

PYROXENE SPECTROSCOPY: EFFECTS OF MAJOR ELEMENT COMPOSITION ON NEAR, MID AND FAR-INFRARED SPECTRA. R. L. Klima¹, C. M. Pieters¹, and M. D. Dyar², ¹Department of Geological Sciences, Brown University, Providence RI 02912; Rachel_Klima@Brown.edu. ²Department of Astronomy, Mount Holyoke College, South Hadley, MA 01075.

Pyroxene is one of the most common minerals in both evolved and undifferentiated solid bodies of the solar system. Various compositions of pyroxene have been directly studied in meteorites and lunar samples and remotely observed by telescopic and orbital measurements of the moon, Mars, Mercury, and several classes of asteroids. Laboratory studies of pyroxene spectra have shown that absorption features diagnostic of pyroxene in both the near and mid infrared are composition dependent. The challenge for remote analyses has been to reduce the level of ambiguity to allow a quantitative assessment of mineral chemistry. This study focuses on the analysis of a comprehensive set of synthetic Ca-Fe-Mg pyroxenes from the visible through far-IR (0.3-50 μm) to address the fundamental constraints of crystal structure on absorption.

Background: Pyroxene spectra are controlled primarily by the distribution of Ca, Fe, and Mg in the M1 and M2 crystallographic sites [1]. Substitution of cations such as Ti^{4+} , Cr^{3+} , Fe^{3+} and Al^{3+} also affects absorption features and can lead to misclassification of pyroxene compositions [2-7]. The presence and distribution of low and high calcium pyroxenes are used extensively in characterization of the igneous evolution of planetary surfaces, so it is critical that we accurately differentiate spectral variations due to Ca-Fe-Mg from those due to minor elements.

Absorption features in the near infrared are controlled by electronic processes, while those in the mid-infrared reflect molecular vibrations. Both these processes are fundamentally controlled by the crystal structure and chemical composition of a mineral. A comprehensive investigation of spectral features from the visible through far-IR for a controlled group of samples provides the opportunity to deconvolve multiple absorptions, and quantitatively investigate the mineral physics controlling diagnostic features.

Approach: Thanks to the generosity of Donald Lindsley and Allan Turnock, we have acquired a set of synthetic Ca-Fe-Mg pyroxenes described in [8], covering the majority of the pyroxene quadrilateral (Fig. 1). This series of pyroxenes with simplified compositions offers a unique opportunity to characterize variations in absorption bands from the visible through far-IR and directly relate them to the composition, crystal structure, and site preference. Although some of the pyroxenes synthesized fall within the 'forbidden' zone of the quadrilateral, and therefore would not relate directly to natural samples, these samples allow us to explore the effects of cation substitution in the crystal lattice in a quantitative and systematic manner.

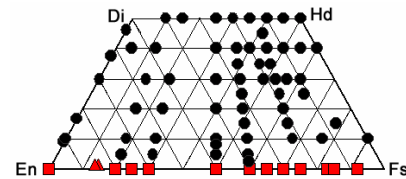


Fig. 1. Synthetic and natural pyroxenes. Current series indicated in red. Natural samples are indicated by triangles, all others are synthetic.

Pyroxenes for this study were synthesized by a variety of methods that were chosen to prevent nucleation of olivine or pyroxenoids, as outlined in [8]. Purity of samples was verified by X-ray diffraction [8]. Our initial analyses concentrate on the En-Fs series. Because no synthetic samples were available with $\sim 10\%$ Fe content, we include two natural pyroxenes, with comparable compositions (Table 1).

The pyroxenes were sieved to $<45 \mu\text{m}$ grain size and spectra were collected as bidirectional reflectance (nearIR) and diffuse reflectance (midIR) in the RELAB. In the mid and far IR where the extinction coefficient (k) is relatively high, reflectance measurements can be related to emissivity by $E = 1 - R$ [9]. For mid and far IR analyses, we avoid regions of the spectrum in which the index of refraction (n) greatly exceeds k , as reflectance measurements produce features that are not observed in emissivity and therefore not relevant to remote measurements.

