

LOW TEMPERATURE CARBONATE CONTROL OF BARIUM IN IGNEOUS Ca-, Al-RICH INCLUSIONS. J. M. Paque^{1,2}, D. S. Burnett¹, J. R. Beckett¹, Y. Guan¹, and H. A. Ishii³. ¹California Institute of Technology, Pasadena, CA 91125; ²julie@paque.com; ³Institute of Geophysics and Planetary Physics, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550.

Introduction: Based on petrography and experimental studies, Type B CAIs formed by fractional crystallization of molten droplets but trace element distributions are often at odds with a simple dynamic crystallization history. Barium is the most egregious example [1]. The experimentally determined partition coefficients (D_i) between melilite and melt [2] show the element to be highly incompatible with D_{Ba} of 0.04 – 0.05. Observed concentrations of Ba in early crystallizing meteoritic melilite would, however, require that D_{Ba} be an order of magnitude higher. Similar, though less extreme, discrepancies exist for Sr, Ti, Sc, and the REE [1,3]; the concentrations are often much more scattered at a given åkermanite content than would be expected for crystallization of melilite from a homogeneous liquid.

Recently we demonstrated for Ti, Sc, and Zr that clinopyroxene inclusions in melilite from the Type B1 CAI Leoville 3537-2 (hereafter LV) caused the scatter and high apparent concentrations of these elements relative to expectations based on the experimental partitioning data [4]. The clinopyroxene inclusions did not, however, contribute significantly to anomalously high Ba or Sr. Here we report nanoSIMS measurements aimed at understanding the origin of observed Ba concentrations in melilite from the Type B1 CAIs LV and Allende USNM 5241 (hereafter 5241), which was previously studied by [3].

Analyses: The Zinner-Crozaz energy offset technique was adapted to the Caltech Cameca 7f Geo ion microprobe. Two standards were used: an Åk₄₀ melilite glass [2] and a CAI Type B bulk composition glass doped with Ba, at levels analyzable by electron probe (nominal 1000 ppm). 7f data on 5241 were obtained for LiBeKCaScTiSrYZrBaCe. Sensitivity factors were as in [4]. Qualitative nanoSIMS imaging was made with the Caltech Cameca 50L in the multicollector mode using positive secondaries for CaScTiSrYBaCe for LV, and negative secondaries for C CN Si S Cl AlO and SrO (LV) and C Si S Cl NaO AlO FeO (5241).

Results for LV: Fig. 1 shows C and Ba ion beam images for the same location in LV mantle melilite near the inclusion rim. The linear feature in the upper portions of the panels is also rich in Ca and Sr (concentrations are higher than in the surrounding melilite). This feature is part of a carbonate vein and it contains high concentrations of Ba and Sr. Leoville is a find,

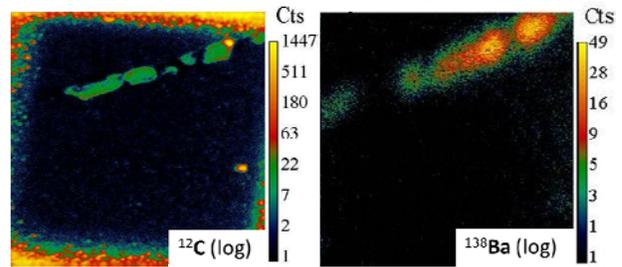


Fig. 1. Leoville mantle melilite 10x10 µm images (mel3-B).

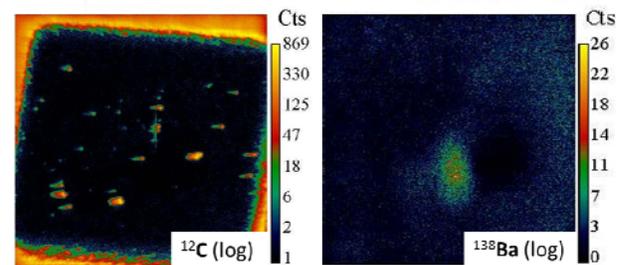


Fig. 2. Leoville mantle melilite 10x10 µm images (rim8-1).

and terrestrial carbonate veins are present in other sections of LV [5] but veins like those imaged in Fig. 1 do not break the inclusion rim and, so, could be pre-terrestrial.

Not every Ba hot spot is due to a carbonate. Fig. 2 shows an LV area with a Ba hot spot, but no corresponding enhancement in C or any other element. Of our 9 Ba images in LV melilite, we obtained negative secondary images of the 4 that had Ba enrichments. Two of the 4 demonstrated that they were carbonates and 2 were produced by some other phase.

Results for 5241: It is likely that the Ba-rich carbonates in LV reflect carbonate precipitation, whether terrestrial or preterrestrial, during secondary alteration and that this material, along with noncarbonate inclusions, significantly affected measured concentrations in melilite by SIMS. No carbonate has been recognized in an Allende Type B1 inclusion but [1] found anomalously high Ba concentrations in the melilite, so we analyzed mantle melilite in 5241 [e.g., 3].

