

SPECTRAL MODELING AND CRYSTALLOGRAPHIC PROPERTIES OF AL-RICH PYROXENES. R. L. Klima¹, M. D. Dyar² and S. E. Peel², ¹Johns Hopkins University/Applied Physics Laboratory, Laurel, MD, 20723 (Rachel.Klima@jhuapl.edu); ²Department of Astronomy, Mount Holyoke College, South Hadley, MA, 01075.

Introduction: Pyroxene is one of the most common and spectrally distinctive minerals on the surfaces of bodies in the inner solar system. Two strong absorption bands near 1 and 2 μm that result from crystal field transitions of Fe^{2+} dominate the pyroxene near-infrared (NIR) spectrum. The positions and shapes of these absorption bands reflect the bulk composition, texture, and cooling history of the pyroxene. The primary octahedral cations Fe^{2+} , Mg^{2+} and Ca^{2+} have the largest effect on the energy (wavelength) of the 1 and 2 μm absorption bands. Previous research has focused primarily on understanding the effect of these quadrilateral cations on the major absorption bands to deduce major element composition from remotely detected spectra [e.g. 1-4]. However, it is recognized that substitutions of minor elements such as Ti and Al result in distortions of the crystal structure and changes in expected band positions [e.g., 2,3,5] (Fig. 1). To tap the wealth of information inherent in pyroxene spectra, systematic laboratory exploration of these complexities with well-characterized samples is needed.

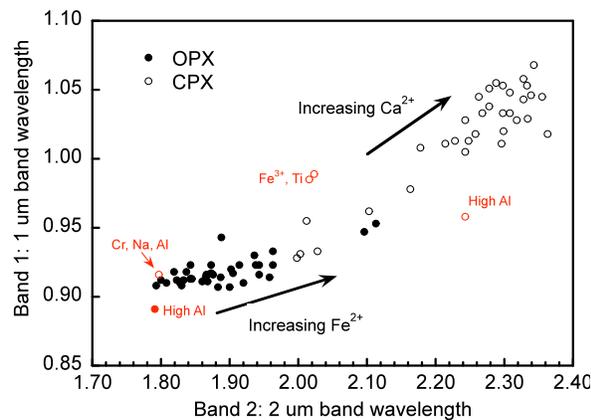


Fig. 1. Band 1 and 2 centers for a suite of natural pyroxenes, measured and analyzed by Adams [1974] and Cloutis and Gaffey [1991]. Al- and Ti-rich pyroxenes plot significantly off the trend for ‘normal’ quadrilateral pyroxenes.

Methodology: Pyroxene NIR spectral features result from electronic transitions in a ligand field, which is determined by the arrangement of adjacent O^{2-} anions around the Fe sites [7]. Two of the most common minor elements in extraterrestrial pyroxenes are Al and Ti. As a transition metal, Ti (3+ and 4+) can exhibit absorption bands of its own, while Al can only distort the crystal structure (Fig. 2) and modify the bands caused by other absorbing species (generally Fe^{2+}). To directly explore the link between structure

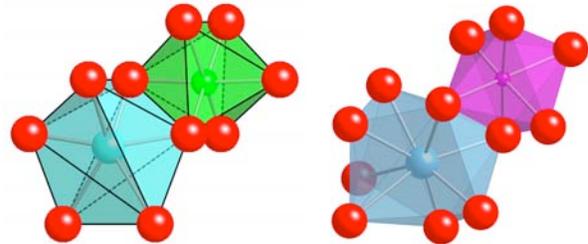


Fig. 2. M2 (blue) and M1 (green for Mg/Fe at left, purple for Al at right) sites in augite (left) and an unusual Al-rich synthetic clinopyroxene at right [6], showing the distortion of the structure when Al is substituted for Fe.

and crystal field absorption bands, our first step has been to calculate a set of structural parameters including combinations of bond angles, octahedral site elongation, and bond length for relatively pure quadrilateral pyroxenes that have had single crystal structural refinements (SREF) performed [8]. SREF data have been collected for 71 pyroxenes that contain stoichiometric Al, including augites, pigeonites, and orthopyroxenes. From these, we have excluded for this work any Al-rich pyroxenes with large cations, such as omphacite or jadeite, because the effect of substituting such a large cation into the lattice is likely to overshadow any effect of the smaller Al^{3+} cation. For Ti-rich pyroxenes, additional absorptions due to charge transfers or Ti^{3+} crystal field absorptions are also present at shorter wavelengths [e.g., 1,2,3,9]. Ultimately, we seek to relate deviations of all crystal field absorption band positions in natural minor element-bearing pyroxenes to structural differences between the Al and Ti bearing pyroxenes and pure quadrilateral pyroxenes.

