

MINOR ELEMENT ZONING REVEALED BY CATHODOLUMINESCENCE AND SUBSTITUTION OF MG and NA INTO SYNTHETIC AND NATURAL ANORTHITE. Ian M. Steele¹, Mark T. Peters², Elizabeth E. Shaffer² and Donald S. Burnett², ¹Dept. of Geophysical Sciences, University of Chicago, Chicago, IL 60637; ²Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125.

Anorthite is a common phase in high-temperature calcium, aluminum-rich inclusions (CAIs) as well as in other igneous samples, including eucrites and many lunar rocks. Cathodoluminescence (CL) of individual crystals shows intricate zoning which can be correlated with the concentrations of Na and Mg in Allende CAIs [1]. Experimental crystallization of anorthite from melts based on CAI compositions results in similar zoning patterns as well as quantitative similarities in minor element concentrations. Zoning can be interpreted as both sector and oscillatory suggesting two different mechanisms of minor element incorporation during growth. Partition coefficients will not be constant but rather are dependent on crystallographic direction and particular growth zones. Correlations among minor elements provide suggestions for substitution mechanisms within the anorthite structure.

Allende anorthite: Anorthite is a late crystallizing phase in Type B CAIs as indicated by its interstitial occurrence and trace element content [2]. These grains contain only several mol% albite and also have Mg, Ti, and Fe as minor elements. Complex patterns of CL intensity have been documented and interpreted as representing sector zoning although no crystallographic relations were obtained [1]. In this same work it was noted that Na and Mg correlated positively with each other and inversely with the CL intensity [1]. No CL spectra were obtained but visually the intensity changes were simple changes in blue intensity with no wavelength change. While one anorthite from inclusion TS-21 showed a 1:1 atomic correlation between Na and Mg, a second anorthite from TS-23 showed a linear correlation, but with Mg>Na on an atomic basis.

Experimental anorthite: Experimental anorthite grown by fractional crystallization from melts simulating type B bulk compositions [3] was imaged using scanning CL and showed complex variation of CL intensity with possibly a 10x range in intensity (Fig. 1). Although no crystallographic orientation was determined, the CL pattern shows two patterns: 1) bands, ~3 to ~15 microns in width, of growth parallel to the growing crystal face; and 2) linear boundaries at high angles to the growing face and sometimes cutting across the parallel type 1 growths. The hue of the CL does not appear to vary, but rather only the intensity.

Microprobe step scans across CL boundaries were made with sufficient spatial resolution to resolve individual lamellae. Analytical conditions (20kV, 100nA) were sufficient to reach detection levels near 50 ppmw for Na, Mg, and Ti. Concentration variations are illustrated in Fig 2 where some eight CL intensity zones are represented as indicated by qualitative estimates of CL brightness at the top of Figure 2. Figure 3 shows an expanded scale for Na. The Ti profile shown in Fig. 2 is relatively flat at Ti = 420ppmw. In contrast, the Mg and Na profiles both show fluctuations where the highest concentrations of both correspond to the duldest CL intensity. Because the excitation volume is at least several microns wide, some lamellae on this scale are not well resolved. This correlation is qualitatively the same as was found for Allende anorthite [1]. Na was not included in the original melt; its presence represents contamination in starting materials.

Discussion: Interpretation of the correlation of Mg and Na content in anorthite in both experimental and natural systems as a coupled substitution is difficult to reconcile with stoichiometry and charge balance. Evidence for non-coupled substitution is the variable Na/Mg ratio, at least for the two Allende grains [1]. A possible alternative is a mechanism where the substitution is independent but influenced by common factors resulting in a correlation. Thus Na would substitute as Na + Si for Ca + Al and Mg would substitute as Mg + Si for 2 Al with Mg in tetrahedral sites [4,5]. One possibility suggested by the CL image of Fig.1 is that the banded CL pattern parallel to the growing face represents oscillatory zoning. While the exact cause of this type of zoning is not well defined, it is generally thought [6] to represent an interaction near the crystal-liquid interface where the composition of the liquid is controlled in part by diffusion of components within the liquid, the rate of attachment (growth), and crystal/liquid partition coefficients (boundary layer phenomena). This type of zoning is well known in feldspar for Na, but not documented to

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our knowledge for Mg.

