NON-EQUILIBRIUM TRACE ELEMENT PARTITIONING AND RELICT GRAINS IN A TYPE B1 CAI;

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In order to investigate the igneous processes involved in the formation of melilite-, fassaite-rich CAIs, crystal/liquid distribution coefficients, D, of trace elements in these phases were experimentally determined by (1) and (2). We now report the application of melilite/liquid D-values to melilite compositions in TS23F1, a well-studied Allende Type B CAI, in order to further understand the history of this inclusion. We also report additional EMP, IMP and SEM data relating to the formation of TS23F1 and Type B1 CAIs in general. TS23F1 is circular in section, $\sim$ 9 mm in dia., with a prominent melilite mantle comprising $\sim$ 45 volume % of the inclusion (3). The inclusion contains several interior melilite grains, $\sim$ 1-1.5 mm long, with complicated zoning patterns (4): the melilite cores are zoned normally ($\sim$ Ak_{25}-Ak_{73}) but the zoning abruptly reverses near the rim (back to $\sim$ Ak_{52}), followed again by normal zoning (to $\sim$ Ak_{60}). This chemical profile has been reproduced experimentally (4) and found to result from the progressive crystallization of melilite, melilite + fassaite, melilite + fassaite + anorthite (all + spinel) at cooling rates < 50 C°/hr.

IMP analyses of the normally zoned core of an interior melilite are shown in Fig. 1a,b. The trend of decreasing La, Ce, Y (=HREE) with increasing X_{Ak} is broadly consistent with that predicted from the decline of $D_{REE^{3+}}$ with increasing X_{Ak} (1,2). At equilibrium, however, D_{LREE}/D_{HREE} is constant over a wide range of melilite compositions, Ak_{12}-Ak_{90} (1,2). Thus, the observed increase in La/Y from 0.26 to 1.67 with increasing X_{Ak} is grossly inconsistent with equilibrium crystallization models. Also, since D_{Ba} $\approx$ 0.04 for all melilite compositions (2), the concentration of Ba (C_{Ba}) should increase in melilite with X_{Ak} as a result of its progressive concentration in residual liquids. Instead, a general decrease in C_{Ba} is observed. Furthermore, although an increase in C_{Sr} with X_{Ak} is expected (D_{Sr} = 0.78 -0.99; (1)), the observed 50 % increase in C_{Sr} from Ak_{31} to Ak_{65} is not (Fig. 1b), as it requires > 90 % crystallization of the liquid over this interval. These irregularities strongly suggest that kinetic disequilibrium in the crystal/liquid partitioning of trace elements played an important role in determining the composition of the interior melilite grains. The observed variation in trace element concentrations for two Ak_{35} analyses (Fig. 1a, pts 4 & 5) suggests that spatial heterogeneities in the liquid composition may have also affected the compositions of the melilite grains. Assuming Type B CAIs cooled at $\sim$ 25 C°/hr from a T_{max} =1420°C (5), complete solidification would have occurred in $\sim$ 24 hrs. A simple calculation using the relationship $x^2 = D^*t$ indicates that ~2 mm is the maximum distance a REE cation could have diffused before solidification ($D_{Gd}^{*1440°C}$ = 1.4 x 10^{-7} cm^2/sec (6)). Thus, it seems likely that chemical heterogeneity produced either during the crystallization of the observed phases, or inherited from pre-melt solids, could be retained and incorporated into the solid phases of the CAI.

EMP step-scans with 1 μm intervals show that mantle melilite grains differ from interior melilite grains by having only normal core-rim zoning profiles. The only mantle melilite analyzed by IMP displays a progressive decrease in Ba, La, Ce, Y and an increase in La/Y and Sr with increasing X_{Ak} similar to that of the interior melilite (Fig. 1) and over a comparable range of X_{Ak}. This suggests that the processes controlling crystal growth and trace element partitioning were also similar between regions. The absolute concentrations of trace elements in the Ak_{31} analysis of the interior melilite, however, are $\sim$ 2X those of the Ak_{29} analysis from the mantle melilite, implying that the trace element concentrations in the liquids from which these two melilite grains crystallized were not the same, despite being only millimeters apart. Using an equation relating Mg/Al of a Type B1 liquid to X_{Ak} of precipitating melilite, extracted from the experimental study of (3), the first-formed melilite to crystallize from a liquid of TS23F1 composition (3) is $\sim$ Ak_5. This estimate compares well with the most Al-rich mantle melilite observed (Ak_7). In contrast, the most Al-rich, interior melilite is Ak_{25}. This difference in minimum X_{Ak} may indicate that a considerable volume of mantle melilite crystallized prior to nucleation and growth of the interior melilite crystals, consistent with the petrographic interpretation of a Type B1 CAI by (7). Furthermore, crystallization of the outer melilite mantle would enrich the residual liquid in incompatible elements and could account, in part, for the trace element enrichment in the interior melilite grains. This enrichment method, however, cannot account entirely for the high concentrations of trace elements in the interior melilite. For example, C_{Ba} in the Ak_{31} analysis implies a coexisting equilibrium liquid with 980 ppm Ba. This corresponds to 98 % crystallization of a liquid which initially contained an average Type B1 concentration of Ba (22.6 ppm), assuming the extreme case of D_{Ba} = 0 in the crystallizing solids. We believe that the high concentrations of trace elements in the interior melilite grains indicate that trace element-rich boundary layers were present during