Aluminum in Terrestrial Pyroxenes: Spectra of over 50 terrestrial pyroxenes with Al contents ranging as high as 14 wt% in some clinopyroxenes are being modeled using the Modified Gaussian Model (MGM). The MGM allows individual bands to be deconvolved from a composite spectrum, isolating absorptions that can be linked directly to specific electronic processes [10]. By using the MGM, we can directly compare the absorption band positions of the high-Al pyroxenes with those for pure quadrilateral pyroxenes [4,11]. The spectra of low-Ca pyroxenes with high amounts of Al appear qualitatively similar to pure quadrilateral pyroxenes. However, their absorption band energies, particularly the position of the 2 μm band, differ from pure quadrilateral pyroxenes of similar composition (minus the Al). This effect can be clearly seen in the case of a high (5.5 wt%) Al orthopyroxene from Mantyhajarja, Finland [3,5] with a composition of $\text{Wo}_{3.3}$

En_{68.5} Fs_{28.2} compared to a synthetic orthopyroxene of Wo₀ En₇₀ Fs₃₀ (Fig. 3). The MGM deconvolution of the same high-Al pyroxene is shown in Fig. 4.

Modeling results indicate that the 1 μ m band occurs at a slightly longer wavelength in the Al-rich pyroxene, consistent with the small amount of Ca in the natural pyroxene. However, the 2 μ m band occurs almost 100 nm shorter than in a comparable composition Al-free orthopyroxene (Fig. 5). This deviation is likely caused by Al³⁺ partitioning into the tetrahedral Si⁴⁺ site and the octahedral M1 site.

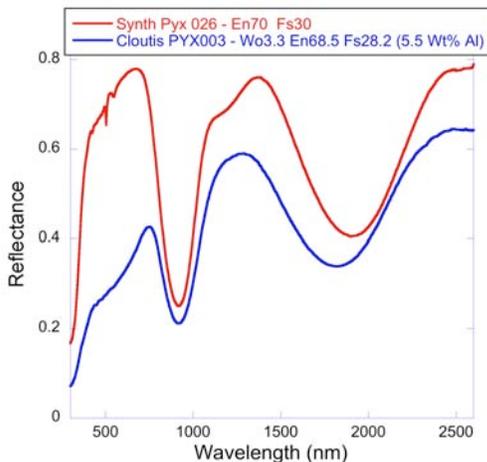


Fig. 3. Comparison of a pure quadrilateral orthopyroxene with a high-Al orthopyroxene of similar major element content.

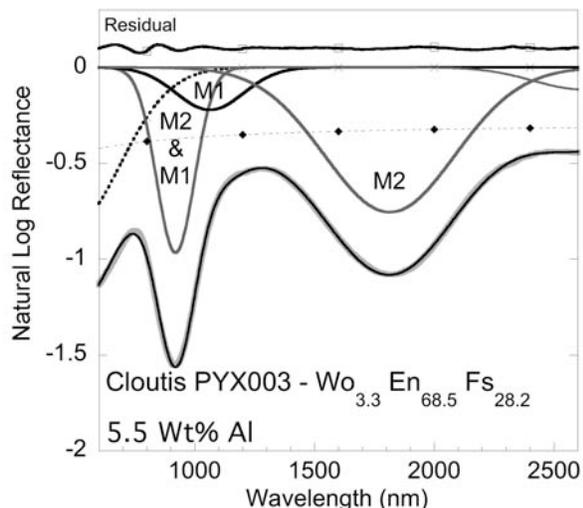


Fig. 4. MGM deconvolution of high-Al PYX003. Crystal field bands caused by Fe²⁺ absorptions in the M1 and M2 sites are indicated. The data are shown as a thick grey line, with the modeled fit overlain as a thin black line. The dashed line indicates the continuum slope used. Natural log reflectance is used to approximate absorbance.

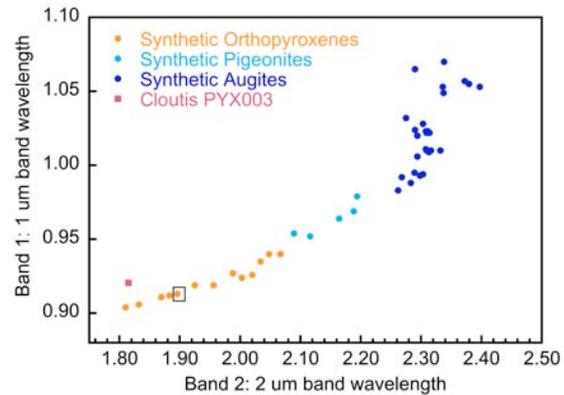


Fig. 5. Band positions for high-Al PYX 003 compared to those of synthetic ortho- and clinopyroxenes. A box has been drawn around the synthetic pyroxene from Fig. 3.

Future Work: Calculation of structural parameters for Al-rich pyroxenes is currently ongoing. Initial results for pure quadrilateral pyroxenes suggest that the mean octahedral elongation of the M2 site is the best structural parameter for predicting the positions of the major 1 and 2 μ m absorption bands [8]. We will test whether the mean octahedral elongation of the M2 site is also predictive of Al-rich pyroxene band positions. We will also explore other crystallographic parameters of the Al-rich pyroxenes and their relationships to the 1 and 2 μ m band positions. Similar analyses will be conducted on Ti-rich pyroxenes, including lunar pyroxenes and angrites, to quantify both the effects of Ti (3+ and 4+) on the Fe²⁺ crystal field bands and the properties of the visible wavelength Ti-absorption band(s).

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