

REFRACTORY LIPHOPHILE ELEMENT CONCENTRATIONS IN MELILITE FROM A TYPE B1 CAI: THE ROLE OF RELICT PHASES. J. M. Paque¹, D. S. Burnett, J. R. Beckett and Y. Guan, California Institute of Technology, Pasadena, CA 91125, ¹jheather@gps.caltech.edu.

Introduction: Based on petrography and experimental studies, Type B CAIs formed by fractional crystallization, but concentrations of refractory lithophile trace elements in Allende Type B1 CAI melilite do not agree with expectations from fractional crystallization [1-4]. As a first step in reinvestigating this problem, we obtained SIMS analyses on melilite in the Type B1 CAI Leoville 3537-2. This choice minimizes the issue of extensive secondary alteration that is present in all Allende CAIs.

Analyses: The Zinner-Crozaz energy offset technique was adapted to the Caltech Cameca 7f Geo ion microprobe. Data are from two sessions: In 2009 we measured: ⁷Li, ⁹Be, ⁴⁹Ti, ⁸⁸Sr, ⁸⁹Y, ¹³⁸Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁵³Eu, plus ⁴²Ca as a reference, and Na and ⁵⁶Fe to monitor the presence of alteration and surface contamination. In 2010, we dropped Na, Fe, La, and Eu, added Sc and Zr, and used ⁴⁰Ca as a reference isotope.

Standards: Two standards were used: an Åk₄₀ melilite glass [5] and a CAI Type B bulk composition glass doped with Sr, Y, Ba, La, Ce, and Eu at levels

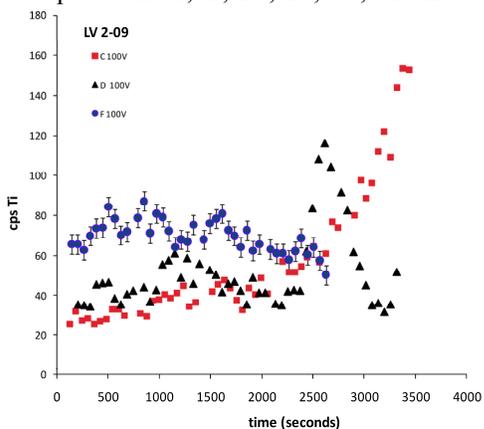


Figure 1. Ti counts as a function of time in mantle melilite.

analyzable by electron probe (nominal 1000 ppm). Li sensitivity factors were calculated from a $1e13/cm^2$ ⁶Li implant into synthetic single crystal åkermanite.

Results: Comparison with fractional crystallization. To avoid potential complications with remelting, as well as the increased uncertainties in modeling changes in liquid composition upon the onset of clinopyroxene and anorthite crystallization, initial analyses were confined to mantle melilite.

As shown in Fig. 1, Ti profiles frequently contain hot spots, indicating Ti-bearing inclusions, up to 0.1-0.2 μ m thick. The identity of these minerals is uncertain. Although high resolution SEM images show rod-

like perovskite or UNK (0.5x1 μ m) near the SIMS pits, these grains are much larger than those generating Ti

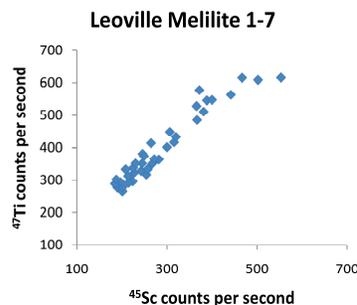


Figure 2. Correlation of Ti and Sc in a single melilite point.

hot spots during SIMS analysis. With the exception of Sc, analyzed elements show no correlation with the Ti hotspots (Zr data are not yet available). Given the large LREE enrichment typical of perovskite

and the absence of Ti-Y or Ti-La correlations, it seems unlikely that the Ti hotspots reflect perovskite inclusions. The Ti hotspots are also unlikely to be associated with WL rim formation because they occur in analyses 100s of μ m from the rim. In many, but not all, profiles there is an excellent correlation between Sc and Ti (Fig. 2) suggesting that the hot spots may be due to clinopyroxene or UNK.

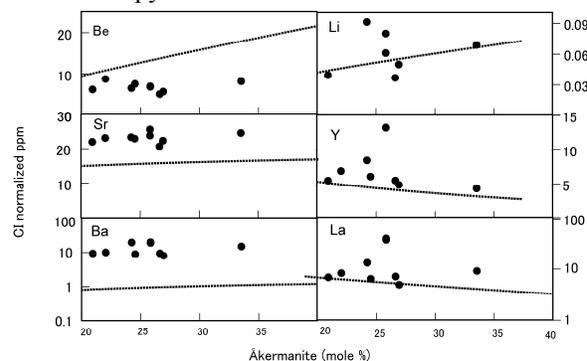


Figure 3. CI normalized trace elements concentrations in melilite as a function of Åkermanite content.

Fig. 3 compares our measured concentrations of trace elements as a function of mole % åkermanite in melilite (Åk) with predictions for fractional crystallization (solid curves) constructed assuming that melilite crystallized from a homogeneous molten inclusion using bulk concentrations for the inclusion from [6]. Note that the Ba and La plots are on log scales. Discrepancies are similar to those found in Allende CAIs by [1-4]. There are significant compositional changes due to evaporation for Type B1 CAIs (e.g., [7]), but this has not been considered in the fractional crystallization models used here. Plots for Ce and Eu are not shown; these elements are almost perfectly correlated

with La and Sr (suggesting that Eu is 2+), respectively. Be differs from the other refractory elements in that measured concentrations are lower than predictions, but the larger number of melilite analyses of [1] show scatter both above and below the fractional crystallization trend. The similarity of our results for an unaltered Leoville CAI with those for Allende Type B1 inclusions [1-4] implies that alteration in Allende CAIs did not disturb melilite refractory lithophile trace element concentrations.

