

ELECTRON PROBE AND ION PROBE DETERMINATION OF MELILITE/LIQUID AND CLINOPYROXENE/LIQUID PARTITION COEFFICIENTS OF TRACE ELEMENTS IN CMAS AND NaCMAS; S.M. Kuehner¹, J.R. Laughlin², L. Grossman¹, M.L. Johnson³ and D.S. Burnett³; ¹Dept. of Geophysical Sci., ²Dept. of Chemistry, Univ. of Chicago, Chicago, IL 60637, ³Geological & Planetary Sci., CalTech, Pasadena, CA 91125.

Types A and B refractory inclusions (1) display complex textural and chemical patterns, suggesting that a variety of processes may have been involved in their genesis. In order to identify those features resulting from igneous processes, Woolum *et al.* (2) initiated a project to determine the partitioning of trace elements between melilite and coexisting liquid using synchrotron X-ray fluorescence and applied these results to measurements of the same elements in CAI melilite. We initiated a parallel study based on ion probe techniques. Previous studies show that energy filtering strongly reduces molecular interferences, but systematics for the accuracy of ion probe data for specific elements in specific minerals are not known. Thus, the first stage of this study has focussed on an electron probe/ion probe comparison of data obtained from synthetic samples with Sr, Y, Zr, La, Sm and Yb present at percent levels. An important advantage of this comparison is that electron and ion probe analyses can be made on the same spot, eliminating potential uncertainty due to sample heterogeneity. At least for melilite, the synthetic samples can be used as standards for ion probe analyses of CAI to an accuracy determined by the electron probe calibration.

Starting materials of melilite Ak₈₀ and Ak₄₀ composition (obtained from J. Beckett) and of Di₂AbAn (weight) composition were spiked with a nitric acid solution of the trace elements, heated in open Pt tubes to 1000°C, then totally fused and ground twice. The typical synthesis procedure was to heat to a superliquidus temperature (1 atm) and then cool quickly into the two phase field for melilite or diopside + liquid. Such a thermal history is not optimum for partition coefficient measurements because of the tendency for rapid crystal growth and disequilibrium partitioning due to formation of compositional boundary layers. To obtain a sample with lower crystal growth rate, one diopside sample was made by cooling about 65 degrees below the liquidus at 2 deg/hr. Superliquidus quench samples of each starting composition were also analyzed. All EPMA data were obtained from an automated CAMECA SX-50 microprobe using wavelength dispersive techniques. Operating conditions were 15 kV, 25 nA for major elements and 25 kV, 200 nA for trace elements, and a 5 µm beam diam. An automatic two-condition analysis routine allowed sequential acquisition of major and trace elements at each point. The synthetic glasses REE2, REE3 and X-glass were used as trace element standards. Diopside glass and a natural albite crystal were used for major elements. Counting times for trace element determinations were 120-360 sec, resulting in detection limits of 0.008-0.001 oxide wt %, and an analytical uncertainty of 0.013-0.004 oxide wt %. Crystals and glass were also measured for major and trace elements by the Chicago ion probe. A 20 nA O⁻ primary beam current was used, resulting in a spatial resolution of ~ 15 µm; energy filtering was used. Relative ion yields are proportionality constants between the ratio of count rates and the ratio of concentrations of two elements. Relative ion yields and their dependence on energy filtering were determined by analyzing X-glass, V-glass and W-glass under various energy conditions. Concentrations of Sm and Yb were based on their ion yields relative to La. Good agreement was obtained between ion and electron probe analyses for 2 melilite quench glasses, 1 diopside sample and particularly for 2 glasses from the Di₂AbAn samples. While the largest difference is 30% relative, many analyses agree to better than 10%. For the melilite glass samples, the greatest disagreement was in SiO₂, which was underestimated by the ion probe by ~ 5% absolute. Therefore, when relative concentrations of all elements present are normalized to 100%, all of the other concentrations are overestimated by ~ 5% relative. Presumably, better agreement between ion and electron probe data for SiO₂ in Di₂AbAn was obtained because the compositions of the standard glasses are much closer to the Di₂AbAn composition than to the melilite. To correct for matrix effects, new ion yields have been calculated to reproduce the electron probe data. In future, ion yields determined from the melilite standards will be used for melilite samples.

