

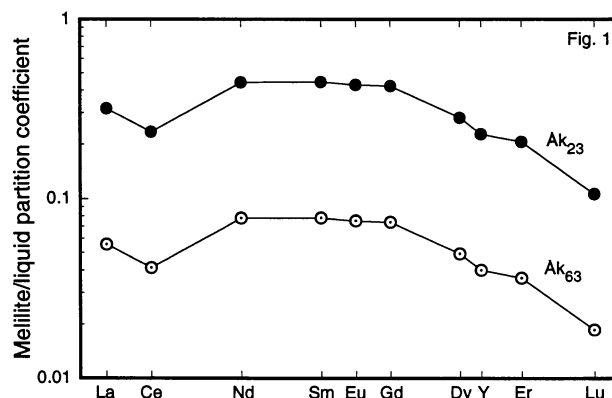
THE EFFECT OF COOLING RATE ON MELILITE/LIQUID PARTITION COEFFICIENTS FOR Y AND REE IN TYPE B CAI MELTS; A. M. Davis¹, F. M. Richter², S. B. Simon² and L. Grossman^{1,2}. ¹Enrico Fermi Inst., ²Dept. of Geophys. Sci., Univ. of Chicago, Chicago, IL 60637.

Abstract. Type B CAIs are widely believed to have crystallized from melts. Beckett *et al.* [1] measured melilite/liquid partition coefficients for La, Ce and Tm for a Type B CAI bulk composition cooled at 2°C/hr and found that they were proportional to the gehlenite to åkermanite ratio of crystallizing melilite. Davis *et al.* [2] reported REE concentrations in melilite from three Allende Type B CAIs. They modeled melilite crystallization in these CAIs using REE partition coefficients [1] and found two important discrepancies: (1) melilite in CAIs is consistently higher in REE than the amount predicted; and (2) REE patterns in CAI melilite become more steeply enriched in LREE than HREE with increasing Åk content, whereas significant fractionation of REE from one another is not predicted. Davis *et al.* [2] proposed that these differences were caused by the formation of trace element-rich boundary layers in melt adjacent to growing melilite crystals and that the fractionation of REE from one another was due to differing diffusion rates of REE in the melt, which caused slower-diffusing LREE to become more enriched in the boundary layer. In order to test for kinetic effects, we have measured melilite/liquid partition coefficients for Y and 9 REE (reported here) and Ti, Sr and Ba [3] in synthetic Type B CAIs grown at a variety of cooling rates. We find that REE partition coefficients for melilite decrease, rather than increase, with increasing cooling rate. Cooling rates in excess of 2°/hr cannot explain REE distributions in Type B CAI melilite.

Experimental. Starting materials of CAIB composition [1,4], doped with about the same levels of Sr, Ba, Y and REE as are observed in CAIs, were placed on platinum loops, held at 1430°C for 3 hr, cooled to 1200° at 2, 20 and 75°C/hr, and air-quenched. All experiments were done in air in a vertical tube furnace. Melilite and glass compositions were measured in starting materials and samples by electron and ion microprobe. The melilite crystals grown are progressively smaller and the initial melilite more åkermanitic with increasing cooling rate [3]. The latter effect is likely due to undercooling and delayed nucleation of melilite and serves to narrow the temperature range of melilite crystallization in experiments with faster cooling rates. Melilite crystal size and temperature range of crystallization compensate for one another, such that linear growth rates of melilite crystals in these experiments are roughly proportional to cooling rates.

Melilite/liquid partition coefficients for Y and REE. The composition of the melt from which melilite grew is only known for the first and last melilite to crystallize in each experiment. Previous experiments [3,5] have established that composition CAIB contains 11 wt% spinel when melilite first crystallizes at cooling rates of 2°/hr or less. The melt composition at the start of melilite crystallization was calculated from the starting composition and the amount of spinel crystallized, assuming spinel/liquid partition coefficients for REE of 0; the composition of glass quenched at the end of melilite crystallization was measured. The compositions of initial (Åk₂₃) and final (Åk₆₃) melilite in the 2°/hr sample were extrapolated from plots of REE concentration vs. distance.

