.021 ($\text{\AA}k_{30}$)-0.012 ($\text{\AA}k_{55}$) at $20^\circ/\text{hr}$, and 0.022 at $75^\circ/\text{hr}$. These are the first reported values for $D^{\text{mel/liq}}$ for Ti.

Discussion. We used the present data and the crystallization model of [3] to calculate melilite Ti, Ba and Sr contents as a function of $\text{\AA}k$ for Allende Type B1 TS34. Results for Ti are illustrated in Fig. 1. The calculated trend passes through the field of low- $\text{\AA}k$ analyses but, at higher $\text{\AA}k$, misses both the high-Ti trend, which is possibly due to fassaite inclusions, and the low-Ti trend, which may be reflecting early fassaite crystallization. While we cannot account for these effects because our model considers only melilite that crystallized before fassaite, the results show that the Ti abundances in $\text{\AA}k_{20-25}$ melilite are consistent with a D of ~ 0.02 and a bulk TiO_2 content of 0.85 wt% [10]. As before, however, the models for Sr (Fig. 2) and Ba (Fig. 3, note log scale) do not fit the analyses. Virtually no variation in D as a function of cooling rate was observed. From modal abundances and average Sr contents of all the phases, we estimate that the bulk Sr content of TS34 is $21\times C1$, whereas an abundance of $\sim 27\times C1$ is required for models to yield even the lowest observed Sr abundances, and the models do not match the steep increase in Sr with $\text{\AA}k$ that is observed. This increase is also too steep to be attributed to boundary layer formation, because D_{Sr} is too high to generate a sufficiently enriched boundary layer. To match the observed trends by conventional Rayleigh fractionation would require lower Ds (to enhance the reservoir effect) and a bulk composition with a Sr abundance $>27\times C1$ (to match the Sr contents of early melilite, using the lower Ds), yet there is no evidence for either. Dissolution of a contaminating, Sr-rich phase and addition of Sr to the melt by condensation during melilite crystallization can both be ruled out for the same reasons. First, it would have to occur in each of the three different inclusions studied. Second, if Sr were added early enough to yield the low- $\text{\AA}k$, Sr-rich melilite, the bulk inclusion would be anomalously enriched ($\sim 27\times C1$). Adding Sr late might account for the high- $\text{\AA}k$, Sr-rich compositions, but the low- $\text{\AA}k$ values would still not be explained. In the case of Ba, the models do not come even close to fitting the data, and the D is so low that the liquid in equilibrium with the melilite observed in TS34 would have to be enriched to $\sim 1000\times C1$ in all 3 inclusions (bulk TS34: $\sim 17\times C1$ Ba). This is not realistic.

These results indicate that a fundamental process occurred during the crystallization of melilite in these CAIs that we still do not understand. Predicted trends do not match observations for Sr, Ba and Ti, even though, in the case of the latter, we can predict initial concentrations in melilite. We have yet to investigate other explanations for the observed trace element abundances and trends, including the possibilities that: 1) Ds are different at lower f_{O_2} ; and 2) loss of Si and Mg by volatilization may have occurred during melilite crystallization, enhancing the enrichment of the residual liquid in refractory trace elements. Future experiments will address these possibilities.

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