REVERSE ZONING IN MELILITE AND CRYSTALLIZATION SEQUENCES IN ALLENDE TYPE B CA-AL-RICH INCLUSIONS. G. J. MacPherson[1], J. M. Paque[2], E. Stolper[2], L. Grossman[1,3]. [1]Dept. of the Geophysical Sciences, University of Chicago, Chicago, IL 60637; [2]Div. of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125; [3]Enrico Fermi Institute, University of Chicago.

The binary melilite system gehlenite ($Ca_2Al_2SiO_7$) - åkermanite (åk--$Ca_2MgSi_2O_7$) exhibits complete solid solution between the end members and a minimum in the liquidus at åk 77 mole % [1]. Equilibrium crystallization of a liquid in the pure system whose bulk composition is more Al-rich than åk77 will produce normally zoned melilite crystals whose cores have higher Al/Mg ratios than their rims. Type B1 Allende Ca,Al-rich inclusions (CAI), whose textures suggest that they crystallized from molten droplets [2], contain melilite crystals which are monotonically zoned from cores of åk20 to rims of åk∿65-70, in accordance with these liquidus phase relations. The interiors of some B1's, however, commonly contain melilite crystals showing reverse zoning near the outermost crystal margins. Here is found a thin (10-50μm) zone that is more Al-rich (åk∿50) than zones immediately adjacent to it (åk∿65-70) towards both the core and margin of the same crystal. Within every such crystal, numerous, irregular, Ti-, Al-rich pyroxene grains exist within the Mg-rich zone just to the interior of the reversal. Pyroxene inclusions are never present in the Al-rich cores of the melilite crystals. These textures indicate that: (a) melilite began to crystallize before pyroxene; (b) pyroxene began to crystallize after the melilite crystals had nearly achieved their final size; and (c) subsequent to the onset of the pyroxene crystallization, the composition of the growing melilite became more Al-rich than just before pyroxene crystallization, i.e. reversely zoned. There is thus a suggestion that pyroxene crystallization may have been responsible for the reversal in the melilite zoning pattern.

Some melilite crystals in Type B2 CAI are reversely zoned in their centers, having cores of åk∿65-70 grading outward to intermediate zones of åk∿50, and normally zoned in their outermost rims, grading outward from åk∿50 to åk∿70. Pyroxene inclusions are present throughout these crystals and are particularly numerous in the cores. Again there is an apparent relationship between melilite reverse zoning and the crystallization of pyroxene.

Equilibrium crystallization experiments on melts of average Type B bulk composition [3] produce melilite zoning patterns similar to those in natural inclusions. Experimental techniques used were similar to those described in [4]. Each charge was held at 1420°C (within the spinel primary phase volume) for several hours, then cooled to the temperature of interest. Cooling rates were linear and varied from 2°C/hr. to 1000°C/hr. Only samples from runs with the slowest cooling rate have melilite crystals showing reverse zoning patterns. Cooling rates of 20°C/hr.-1000°C/hr. produced normal zoning in melilite. The crystallization sequence for this bulk composition at 2°C/hr. is spinel, melilite, pyroxene and anorthite. In those runs quenched within the melilite field (1260°C>T>1199°C), the melilite is normally zoned from cores of åk∿30 to rims of åk∿40-55. Runs containing the assemblage spinel + melilite + pyroxene + glass (1100°C<T<1199°C) have melilite crystals with reversely zoned rims on normally zoned cores. The rims zone outward from åk∿60-64 to åk∿37 in the most extreme case. These results support the idea that co-precipitation of pyroxene and melilite in Type B melts will cause reverse zoning in the melilite. At the temperature at which pyroxene starts

to crystallize from the liquid in our experiments, the liquid contains 20.3 wt. % Al_2O_3 and 6.6 wt. % MgO. The onset of voluminous precipitation of pyroxene containing 20-26 wt. % Al_2O_3 and ∿10% MgO drives up the Al/Mg ratio of the residual liquid, causing the equilibrium melilite composition to become more Al-rich.

The effect of the onset of anorthite precipitation is less clear, as the experimental results are not entirely in accord with textures in the natural samples. Runs cooled down to the anorthite field ($T \lesssim 1100^{\circ}C$) have melilite crystals that show monotonic, normal zoning from cores of $\mathring{a}k \sim 30$ to rims of $\mathring{a}k \sim 83$, in contrast to many natural Type B's whose melilite crystals pass from normal to reverse and back to normal zoning again. In natural inclusions, anorthite crystallization is probably responsible for the outer, normally zoned mantles on the melilite crystals, as its precipitation lowers the Al/Mg ratio of the liquid, reversing the earlier effect of pyroxene crystallization on the liquid composition. The reason why this has not occurred in the anorthite-bearing experimental runs is unclear but one other peculiarity of the experimental results may provide a clue. The amount of anorthite present in runs quenched at $T<1100^{\circ}C$ is much greater than can be accounted for by solidification of the volume of glass present in anorthite-free runs quenched above $1100^{\circ}C$. This suggests the possibility that anorthite formed by reaction of another phase, possibly pyroxene or melilite, with the liquid. Textural evidence to support this interpretation, however, such as anorthite rims on another phase, is lacking. This problem remains unresolved.

The fact that reversely zoned melilite was produced only in runs having cooling rates of $\sim 2^{\circ}C/hr$. further supports the earlier suggestion [4] that CAI cooled at very slow rates, much slower than those inferred for olivine chondrules. This suggests that the temperature of the ambient nebular gas was comparable to the solidus temperatures of the CAI droplets, probably $\sim 1100^{\circ}C$. The general agreement in textures and inferred parageneses between the natural CAI and experimental runs indicates that liquid crystallization provides a simpler explanation for the origin of melilite in Type B CAI than the model proposed by others [5] involving metamorphic and metasomatic resorption and replacement of pyroxene. The reverse zoning observed in melilite requires that pyroxene components be progressively subtracted from the system during melilite growth, not added to the system as would be the case in the metamorphic model.

References: [1] Osborn, E. F. and Schairer, J. F. (1941) Am. Jour. Sci. 239, p. 715. [2] MacPherson, G. J. and Grossman, L. (1981) E.P.S.L. 52, 16-24. [3] Stolper, E. (1982) G.C.A. 46, 2159-2180. [4] Paque, J. M. and Stolper, E. (1982) Conf. on Chondrules and their Origins, Abstract Vol., p. 49. [5] Meeker, G. P. *et al.* (1982) L.P.S. XIII, 505-506.