A relict phase model for lithophile trace element abundances. Similar to [4], we assume that refractory lithophile trace element carrier phases (e.g., perovskite, allendeite, davisite, barioperovskite) were among the precursor crystals that were present in the outer regions of the inclusion during melting and either (a) dissolved to produce local heterogeneities in liquid composition leading to anomalously high concentrations of trace elements in mantle melilite that crystallized from these liquids, or (b) were trapped as undissolved grains in mantle melilite, or (c) reacted with the liquid to produce other phases that were then incorporated into the crystallizing melilite. These alternatives are not mutually exclusive. SIMS analyses are sensitive to nano-sized inclusions because of the small volume sampled

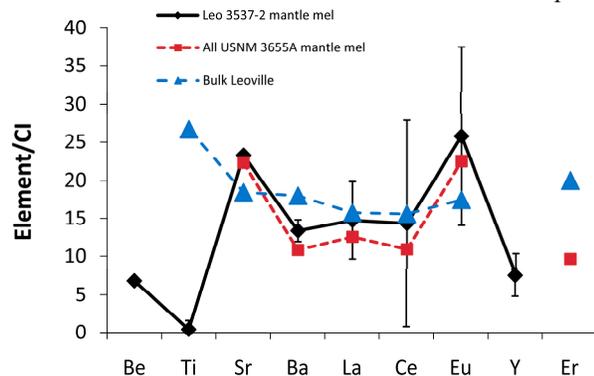


Figure 4. CI-normalized abundance pattern for representative mantle melilite in Leoville 3537-2. Shown for comparison are patterns for the bulk inclusion [6] and a typical mantle melilite pattern for Allende Type B1 inclusion 3655A [4].

at any given moment. The relict phase model can explain the observed large amount of variability. In an extreme version of this model, crystal-liquid partitioning is irrelevant; melilite is simply a carrier for the dispersed grains, and the melilite abundance pattern then reflects the bulk concentrations (approximately flat CI-normalized pattern for Leoville 3537-2). Fig. 4 shows abundance patterns for melilite from Leoville 3537-2 and Allende USNM 3655A [4] as well as the bulk Leoville pattern [6]. "Error bars" are the standard deviations among all mantle analyses. Note that Sr, Ba,

La, Ce, and Eu data have *average* concentrations close to those of the bulk CAI, consistent with expectations for relict phases, provided that, initially, they were relatively uniformly distributed on average. The depletion of Ti (and perhaps Y and heavy REE, represented here by Er), reflects partitioning after dissolution of the Ti carrier. Perovskite as a relict phase was suggested by [4], Figs. 1-3 suggest that phases in addition to perovskite were/are present.

If the melilite refractory lithophile trace element abundances are due to solid precursor grains, progressive dissolution of the grains with increasing melilite crystallization should generate progressively higher concentrations in the liquid because these are all incompatible elements for aluminous melilites. This ef-

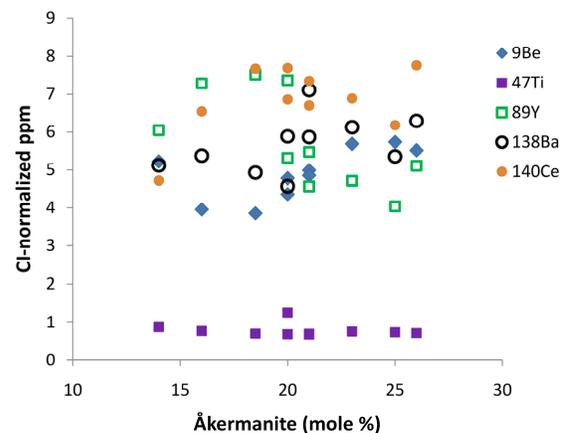


Fig. 5. CI normalized trace elements in a single crystal of melilite from the mantle of Leoville 3537 as a function of Åk.

fect is not seen in terms of Åk correlations for analyses obtained from random points (Fig. 1). In single crystals near the rim of the inclusion, we observe systematic behavior (e.g., Fig. 5) but monotonic trends with either Åk or distance from the rim, as expected for simple fractional crystallization, are not present. The role of evaporation remains to be considered.

Summary: Control of refractory lithophile abundances in CAI Type B1 melilite by relict phases other than perovskite is strongly indicated. Looking forward we will consider the role of evaporation and use ratios derived from interelement correlations to try to indentify the relict phases.

References: [1] Davis A. M. et al. (1992) *LPS XXIII*, 281-281. [2] Simon S. B. et al. (1996) *LPS XXVII*, 1201-1202. [3] Davis A. M. et al. (1996) *LPS XXVII*, 291-292. [4] Kennedy A. K. et al. (1997) *GCA 61*, 1541-1561. [5] Beckett J. R. et al. (1990) *GCA 54*, 1755-1774. [6] Sylvester P. J. et al. (1992) *GCA 56*, 1343-1363. [7] Grossman L. et al. (2008) *GCA 72*, 3001-3021.