INTRODUCTION: The diagnostic power of near-infrared spectra to determine pyroxene compositions was established more than three decades ago by the seminal work of Burns [1] and Adams [2]. Subsequent work has expanded and deepened our understanding of pyroxene spectra [4-6]. Cloutis and coworkers [7] developed a calibration for determining the relative abundance of pyroxene in olivine-orthopyroxene mixtures. Several groups investigated the effects of temperature on pyroxene band positions [8-11].

Gaffey and coworkers [12] developed a set of equations to derive pyroxene compositions from pyroxene band centers. These involved a means of removing the effect of olivine on the Band I position for olivine-pyroxene mixtures. These calibrations work well for the spectra of pure pyroxene samples, for spectra of mixtures of olivine and orthopyroxene, and for spectra of HED meteorites. However, these equations produce erroneously high values of the iron content (ferrosilite, Fs) for ordinary chondrite spectra. Since one of the main goals of asteroid spectroscopy is to identify potential meteorite parent bodies, this problem raises issues concerning the interpretation of asteroid spectra using these calibrations.

NATURE OF THE PROBLEM: The positions of the 1 & 2 μm Fe²⁺ crystal field features in pyroxene spectra are directly related to the crystal symmetry and composition of the individual pyroxene sample. Although assemblages containing a single pyroxene species are found in nature, it is common to find assemblages with two or more coexisting pyroxenes. In such cases, the position of the absorption features in the reflectance spectrum is a weighted average of the positions of the bands arising from each individual pyroxene phase. This can be defined schematically by the equation:

\[ \lambda_{\text{band}} = \sum_{i=1}^{N} \lambda_i A_i I_i \]  

Eq. 1

where \( \lambda_i \), \( A_i \), and \( I_i \) are the band position, phase abundance, and band intensity of the \( i \)-th pyroxene species in the mixture.

Thus the equations of [12] will return the composition which corresponds to the weighted average band positions for the assemblage whose spectrum is being analyzed. The procedure successfully returns the correct compositions for samples containing a single pyroxene species such as pure pyroxenes, mixtures of olivine and orthopyroxene, and HED meteorites. (Strictly speaking, the HED meteorites contain two pyroxenes – a low-calcium orthopyroxene phase hosting tiny high-calcium augite exsolution lamellae [e.g., 13,14].) The compositions of HED pyroxenes reported in the literature are commonly of the bulk phase including both the low-Ca Opx host and the high-Ca augite lamellae. Thus, the spectral derived composition correspond well to the analytical compositions.

ORDINARY CHONDRITE SPECTRA: Discrete augite grains are the third most abundant silicate phase in ordinary chondrites [15]. The augite comprises ~12%, ~17%, and ~19% of the total pyroxene in H-, L-, and LL-chondrites respectively [16]. Thus, ordinary chondrites are two-pyroxene assemblages. Although additional work is required to develop calibrations to interpret the suite of possible two-pyroxene assemblages, a procedure has been developed for the limited two-pyroxene suite present in ordinary chondrites. The procedure has been set up as an Excel spreadsheet (available upon request).

The first step is to determine the wavelengths of the Band I and Band II features and the band area ratio (BAR) from the spectrum of the potential OC asteroid. These band centers are entered into the appropriate cells on the spreadsheet which uses the set of equations defined by Gaffey and coworkers [12]. The Fs and Wo values that satisfy the conditions of the equations are identified. If the asteroid consists of an olivine-free one-pyroxene assemblage, or a two-pyroxene HED-type assemblage [as indicated by BAR > ~1.5], these values are the pyroxene chemistry.

If the spectrum contains a spectrally significant olivine component [BAR < ~1.5], the correction factor shown on Figure 1 needs to be applied. The appropriate correction factor can be computed by entering the BAR value into the appropriate cell on the spreadsheet. This correction factor is subtracted from the Band I center position and the Fs and Wo values that satisfy the conditions of the equations are identified.

To test for an OC assemblage, the process is repeated for the H-, L-, and LL-chondrite options by compensating for the presence of augite on the Band II position (subtracting 0.063 \( \mu \)m, 0.061 \( \mu \)m, and 0.083 \( \mu \)m, respectively (Fig. 2). [Note: These parameters are still being adjusted and refined values will be available in the Excel spreadsheet that is distributed.] If the assemblage is an ordinary chondrite, the resulting Fs and Wo values will fall in the OC range [indicated on the worksheet]. Falling in the OC range maintains the OC option but does not prove it. Falling outside the OC range eliminates the OC option. Figures 2 & 3 show the effect of applying these correction fac-
tors to OC chondrite spectra. Figure 3 compares the band positions corrected from OC spectra to the band positions computed from the measured OC low-Ca pyroxene compositions, showing good agreement. The analytic and spectrally-derived compositions agree to within ±1-2 mole percent in iron and calcium.

Partial Melt Assemblages: A number of asteroid spectra have recently been interpreted as indicating partially melted assemblages [17-20]. It has been suggested that partial melting should be the end-state for a large fraction of the asteroid population [21]. If an asteroid fails the OC test described above and indicates a pyroxene composition with Fs and Wo above the OC range, this is a strong indication of a partial melt assemblage where the melt phase was not efficiently extracted from the source region (or was enriched). Although the bulk pyroxene composition is conserved in the partial melting process, the process affects the band positions because of the redistribution of the Ca and Fe cations. The initial melt phase is enriched in both Fe and Ca and – if crystallized – resembles a eucritic assemblage, resulting in a three-pyroxene assemblage. During the melting process both the abundance and the Fe contents of the low-Ca Opx and augite are depleted. If Equation 1 is applied to the new system, it is evident that the spectrum will be disproportionally affected by the Fe- & Ca-rich eucrite-like pyroxene. Although the calibration is failing, its failure is diagnostic. Future work is needed to establish a calibration to disentangle the third-pyroxene effect.

Figure 1 – The correction factor applied to (subtracted from) the Band I position measured for olivine-bearing olivine-orthopyroxene assemblages from [12].

Figure 2 - The effects of applying the correction factors to the band positions measured from average ordinary chondrite spectra: Red = H Chon., Green = L Chon., Blue = LL Chon. Diamonds (ranges indicated by bars) = average measured OC Band centers. Squares = Band centers corrected for olivine. Triangles = Band centers corrected for olivine and augite. The approximate band positions of the OC augite is indicated by the pink square. Band positions for pyroxenes from [2,4] are plotted as small black symbols.

Acknowledgments: This research was supported by NASA PGG Grant NNG04GJ86G and NASA NEOO Grant NNG04GI17G.