Our data for Åk₂₃ and Åk₆₃ for the 2°/hr run (Fig. 1) are consistent with the finding of Beckett *et al.* [1] that $D_{REE} = k \times X_{Ge}/X_{Åk}$ and are in excellent agreement with Beckett *et al.* for the proportionality constant for the two REE measured in both studies, La and Ce. The following values of k were found for the 2°/hr run: Y, 0.068; La, 0.095; Ce, 0.070; Nd, 0.133; Sm, 0.133; Eu, 0.128; Gd, 0.126; Dy, 0.084; Er, 0.062; and Lu, 0.032. The shapes of the curves in Fig. 1 are similar to that reported by Nagasawa *et al.* [6] for Åk₁₅ melilite. We found, in agreement with Beckett *et al.* [1], that D_{Ce} is significantly lower than D_{La} and that there is a negative Ce anomaly among the Ds. This is caused by the presence of tetravalent Ce in the melt, due to the oxidizing conditions of the experiments. There is no Eu anomaly in the Ds, because all Eu is trivalent



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under the oxidizing conditions of the experiments.

There is some decidedly anomalous partitioning behavior in our experiments compared to expectations from the $D_{\text{REE}} = k \times X_{\text{Ge}}/X_{\text{Ak}}$ relationships. An example is shown for La in Fig. 2. Here we have plotted measured La concentrations in melilite in all of our experiments, along with a calculated fractional crystallization curve using $k_{\text{La}} = 0.095$. In calculating this curve, we have followed Beckett *et al.* [1] and assumed that $F = A + B/X_{\text{Ak}}$, where F is the fraction of melt. A and B were calculated from the beginning and end points of melilite crystallization in the 2°/hr experiment, 89% melt and Ak_{23} at the beginning and 38% melt and Ak_{63} at the end. While calculated melilite La contents agree with measured ones at the low-Ak and high-Ak ends, all intermediate Ak melilites have La contents that are lower than expected, regardless of cooling rate. Furthermore, over narrow ranges of Ak content at the beginning of crystallization of the 2 and 20°/hr runs, La contents vary by a factor of 2. Over this narrow range, D_s should vary little and reservoir effects are insignificant. The D_s for all REE at faster cooling rates appear to be lower than those measured at 2°/hr.

Crystallization history of Type B CAIs. In Fig. 3, we compare the La contents of a single melilite crystal in each of three Type B CAIs with those calculated from a simple fractional crystallization model. The latter were calculated in the same way as in Davis *et al.* [2], except that we used our new k value, above, and we calculated the bulk composition of each CAI from modal abundances of phases [7] and average La contents of these phases [2, 8, unpublished data]. As found earlier [2], CAI melilite contains far more La than that calculated from simple fractional crystallization models using measured melilite/liquid partition coefficients. Plots for other REE show a similar discrepancy between models and CAIs. There is another discrepancy between CAIs and experiments: in CAI melilite, REE abundances (except for Eu) drop fairly smoothly from La to Lu and REE patterns become more steeply LREE-enriched with increasing Ak. According to models using measured partition coefficients, melilite crystallized from a CAI with a flat bulk REE pattern should have REE patterns with shapes like those in Fig. 1; in addition, those models do not predict significant fractionation of REE from one another.

It is now clear that CAI crystallization at cooling rates faster than 2°/hr cannot explain the enhanced trace element contents or the shapes of the REE patterns of Type B CAI melilite. Dissolution of trace element-rich precursors during melilite crystallization also does not work [3]. There are several other possibilities, which we plan to test experimentally: (1) partition coefficients of REE are significantly enhanced under reducing conditions; (2) evaporation of Mg and Si from the melt during melilite crystallization concentrated refractory trace elements in the melt; (3) postcrystallization diffusive reequilibration altered trace element abundances without significantly changing melilite major element composition.

References: [1] Beckett J. R. *et al.* (1990) *GCA* **54**, 1755–1774. [2] Davis A. M. *et al.* (1992) *LPS* **23**, 281–282. [3] Simon S. B. *et al.* (1996) this volume. [4] Stolper E. (1982) *GCA* **46**, 2159–2180. [5] Stolper E. & Paque J. M. (1986) *GCA* **50**, 1785–1806. [6] Nagasawa H. *et al.* (1980) *EPSL* **46**, 431–437. [7] Beckett J. R. (1986) Ph.D. dissertation, U. of Chicago. [8] Simon S. B. *et al.* (1991) *GCA* **55**, 2635–2655.