SEM study shows that melilite grains typically have blocky shapes, ~ 150 x 200 µm in size, occurring singly or in small clusters. BEI shows that a bright fringe region, ~ 2 µm wide, occurs along the margin of each melilite grain and grades outward into the adjacent glass. Analysis of these boundary layers shows that they are enriched in the elements incompatible in melilite (all trace elements except Sr), with concentrations up to 3X that of the homogeneous glass away from the crystals. Electron probe traverses across individual melilite grains from Ak₈₀ starting compositions show them to be homogeneous in major elements (Ak₈₀) but result in U-shaped trace element patterns having a maximum enrichment in crystal rims of 3-4X that of the crystal interiors. In the

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Ak40 starting composition, one large crystal fragment (950 x 500 μm) has a distinct outer rim, $\sim 100 \mu\text{m}$ wide, defined in BEI by having a lower albedo than the core. Major element concentrations are identical in the two regions (Ak12) but the core is $\sim 10\%$ richer in REE than the rim. The range of minor element concentrations in the large grain overlaps concentrations obtained from random analyses of smaller melilite fragments. Unlike the melilite-bearing samples, pyroxene grains from the Di2AbAn starting composition do not have distinct trace element-enriched boundary layers, but glass adjacent to crystal boundaries shows a very subtle, $\sim 10\%$, increase in ZrO_2 compared to glass away from the grains, and a distinct enrichment of Al_2O_3 and depletion of MgO at the crystal boundary. In the rapidly-cooled sample, individual pyroxene grains are $> 1000 \mu\text{m}$ long and very uniform in major element composition. Trace element contents vary by as much as a factor of 2 between grains, however, indicating that equilibration of trace elements was incomplete. The slowly-cooled sample has many large crystals, up to 700 μm long, with more uniform major and trace element contents.

SEM and EPMA studies show a high degree of variability of trace element contents in melilite crystals, presumably due to boundary layer enhancements accompanying rapid crystal growth. For melilite, partition coefficients were estimated by assuming that crystal core concentrations are representative of the initial stages of crystal growth and presumably the growth conditions with the minimum boundary layer formation. Thus, partition coefficients plotted in Fig. 1 were calculated using compositions of melilite crystal cores and the initial glass. D values for REE and Y are 15-30X greater in Ak12 than in Ak90 and are in reasonable agreement with the partition coefficients of Nagasawa *et al.* (3), who also used starting materials of \sim melilite composition. The partition coefficients of Woolum *et al.* for melilite (\sim Ak30) grown from a liquid of Type B CAI composition are intermediate between our Ak12 and Ak90 results. All data are regarded as preliminary at present, but a strong composition/temperature dependence of melilite partitioning is clear.

For the Di2AbAn composition, clinopyroxene partition coefficients for the slowly-cooled sample are closer to equilibrium values, although intrasample variability is observed due to the temperature dependence of partitioning (4). Differences between ion and electron probe data tend to cancel when partition coefficients are calculated. Results (Fig. 2) agree fairly well with previous work (5). These data will provide a basis for comparison with those obtained in future studies on Ti-rich clinopyroxene samples more analogous to those of CAI.

Refs.: (1) Grossman, L. (1980) *Ann. Rev. Earth Planet. Sci.* 8, 559. (2) Woolum, D.S. *et al.* (1987) 50th Met. Soc. Mtg. (3) Nagasawa, H. *et al.* (1980) *EPSL* 46, 431. (4) Jones, J. & Burnett, D.S. (1987) *GCA* 51, 769. (5) Grutzeck, S. *et al.* (1974) *GRL* 1, 273.

