

SECTOR ZONING OF MINOR AND TRACE ELEMENTS IN SYNTHETIC PYROXENES: C.S. Schwandt, and G.A. McKay, Planetary Sciences Branch, Johnson Space Center, SN4, Houston, TX 77058.

Enstatite ($\text{En}_{80}\text{Fs}_{19}\text{Wo}_1$) crystals grown from hypersthene normative volatile-free basaltic melts under iron-wüstite fugacity conditions contain dramatic sector zoning of minor (Al, Cr, Ti) elements and trace elements (Yb, other REE under investigation) (Fig. 1). Enstatite crystals are synthesized at constant furnace temperature a couple of degrees below the liquidus of 1210 °C, for a duration of 1 to 2 days, resulting in crystals with dimensions of 50 x 100 x 500-1000 µm. The mineral/melt partition coefficients determined for each of the sectors can vary from one another by more than a factor of three. Sector development appears to be kinetically and crystallographically controlled. The largest concentration differences occur between the fastest and slowest growing sectors. Growth of these pyroxenes is fastest parallel to the c-axis, therefore in the case of Al, the {001} and {011} sectors are the most depleted and the prism sectors are most enriched, with the {010} sectors containing the most Al. To accurately determine a single equilibrium partition coefficient, one could algebraically average the partition coefficients on a sector volume percentage basis. However, sector differences between the prism sectors are minor and the prism sectors comprise the largest volume, such that use of partition coefficients determined from the prism sectors is perhaps appropriate for most modeling.

Recent technological improvements to the collection of X-ray spectrometric data now allow the visualization of concentration variations of minor and trace elements in a digital format. Digital maps of synthetic pyroxenes indicate that sector zoning is common [1,2]. Sector zoning occurs in pyroxenes grown under experimental conditions that approximate, as closely as possible in the laboratory, equilibrium conditions; e.g. constant furnace temperature a couple of degrees below the liquidus, low percentage of nucleation, constant melt composition. The presence of the sector zoning is important because it impacts the determination of elemental partition coefficients, but more importantly it provides clues about the mechanisms of mineral growth.

Several models have been proposed to explain the development of sector zoning. These include: (1) preferential adsorption of elements onto specific mineral faces during growth [3,4,5,6,7]; (2) kinetically induced enrichments and depletions of elements at the crystal/melt interface [8,9,10,11]; (3) crystal chemical characteristics of cation sites within the minerals relative to cation size [10,12]; (4) slow volume diffusion in minerals [13]; (5) growth mechanisms that differ for each crystal form because of different surface structure [14,15]. However, the present data indicate that none of these models completely explain the formation of sector zoning.

The sector enrichment of Al follows the scheme of {010} > {100} ≈ {110} > {101} > {001}. The concentration of aluminum is unique for each sector with only minor variation within each sector, due to normal growth zoning. The concentrations of Cr and Ti within each sector correlate with Al concentration. Increased amounts of Al, Cr, and Ti within a specific sector are offset by depletions of Mg and Si. Ca and Fe exhibit no sector zoning and only minor growth zoning. Therefore the incorporation of Al is occurring via charge compensating coupled substitutions, the primary mechanism being ${}^{VI}\text{Al}^{3+} + {}^{IV}\text{Al}^{3+}$ for ${}^{VI}\text{Mg}^{2+} + {}^{IV}\text{Si}^{4+}$. The charge compensating coupled substitutions of ${}^{VI}\text{Cr}^{3+} + {}^{IV}\text{Al}^{3+}$ for ${}^{VI}\text{Mg}^{2+} + {}^{IV}\text{Si}^{4+}$ and ${}^{VI}\text{Ti}^{4+} + 2{}^{IV}\text{Al}^{3+}$ for ${}^{VI}\text{Mg}^{2+} + {}^{IV}\text{Si}^{4+}$ are respectively less prominent, as indicated by the less prominent sector zoning of Ti and Cr relative to Al. Preliminary analyses by electron microprobe suggest that Yb enrichment also parallels the Al sector enrichment scheme.

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Clearly, sector zoning is evident in synthetic enstatite, as predicted for rapidly grown crystals [13]. However, in addition to experimentally grown minerals, sector zoning is important in natural volcanic [3, 7, 10, 12] and possibly plutonic minerals. Therefore this disequilibrium phenomena indicates there is commonly insufficient time for volume diffusion to erase the development of sector zoning and that diffusion limitations do not address the reason for formation of sector zoning. Also, the experimental samples suggest that diffusion limitations within the melt or boundary layer are not the cause of sector zoning. Composition gradients in the melt glass, which should be of similar magnitude as those in the crystals, are not detectable. If crystal growth rate were to be controlling the speciation of the boundary layer, Al which is incompatible in enstatite ($D = 0.05$ to 0.3), would tend to build up in the boundary layer of the fastest growing faces. Such a buildup of Al should increase the concentration of Al in the melt boundary layer and thereby decrease the partition coefficient (concentration of Al in enstatite/concentration of Al in melt) relative to more slowly growing faces. This is observed, but Al is not the only element. The mechanism is inconsistent with the Cr sector zoning, which shows the same relative sector enrichments as Al. Cr is compatible ($D = 3.0$ to 5.4) in enstatite and should then become depleted in the melt boundary layer of the fastest growing faces leading to higher partition coefficients and producing relative sector enrichments that would be opposite those for Al, which is not observed. In addition, growth rates for the {100} and {010} forms are similar, yet there are very distinct sector concentration differences between these forms (Fig. 1).

These experiments suggest that it may be the substitution of Al into the tetrahedral sites that is a dominant controlling factor for sector formation, and that the octahedral impurity cation substitution is charge compensating. Further sector zoning work will better characterize mineral growth mechanisms and the definition of experimental partition coefficients.

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Fig. 1. Digital Al map of enstatite in glass. Bright sectors are {010}. White line is 50 μm scale bar.