Preliminary Results: We have currently measured the series of calcium-free pyroxenes over the wavelength range of 0.3-50 μm . Measurement and analysis of the Ca-rich and intermediate pyroxenes will follow over the coming year.

Near-Infrared. Most pyroxenes are characterized by two absorption bands near 1 and 2 μm [1-4]. Both features are caused principally by Fe^{2+} in the larger, more distorted M2 site. As has been previously observed, both absorptions shift to longer wavelengths with increasing iron content as shown in Fig. 2. In pure enstatite, no absorptions are observed because there is no absorbing species (Fe^{2+}).

Because Fe^{2+} is a larger cation than Mg, Fe^{2+} prefers the M2 site in Ca-free pyroxenes. If site ordering is non-ideal or if $\text{Fe}^{2+} > 1$ cation pfu, it will enter the M1 site and produce additional absorptions [1]. Because the M1 site is more symmetrical, these bands are weaker [1]. However, with increasing iron content, the strength of the M1 band centered near 1.2 μm is observed to increase dramatically (Fig. 2). Even at Fe contents below 20%, an additional band at 1.2 μm was found to be necessary to properly model the orthopyroxene spectrum [7]. Our new data in Figure 2 highlight the importance of the 1.2 μm band and its asso-

ciation with Fe content. These data suggest that most observations of a 1.2 μm band in conjunction with the two M2 pyroxene bands are the result of Fe^{2+} in the M1 site (and should *not* be interpreted as plagioclase or olivine species).

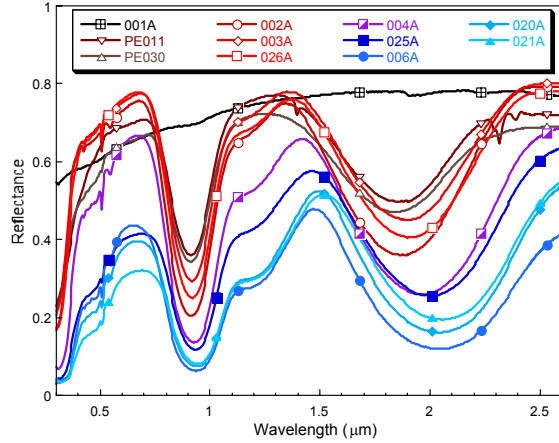


Fig. 2. NIR spectra of synthetic and natural pyroxenes. Red spectra have $<50\%$ Fe; blue have $>50\%$ Fe. Specific compositions for each sample are listed in Table 1.

Table 1. Compositions of Synthetic and Natural Pyroxenes.

Sample	Ca	Mg	Fe	Sample	Ca	Mg	Fe
001A	0	100	0	004A	0	50	50
PE011*	1.65	84.4	14.0	025A	0	35	65
PE030*	1.51	85.6	12.9	006A	0	25	75
002A	0	80	20	020A	0	17	83
003A	0	75	25	021A	0	8	92
026A	0	70	30				

*Natural samples

Mid-Far Infrared. Spectra for our En-Fs series in the mid and far IR are shown in Fig. 3. Absorption features are consistent with those identified by Hamilton (CA#n) with more limited data [5]. Our initial analyses of mid IR features indicate that bands 1-3 migrate toward longer wavelengths as Fe increases, while band 4 migrates to shorter wavelengths. There is very little movement of bands 2 and 3 once 1 cation pfu Fe content (in this case, 50%) is exceeded. Bands 5-8 also migrate towards longer wavelengths with increasing Fe, and band 8 disappears above 50% Fe. There are a large number of absorption features in pure enstatite beyond about 25 μm , but these become muted and disappear at intermediate Fe-Mg compositions. Our long-term goal is to identify the structural changes associated with these features.