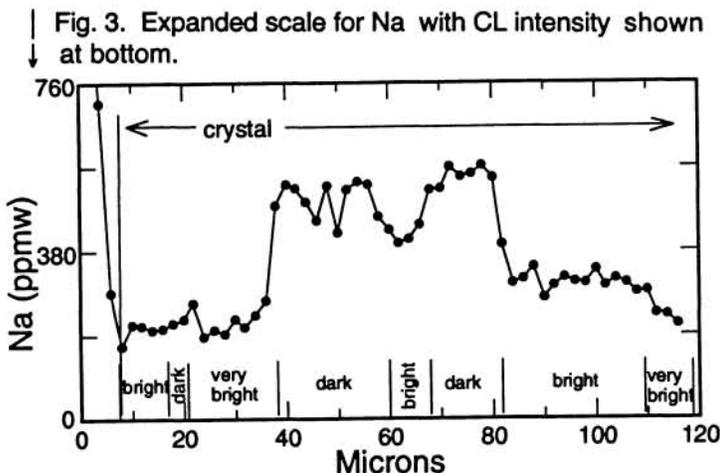
While the mechanism may not be well known, it is clear that the Mg content of anorthite both in experiments and in natural samples is variable, and thus crystal/liquid partition coefficients would show a variation depending on where within a single crystal measurements are made. Documentation using CL is rapid and serves as a useful tool in studying minor element partitioning.

Our fractional crystallization experiments have essentially reproduced the observed CL patterns in CAI anorthite, strongly suggesting that the CAI patterns are also a consequence of crystal growth from a melt. A somewhat less firm conclusion is that the complex Mg distributions in CAI anorthite are also igneous in origin. This is an important conclusion because it implies that the CAI ²⁶Mg-²⁶Al systematics (based almost entirely on anorthite) have not been modified by subsolidus redistribution or alteration.

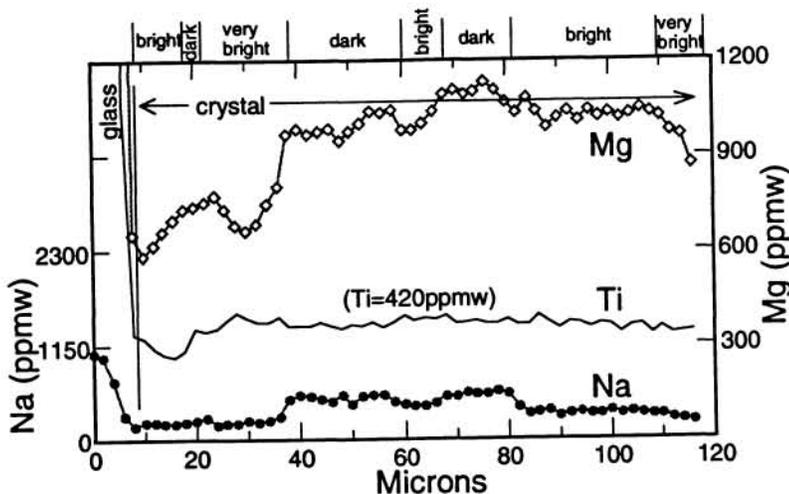
References: [1] Hutcheon, I.D. et al. (1978) Proc. 9th Lunar Planet. Sci. Conf., 1345-1368; [2] Simon, S. et al. (1994) Geochim. Cosmochim. Acta 58, 1507-1523; [3] Peters, M.T. et al. (1994) Mineral. Mag. 58A, 713-714; [4] Longhi, J. et al. (1976) Proc. 7th Lunar Planet. Sci. Conf., 1281-1300; [5] Peters, M.T. et al. (1995) Geochim. Cosmochim. Acta (submitted); [6] L'Heureux I. and Fowler A.D. (1994) American Mineral. 79, 885-891.



←----- Fig. 1. Scanning CL image of synthetic anorthite. Dark area at bottom is glass while successive bands are parallel to this glass-crystal interface. Indicator arrows indicate position of scan profile represented in Figs. 2 and 3. (Row of dots indicate electron probe damage).



| Fig. 3. Expanded scale for Na with CL intensity shown at bottom.



←----- Fig. 2. Variation of Mg, Na and Ti concentration across profile indicated in Fig. 1. Left is glass-crystal interface. Qualitative CL intensities are indicated at top of Figure.