LUNAR PYROXENES: CRYSTAL CHEMICAL RATIONALIZATION OF REE ZONING, PATTERN SHAPES, AND ABUNDANCES - AN ION MICROPROBE INVESTIGATION; J.J. Papike¹, C.K. Shearer¹, S.B. Simon¹, and N. Shimizu²,¹Inst. for the Study of Mineral Deposits, S.D. School of Mines & Tech., Rapid City, SD 57701-3995, Dept. of Earth, Atm. & Planetary Sciences, M.I.T., Cambridge, MA 02139

Introduction. It was recognized in the early days of Apollo that the integrity of the lunar samples must be maintained for second generation experiments based on new technological developments. This study is a direct result of such technological development in data acquisition and reduction utilizing the ion microprobe.

Bence and Papike [1] documented the utility of chemically zoned lunar pyroxenes as effective recorders of crystal-liquid interaction. That study utilized the electron microprobe to document major and minor zoning trends. We now have analyzed these zoned lunar pyroxenes for a number of trace elements including seven REE with the ion microprobe. Two companion abstracts [2,3] document the chemical zoning systematics in pyroxenes from mare and KREEP basalts, respectively. Here we attempt to explain such systematics based on pyroxene crystal chemical principles.

Observations. Several basic observations documented in companion abstracts [2,3] are: (1) Relative REE enrichments in lunar pyroxenes are in the order augite > pigeonite > orthopyroxene; (2) The patterns have negative Eu anomalies with the size of the anomaly changing systematically with the augite anomaly < pigeonite < orthopyroxene; (3) The REE abundances increase with Fe²⁺/Mg; (4) The positive slope of the pattern defined by Yb/Ce increases in the order augite < pigeonite < orthopyroxene; (5) The slope of the REE from Ce to Sm is much steeper than from 6d to Yb.

Crystal chemical rationalization of observations. Figure 1 illustrates the basic features of the C2/c augite crystal structure. The pyroxene group minerals crystallize in a variety of space groups but for our purposes only three are important: C2/c for augite, P21/c for pigeonite, and Pbca for orthopyroxenes. The structure of all pyroxenes can be described in terms of alternating tetrahedral and octahedral layers that lie parallel to the (100) plane. The tetrahedral layer is composed of infinite chains of corner-sharing tetrahedra running parallel to c. The "octahedral layer" is composed of the 6-8 coordinated M2 site and the octahedral M1 site. M1 octahedra share edges to form infinite chains parallel to c. The M2 polyhedra are either 8- or 6-coordinated depending on their occupancy. The site is 8-coordinated when it contains Ca or Na but is approximately 6-coordinated when containing the smaller Mn²⁺, Fe³⁺, Mg, and Li cations.

The three structure types considered here (C2/c, P21/c, Pbca) differ mainly in the manner in which the octahedral and tetrahedral layers are linked. These three
different pyroxene structural topologies have a profound effect on the nature of the coordination and size of the M2 site. In orthopyroxene, as a direct result of the octahedral stacking sequence \([4,1]\), the M2 site is constrained to be a relatively small octahedral site with very little ability to accommodate ions larger than Mn\(^{2+}\). However, the M2 site in augite and pigeonite has a great deal of flexibility to accommodate ions as large as Ca and Na in 8-coordination or as small as Mg in 6-coordination.

Figure 2 illustrates the range of cation sizes that the M2 and M1 sites can accept, and the X-site of feldspars, for comparison. Based on these systematics we would predict that the REE in pyroxene are essentially restricted to the M2 site, and that Eu\(^{2+}\) must be totally excluded from the M2 site of orthopyroxene and is almost too large to fit into the expanded M2 site of augite.

We now return to observations 1-5 listed above: (1) The REE enrichments of augite > pigeonite > orthopyroxene is directly related to the amount of Ca in the M2 site which "props open" the site for the relatively large REE; (2) The relative size of the Eu anomaly augite < pigeonite < orthopyroxene is a result of the large Eu\(^{2+}\) being excluded from the octahedral M2 site of opx and being enriched in augite over pigeonite, again following the amount of Ca; (3) The REE increase with Fe/Mg not only because the REE concentrations are building up in the melt as a result of their incompatible behavior but also because the Fe for Mg substitution in both the M2 and M1 sites results in a larger M2 site which more readily accommodates REE; (4) The slope measured by Yb/Ce reflects the fact that the large REE are excluded from the M2 pyroxene site in the order opx < pig < aug; (5) The change in slope from Ce to Sm compared to that from Gd to Yb reflects the fact that in the ionic size range Ce to Sm the larger REE tend to be excluded from the M2 site but in the ionic size range Gd to Yb the REE are readily accommodated by the M2 site. Based on ionic radii and charge balance considerations we predict the most important trivalent REE component in these pyroxenes is \(\text{M}^2(\text{REE})^3^+ + \text{M}^1\text{R}^2^+ \text{IV}(\text{Si}, \text{Al})\text{O}_6\) where \(\text{R}^2^+ = \text{Fe}^{2+}, \text{Mg}\) and the Eu\(^{2+}\) component is \(\text{M}^2\text{Eu}^{2+} + \text{M}^1\text{R}^2^+ \text{Si}_2\text{O}_6\).