Pyroxene spectroscopy has been the focus of much research since the 1970's [e.g. 1,2,4]. Most of this research has centered on the behavior of the prominent 1 and 2 µm crystal field (CF) absorptions that easily distinguish pyroxene from other minerals [1,5]. In addition to these absorption bands, there are a number of spin-forbidden crystal field absorptions in visible spectra of Fe-bearing pyroxenes. Although these features are orders of magnitude weaker than those in the near-infrared, they have been clearly observed on Vesta and other smaller asteroids [6]. With the exception of early transmission spectroscopy of lunar and terrestrial pyroxenes [2,3,7,8], there has been little systematic characterization of visible wavelength pyroxene features with chemical composition. We focus on visible reflectance spectra of a series of synthetic Ca-free pyroxenes to investigate variations in spin-forbidden features with Fe\textsuperscript{2+} content. These features are of interest because sensitive high spectral resolution detectors are available to detect their presence in remote observations.

**Background:** Absorption features at visible wavelengths are attributed to four processes [e.g. 5]: (1) Oxygen metal charge transfers (OMCT); (2) Intervallence charge transfers (IVCT); (3) Spin-allowed crystal field transitions (CFT); and (4) Spin-forbidden crystal field transitions (SFT) [5]. CF transitions are responsible for the prominent 1 and 2 µm Fe\textsuperscript{2+} absorptions in pyroxenes and may also produce absorptions in the visible when Ti or Cr are present [e.g. 5]. OMCT may be 1-2 orders of magnitude more intense than spin-allowed crystal field absorptions, and are responsible for the strong absorption edge seen in Fe\textsuperscript{2+} silicates near 300-400 nm [5].

SFT produce a series of sharp absorptions that are several orders of magnitude weaker than CFT. For example, polarized transmission spectra of a clinopyroxene from Apollo 11 show seven total absorption features between 400 and 700 nm, five of which have been assigned to spin-forbidden transitions in Fe\textsuperscript{2+} and two of which are assigned to CFT in Ti\textsuperscript{3+} [3]. These assignments are based on comparison of the positions of the observed bands with energy level diagrams for Fe\textsuperscript{2+} in octahedral coordination. Spectra of terrestrial and lunar pyroxenes may exhibit four or fewer spin-forbidden features [2,3,7,8]. In terrestrial pyroxenes, these are most likely due to the presence of Fe\textsuperscript{3+}, which causes an Fe\textsuperscript{2+}-Fe\textsuperscript{3+} IVCT band at a similar wavelength, obscuring the weak spin-forbidden features. In extraterrestrial materials, space weathering or shock effects may mask or erase the weaker spin-forbidden features [9].

**Approach:** This study focuses specifically on the Ca-free orthopyroxene sequence, allowing the effects of Fe\textsuperscript{2+} substitution on the spin-forbidden features in pyroxene to be explored (Ca-bearing pyroxenes will be included later).

Through the generosity of Donald Lindsley and Allan Turnock, we have acquired the set of synthetic Ca-Fe-Mg pyroxenes described in [10]. Pyroxenes for this study were synthesized by a variety of methods that were chosen to prevent nucleation of olivine or pyroxenoids. Purity of samples was verified by X-ray diffraction and electron microprobe [10].

Although all of the samples were prepared as fine powders, all pyroxenes were sieved to <45 µm grain size. Spectra were collected from 410-590 nm with a 0.5 nm resolution using the bidirectional reflectance spectrometer at RELAB. Position, width, and intensity of absorption bands were determined using the Modified Gaussian Model (MGM) [11]. Although the MGM was created to model CFT absorption features, SFT are also dependent on the crystal field environment, and SFT absorption energies may be similarly related to the average bond length.