Summary: Coordinated spectral analyses of pyroxenes with a broad range of controlled compositions allow a unique opportunity to disentangle the complex absorption features of this mineral group. Electronic absorptions in the near infrared offer insight into the ordering of cations between the M1 and M2 sites, which in turn can be used to constrain the complex molecular vibrational bands of the mid and far IR.

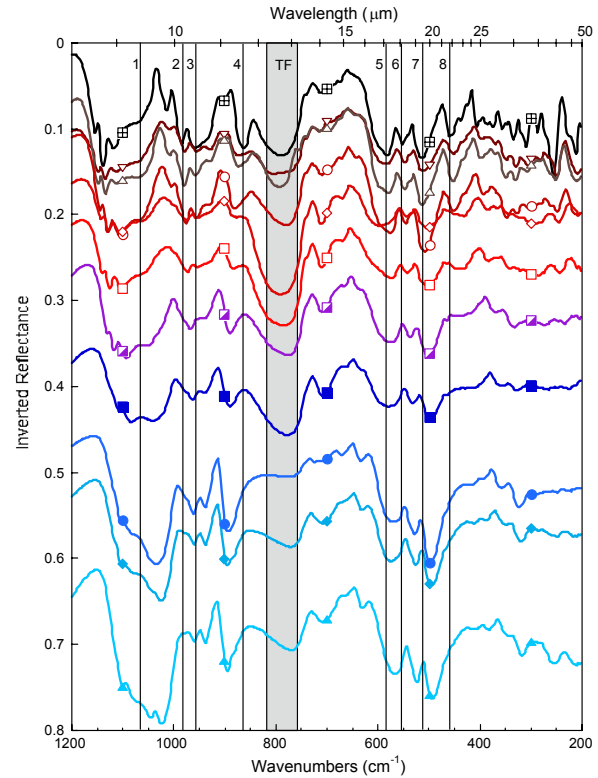


Fig. 3. Mid IR spectra for synthetic and natural pyroxenes. See Fig. 2. for legend. Spectra are offset for clarity and inverted for comparison with emissivity. Around 800 cm^{-1} , the index of refraction produces a transparency feature in reflectance spectra that is not observed in emission spectra. This feature is highlighted in grey. Critical absorptions observed by [5] are indicated by vertical lines.

Acknowledgments: We are grateful to Donald Linsley and Allan Turnock for so generously making this suite of samples available to us. We thank Takahiro Hiroi for his dedication and hard work in the RELAB. We thank NASA grants NNG04GB53G, NNG04GG12G and NAG5-12687. RELAB is supported by NASA grant NAG5-13609.

References: [1] Burns, R.G., *Mineralogical Applications of Crystal Field Theory*. 2 ed. Cambridge Topics in Mineral Physics and Chemistry. 1993, Cambridge: Cambridge University Press. 551. [2] Cloutis, E.A. and M.J. Gaffey, (1991) *Earth Moon and Planets*, 53, 11-53. [3] Cloutis, E.A., (2002) *JGR*, 107, 10.1029/2001JE001590 [4] Adams, J.B., (1974) *JGR*, 79 4829-4836. [5] Hamilton, V.E., (2000) *JGR*, 105, 9701-9716. [6] Sunshine, J.M. and C.M. Pieters, (1993) *JGR*, 98, 9075-9087. [7] Sunshine, J.M., C.M. Pieters, and S.F. Pratt, (1990) *JGR*, 95, 6955-6966. [8] Turnock, A.C., D.H. Lindsley, and J.E. Grover, (1973) *Am. Mineral.*, 58, 50-59. [9] Salisbury, J.W., *Mid-Infrared Spectroscopy: Laboratory Data*, in *Remote Geochemical Analysis: Elemental and Mineralogical Composition*, C.M. Pieters and P.A.J. Englert, Editors. 1993, Cambridge University Press: Cambridge.