We have not yet conducted Ba imaging in 5241 but we did test for carbonates and other inclusions in 5241, through 24 10x10 micron negative secondary nanoSIMS images of mantle melilite on locations previously analyzed for Ba with the 7f, mostly at the bottom of the roughly 40 micron wide, 0.5-1 µm deep pits. We resorted to imaging within SIMS pits because in 5241, unlike LV, confusion in C images from sur-

face contaminant particles was a serious problem, that was not entirely eliminated by typical amounts of presputtering. Within the 7f pits, ion-beam mixed surface contamination, e.g., of Li or Na, is completely removed. Figure 3 shows an image of a C-, Na-rich vein in a high Ba 7f pit. The vein is also Fe-rich, and has S and a small amount of Cl. NanoSIMS CaSrBa positive secondary images can unambiguously settle whether this or other C rich features are carbonate. We emphasize that the features in Fig. 3 are present 0.5-1 micron below the section surface and are not obviously due to particulate surface contamination.

We observe variable Ba concentrations on all scales but, compared to the spectacular variability in intraspot depth profiles for TiScZr in LV [4] due to

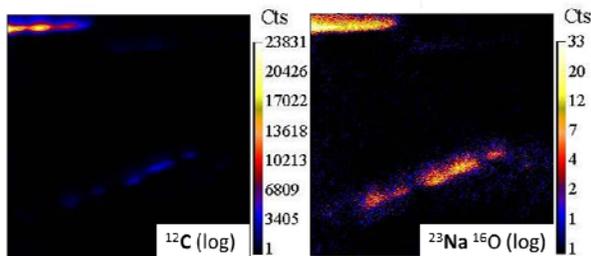
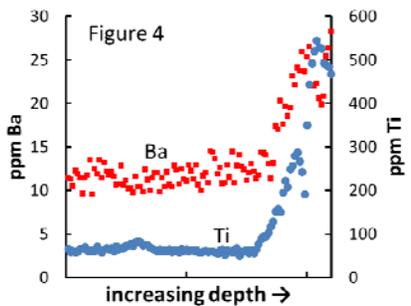
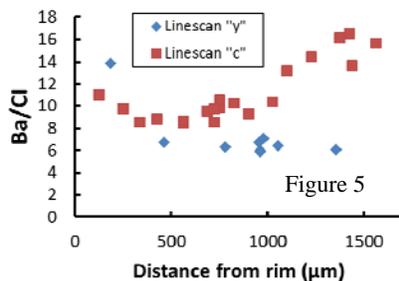


Figure 3. 5241 images from 10x10 μm area near the rim. micron size clinopyroxene inclusions, intraspot variability for Ba is muted. For Ba in 5241, the overall variations are within 2 sigma counting statistics for 80-90% of the profiles. Generally, intraspot variation

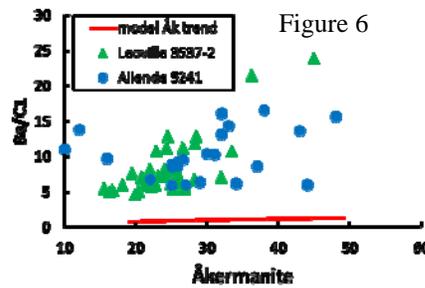


within LV Ba profiles is larger than in 5241 analyses, probably the effect of the carbonate alteration. However, one 5241 profile (Fig. 4) show clear evidence for a Ba and Ti-rich inclusion. The inclusion is rich in Y and Ce, but not Sc or Zr, and so is probably a Ba-rich perovskite.

The mm-scale interspot variations in 5241 show regular behavior in terms of distance from the inclusion rim (Figure 5). Both profiles in Figure 5 are



within large melilite single crystals. The trends similar over the first 500 microns in that Ba decreases monotonically, but are very different at greater depths, with Ba flattening in profile y and rising as a function of



distance in profile c. Analogous profiles in LV are scattered. Ba in melilite from LV and 5241 are plotted vs. Åk content in Fig. 6. Overall, Ba concentrations are similar in the two CAIs and much higher than expected from fractional crystallization, as shown by the red curve.

Discussion: The anomalous behavior for Ba in CAIs, recognized as far back as [6], remains unexplained. However, feasible extensions of the measurements reported here can result in significant progress: For example, positive secondary nanoSIMS and SEM imaging on the same spots in 5241 that show C concentrations can settle whether the carbonate control of Ba, which is seen in LV, is also significant in Allende inclusions. FIB/TEM studies of the non-carbonate Ba hot spots in LV can additionally constrain the nature of Ba host phases (the Ba hotspot in Fig. 2 is not perovskite). These could be primary nebular condensates, phases precipitated in the residual liquid during volatilization, or secondary phases other than carbonates that precipitated during metasomatism. It is somewhat ironic that, for this study, the distribution of Ba in the nominally-unaltered LV CAI may be more sensitive to alteration than an obviously altered Allende CAI. Even if carbonate alteration has no role in introducing Ba in general, the possibility of Ba introduction during the alteration associated with melilite O exchange is a model worth considering. Finally, although we emphasized Ba in this report, nanoSIMS imaging also revealed a large amount of interesting structure in other elements potentially related to secondary alteration processes.

References: [1] Davis A. M. et al. (1992) *LPS XXIII*, 281-282. [2] Beckett J. R. et al. (1990) *Geochimica et Cosmochimica Acta*, 54, 1755-1774. [3] MacPherson G. J. et al. (1989) *Geochimica et Cosmochimica Acta*, 53, 2413-2427. [4] Paque J. M. et al. (2011) *LPS XLII*, Abstract #2096. [5] Patzer A. et al. (2012) *Meteoritics & Planet. Sci.*, 47, 142-157. [6] Grossman L. et al. (1977) *Geochimica et Cosmochimica Acta*, 41, 1647-1664.