**Preliminary Results:** High-resolution visible spectra of the Ca-free synthetic pyroxene suite are shown in Figure 1. Spectra have been scaled to endmember enstatite at 525 nm. The strongest discernable absorption feature occurs near 506 nm. Absorptions near 425 and 550 nm are also present in all but the endmember enstatite spectrum. With increasing Fe content, additional bands between roughly 450-490 nm become more prominent.

![Fig. 1. Reflectance spectra of Ca-free synthetic pyroxenes from 410-590 nm. Spectra have been scaled to endmember enstatite (black line) to allow comparison of band positions and slope changes with Fe\textsuperscript{2+} content. Spectra of pyroxenes containing <50% Fe\textsuperscript{2+} are shaded red, and those with >50% Fe\textsuperscript{2+} are shaded blue.](image-url)
Fe$^{2+}$ and moving to near 507.4 nm at 92% Fe$^{2+}$. The movement of the 506 nm absorption band center with increasing Fe content is illustrated in Figure 3.

![Image](image_url)

**Fig. 2.** Close-up view of the 506 nm Fe$^{2+}$ feature in the Ca-free synthetic pyroxenes. See Fig. 1 for legend.

**Fig. 3.** Shift of the 506 nm band center for Ca-poor pyroxenes with increasing Fe content.

**Discussion:** Band positions of the three most prominent spin-forbidden features in this suite of synthetic pyroxenes agree well with those measured by previous authors [2,3,7,8]. These bands, located at roughly 425, 506 and 550 nm, have been previously assigned to Fe$^{2+}$, which is consistent with their detection and variations in this Mg-Fe series. Similar to spin-allowed crystal field transitions, these features move to longer wavelengths with increasing Fe contents. Hazen et al. [2] show an additional triplet absorption in FeSiO$_3$ centered near 480 nm. This may correspond to three weak absorptions around 452, 467 and 487 nm in the >50% Fe pyroxenes.

Burns [8] and Hazen [2] both report a sharp doublet near 505 nm in lunar pigeonite spectra. Burns [8] notes a correlation between the relative strengths of the doublet peaks and the distribution of Fe$^{2+}$ between the M1 and M2 crystallographic sites as measured by Mössbauer spectroscopy, and thus suggests that the doublet is caused by Fe in each site. However, although a large portion of the Fe$^{2+}$ in our 92% Fe pyroxene must reside in the M1 site, a doublet is not observed in any of our spectra. There are two potential explanations for this discrepancy. (1) The pigeonites observed by Burns et al. were exsolved (as is common in most pigeonites), and the measured doublet represents a superposition of the 506-nm position of a low-Ca band with that of a high-Ca exsolved phase; or, (2) sharp doublets that are detectable in high-resolution transmission spectra are not resolved in our reflectance spectra. Because of the current uncertainty in interpretation, mineralogic implications based on the presence or absence of a doublet 506 nm are ambiguous (see below).

**Application to Telescopic Data:** High resolution laboratory data of pure Fe-Mg pyroxenes suggest that the spin-forbidden features move to longer wavelengths with increasing Fe content. However, a large number of processes produce absorptions at visible wavelengths, particularly when other transition metals are present in a pyroxene. The assignment of spin-forbidden features to specific electronic transitions is not necessarily unique. Until more detailed investigation is undertaken, caution should be exercised when using spin-forbidden or other minor absorption features to determine chemistry of unknown surfaces from remote measurements.

**Ongoing/Future Work:** Preliminary investigation of a series of intermediate Ca content synthetic pyroxenes (10-30% Ca) reveals that the 506 nm band is indeed often a composite Gaussian with two distinct bands necessary. As more detailed chemical analyses are completed (including Mössbauer spectroscopy), we will address whether a 506 nm doublet is due to Fe$^{2+}$ in the M1 and M2 sites or due to the presence of two pyroxenes (ie., exsolution).

**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 careful work in the RELAB making these measurements possible. We thank NASA grants NNG-05G100G, NNG04GG12G and NSF EAR-0439161. RELAB is supported by NASA grant NAG5-13609.

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