

EXPERIMENTAL DETERMINATION OF Li, Be AND B PARTITIONING DURING CAI CRYSTALLIZATION F.J. Ryerson¹, J.M. Brenan² and D.L. Phinney³, ¹IGPP, Lawrence Livermore National Laboratory, Livermore, CA 94530; ryerson1@llnl.gov, ²Department of Geology, University of Toronto, 22 Russell St, Toronto, Canada M5S 3B1; brenan@geology.utoronto.ca, ³Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, CA 94530; phinney1@llnl.gov.

Introduction: The main focus of the work is to develop a better understanding of the distribution of the elements B, Be and Li in melilite, fassaite clinopyroxene, anorthite and spinel, which are the primary constituents of calcium-aluminum-rich inclusions (CAIs). These elements are the parent or decay products of short-lived nuclides (specifically, ⁷Be and ¹⁰Be) formed by cosmic ray spallation reactions on silicon and oxygen. Recent observations suggest that some CAIs contain “fossil” ⁷Be and ¹⁰Be in the form of “excess” amounts of their decay products (B and Li). The exact timing of ⁷Be and ¹⁰Be production is unknown, but if it occurred early in CAI history, it could constrain the birthplace of CAIs to be within a limited region near the infant sun. Other interpretations are possible, however, and bear little significance to early CAI genesis. In order to interpret the anomalies as being “primary”, and thus originating at high temperature, information on the intermineral partitioning of both parent and daughter elements is required.

Experimental Technique: Partitioning experiments were performed over a range of temperatures (1220–1350°C) using a bulk composition corresponding to the CAIB eutectic, as determined by Stolper [1] (glass composition from experiment CAI20). The CAI20 composition was synthesized from high-purity oxides and carbonates, calcined at 1100°C for 12 hours, ground, then fused at 1500°C for four hours and reground. To this composition we added various proportions of synthetic melilite (Ge60) oxide mix or fassaite glass to produce the desired mineral assemblage at a specific temperature. Preliminary experiments to measure spinel-melt partitioning employed a CAI20 composition that had been pre-saturated in a spinel crucible. Samples were prepared by adding a predetermined amount of B, Be and Li (as ICP standard solutions) to a 2 mm ID Pt capsule, then approximately 25 mg of sample powder. Experiments were done using trace element additions at the 10 and 100 ppm level. The powder plus solution were then dried at 350°C for several hours, and the capsule was crimped and welded shut. Samples were homogenized by fusion at 1400°C for 15–20 minutes. For the case of experiments to measure anorthite- or fassaite-melt partitioning, the capsule was cut open after the fusion step, and a small amount of natural diopside or anorthite powder was added to promote nucleation. Such samples were then crimped and rewelded. All partitioning

experiments were conducted by plunging capsules into the predetermined hotspot of a vertical tube furnace, isothermal soaking for 24–72 hours, then quenching in a water bath. Temperature was monitored throughout the run with an adjacent Pt-Pt10%Rh thermocouple. Capsules were weighed before and after each experiment, and those showing any post-experiment weight loss, or visible glass on their exterior were discarded.

Analytical methods: The major element composition of run-product phases was determined by electron microprobe, and backscattered electron images were also collected for phase identification and to assess gross sample homogeneity. Concentrations of B, Be, and Li were measured using a Cameca IMS-3F ion microprobe at LLNL employing methods previously described in Brenan *et al.* [2, 3]. Trace element concentrations were determined by comparing the ³⁰Si-normalized isotopic ratios of the samples to those of NIST glass standards. As a result of surface contamination, the count rate for ¹¹B usually decayed from somewhat elevated values to a constant level only after the first 10–15 counting cycles (i.e., 10–15 min on most mineral specimens); only the data obtained in subsequent cycles was considered to reflect the intrinsic abundance within the sample. Partition coefficients were calculated from the ratio of the average ³⁰Si-normalized count rate of an isotope in the mineral to that in the glass. In most cases, analyses of quenched melt and crystals yielded a standard deviation from separate spots that was similar to errors based on counting statistics (i.e., ~1%).

Results and Discussion: Run products consist of 1–3 crystalline phases (1–200 mm in diameter, Figure 1) in contact with melt. Partition coefficients for melilite, ~Ak₅₀, are highest (Table 1), with $D^{\text{mel-melt}}$ for Be approaching unity, in rough agreement with previous results [4]. Melilite does not strongly fractionate Li and Be, with D(Be)/D(Li) ~ 1.6 for Ak₅₀. Boron is more incompatible, with D(Be)/D(B) ~ 4. Though more incompatible, the pattern of anorthite-melt partitioning, D(Be) > D(Li) > D(B), is similar to melilite, with absolute values ~10 X lower. For anorthite D(Be)/D(Li) ~ 1.6 and D(Be)/D(B) ~ 12. The fractionation of Li and B observed here is similar to that determined for plagioclase in equilibrium with melts of Martian basalt compositions [5], but with absolute values for CAIs are ~10 X lower. Clinopyroxene compo-