crystallization of the melilite. In the isothermal study of (1), and in our crystallization experiment on an average Type A composition cooled at increments of 10 C°/hr (unpublished), the restricted diffusion of incompatible elements away from the melilite/liquid interface produced boundary layers ~ 2 μm wide. The trace element concentrations in the boundary layers are up to 4X those of the glass away from the crystal/liquid interface, and these enhancements caused corresponding increases in the concentrations of trace elements in the growing melilite crystal. Boundary layers are due to an imbalance between the diffusion rate of a trace element away from the crystal/liquid interface and the rate of crystal growth. Such boundary layer effects may also be responsible for the deviation of trace element profiles in mantle and interior melilite crystals from those expected from equilibrium partitioning. Calculations are now underway in an attempt to model these processes, and to further evaluate the observed trace element variations.

Another factor which may complicate the distribution of trace elements in Type B CAIs is the partial dissolution of relict (pre-inclusion) phases (8). A detailed examination of interior and mantle melilite crystals using BSE and X-ray mapping techniques has located numerous spinel grains with fassaite rims (< 10 μm wide). Unlike (4), we interpret the fassaite and accompanying spinel grains as relict phases. This is based on the occurrence of these fassaite-spinel grains within melilite crystal cores which have X_{Ak} contents as low as 0.31. Such melilite compositions are very Al-rich compared to that which existed at the onset of fassaite precipitation marked by the beginning of the reversely-zoned profile at Ak_{73} (4). EMP analyses of the fassaite rims show that they have TiO_2 (total Ti) and Al_2O_3 contents which overlap the range of concentrations in the large fassaite crystals in the interior of TS23F1 (3-11 wt % TiO_2, 13-22 wt % Al_2O_3). No difference in Ti^{4+}/Ti^{3+}, V, Cr, Fe or Zr was found between these two fassaite populations. The high TiO_2^{tot} concentrations in the fassaite rims indicate that they could not have crystallized from a liquid of TS23F1 composition (TiO_2^{tot} = 1.29) prior to their incorporation within Ak_{31} melilite. For $D_{Ti^{3+}}^{cpx/liq}$ ~6 and $D_{Ti^{4+}}^{cpx/liq}$ ~1 (3), ~ 75 % of the inclusion would have had to crystallize (D_{Ti}^{solid}= 0) in order to obtain a liquid whose TiO_2^{tot} concentration was high enough to precipitate the observed fassaite rim compositions (e.g. Ti_2O_3 = 3.76 %, TiO_2= 4.21 %, based on 4 cations). This is an unrealistic proportion, requiring complete solidification of the melilite mantle and half of the inclusion's interior prior to crystallization of Ak_{31} melilite. EMP analyses of spinel grains with and without fassaite rims were also compared. No distinctions could be made based on Fe,Ti, Cr, V or Ca concentrations. If the spinel-fassaite assemblages are indeed relict grains, the chemical compositions of the precursors of the inclusion are indistinguishable from their present counterparts.

Refs.: (1) Kuehner, S. *et al.* (1988) LPS XIX, 653. (2) Beckett, J. *et al.* (1988) LPS XIX, 49. (3) Beckett, J. (1986) Ph.D. Thesis, Univ. of Chicago. (4) MacPherson, G. *et al.* (1984) J. Geol. 92, 289. (5) Stolper, E. & Paque, J. (1986) GCA 50, 1785. (6) Magaritz, M. & Hofmann, A. (1978) GCA 42, 847. (7) MacPherson, G. & Grossman, L. (1981) EPSL 52, 16. (8) Johnson, M. *et al.* (1988) Meteoritics 23, 276.