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

The binary melilitc system gehlenite (Ca\textsubscript{2}Al\textsubscript{2}Si\textsubscript{2}O\textsubscript{7}) − åkermanite (\textsubscript{\textalpha}k−Ca\textsubscript{2}Mg\textsubscript{2}Si\textsubscript{2}O\textsubscript{7}) exhibits complete solid solution between the end members and a minimum in the liquidus at \textsubscript{\textalpha}k 77 mole % [1]. Equilibrium crystallization of a liquid in the pure system whose bulk composition is more Al-rich than \textsubscript{\textalpha}k77 will produce normally zoned melilitc crystals whose cores have higher Al/Mg ratios than their rims. Type B1 Allende Ca\textsubscript{2},Al-rich inclusions (CAI), whose textures suggest that they crystallized from molten droplets [2], contain melilitc crystals which are monotonically zoned from cores of \textsubscript{\textalpha}k20 to rims of \textsubscript{\textalpha}k\textless65−70, in accordance with these liquidus phase relations. The interiors of some B1’s, however, commonly contain melilitc crystals showing reverse zoning near the outermost crystal margins. Here is found a thin (10−50µm) zone that is more Al-rich (\textsubscript{\textalpha}k\textless50) than zones immediately adjacent to it (\textsubscript{\textalpha}k\textgtrsim65−70) 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 melilitc crystals. These textures indicate that: (a) melilitc began to crystallize before pyroxene; (b) pyroxene began to crystallize after the melilitc crystals had nearly achieved their final size; and (c) subsequent to the onset of the pyroxene crystallization, the composition of the growing melilitc 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 melilitc zoning pattern.

Some melilitc crystals in Type B2 CAI are reversely zoned in their centers, having cores of \textsubscript{\textalpha}k\textless65−70 grading outward to intermediate zones of \textsubscript{\textalpha}k\textgtrsim50, and normally zoned in their outermost rims, grading outward from \textsubscript{\textalpha}k\textgtrsim50 to \textsubscript{\textalpha}k\textgtrsim70. Pyroxene inclusions are present throughout these crystals and are particularly numerous in the cores. Again there is an apparent relationship between melilitc reverse zoning and the crystallization of pyroxene.

Equilibrium crystallization experiments on melts of average Type B bulk composition [3] produce melilitc 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 melilitc crystals showing reverse zoning patterns. Cooling rates of 20°C/hr.–1000°C/hr. produced normal zoning in melilitc. The crystallization sequence for this bulk composition at 2°C/hr. is spinel, melilitc, pyroxene, and anorthite. In those runs quenched within the melilitc field (1260°C<T<1199°C), the melilitc is normally zoned from cores of \textsubscript{\textalpha}k\textgtrsim30 to rims of \textsubscript{\textalpha}k\textgtrsim40−55. Runs containing the assemblage spinel + melilitc + pyroxene + glass (1100°C<T<1199°C) have melilitc crystals with reversely zoned rims on normally zoned cores. The rims zone outward from \textsubscript{\textalpha}k\textgtrsim60−64 to \textsubscript{\textalpha}k\textgtrsim37 in the most extreme case. These results support the idea that co-precipitation of pyroxene and melilitc in Type B melts will cause reverse zoning in the melilitc. At the temperature at which pyroxene starts
to crystallize from the liquid in our experiments, the liquid contains 20.3 wt. % Al₂O₃ and 6.6 wt. % MgO. The onset of voluminous precipitation of pyroxene containing 20-26 wt. % Al₂O₃ 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<1100°C) have melilite crystals that show monotonic, normal zoning from cores of Åk=30 to rims of Åk<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°C is much greater than can be accounted for by solidification of the volume of glass present in anorthite-free runs quenched above 1100°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 ~2°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 ~1100°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.