sitions lie in the Di-CaTs-CaTiAl₂O₆ ternary, and require no Ti⁺³. Major element zoning is absent, but Al₂O₃ concentrations vary from 10-18 wt% between experiments. Li, Be and B are all incompatible in Cpx and, in general, D^{cpx-melt} is positively correlated with Al concentration (Table 1). For the Cpx-melt pairs in which the in Cpx is ~ 10 wt%, D(Be)>D(B)>D(Li). For Al₂O₃ in Cpx ~ 18 wt% D(Be)>D(Li)>D(B), suggesting that the relative fractionation of these elements is composition dependent. This is more strongly demonstrated by comparison with the results from Cpx-haplobasaltic melts in which the pattern is D(Li)>D(B)>D(Be) [3] where D(Be)/D(Li) in the haplobasaltic compositions reaches values as low as ~0.02, while D(Be)/D(Li) for CAI are 4-6.

The range of Be/B and Be/Li in melilite, anorthite and clinopyroxene generated by igneous processes can be simulated using these partition coefficients (assuming D(Li, Be, B)=0 for spinel) in conjunction with the phase proportions from Stolper [1]. We use the data for Ak₅₀ presented here, as there is currently no data on the composition dependence of D^{mel-melt} for Li and B. The model predicts a limited range of melilite compositions. Be/B and Be/Li for the first-crystallized melilite will be ~4 × and ~ 1.6 × that of the bulk CAI. Be/B and Be/Li in melilite decrease crystallization by factors of 1.7 and 1.3, respectively, over 75% crystallization of the CAI. The first-crystallized anorthite would have Be/B and Be/Li ~8 × and 1.4 × that of the bulk CAI, respectively, and decrease by only 10% between 55% and 73% crystallization. Finally, at 73% crystallization, the first-crystallized Cpx would have Be/B and Be/Li ~5 × and 3 × that of the bulk CAI, respectively. While the range of melilite compositions predicted is small, a majority of observed melilite compositions fall within a factor of two of the predicted range. More extreme compositions can be generated in the last phases of crystallization.

The model predicts that Be/Li(Cpx) > Be/Li(Mel) and that Be/B(Cpx) ≥ Be/B(Mel). Of 29 melilites in an Allende CAI (3529-41)[6] and two Vigarano CAIs (Vig. 1623-9, and 477-4b) [7], 18 have Be/Li less than or equal to that of the measured fassaite in each sample. Conversely, the Be/B data disagree with the model as Be/B is always greater in melilite than in Cpx by factors of 3 to 6000. Using the Cpx-melt partitioning data from haplobasaltic compositions [3] reduces the Be/B(Cpx) yielding predicted compositions in much better agreement with observation. The disparity is largely due to the anomalous compatibility of Be in Cpx relative to Li and B the CAI compositions relative to haplobasaltic system. If this pattern can be confirmed by further experiment and analysis, it would indicate that the Be/B compositions in CAIs are effected by processes other than mineral-melt partition-

ing, or that compositions of Cpx in these experiments (performed in air, Ti⁺³ absent) does not mimic crystallization under more reducing conditions.

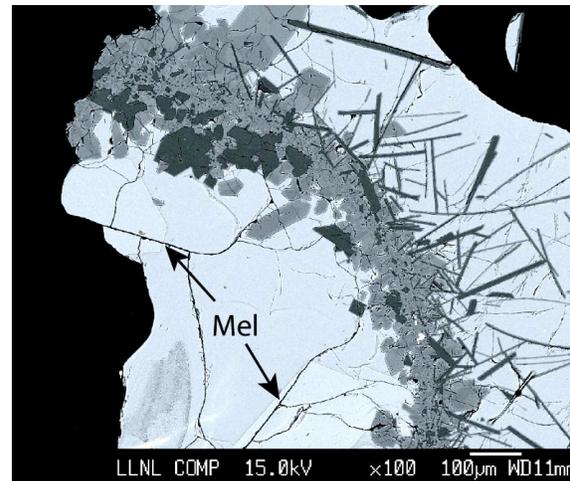


Figure 1. Backscattered electron image of a portion of an experiment run at 1220°C. Run contains An (dark), Cpx (med. gray), Melilite (arrows) and glass.

Table 1. Mineral-melt partitioning data

Mineral, T, ppm added	Li	Be	B
Mel. (Ak ₁₀₀) 1220, 100	0.534	0.550	0.054
Cpx 1220, 100 ppm (1)	0.009	0.073	0.015
Anorthite 1220, 100	0.033	0.054	0.004
Cpx, 1220, 10	.0048	.0289	.0155
Mel. (Ak ₅₀) 1245, 100	0.450	0.749	0.186
Mel. (Ak ₅₀) 1245, 10 (6)	0.368	0.600	0.130

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