GAUSSIAN ANALYSIS OF PYROXENE REFLECTANCE SPECTRA. Jessica M. Sunshine, Carle M. Pieters and Stephen F. Pratt, Department of Geological Sciences, Brown University, Providence, R. I., 02912.

Introduction Studies of visible and near-infrared reflectance spectra have provided a basis for estimating the mineralogy of many terrestrial and extra-terrestrial surfaces. Current and future exploration programs call for increased utilization of mapping spectrometers from telescopic, airborne and orbiting platforms. The large influx of data from any one these sources, e.g. MO-VMIS, requires a consistent and perhaps automated approach to the classification of absorption features [e.g. 1, 2]. A Gaussian analysis of the diagnostic features in reflectance spectra of common silicates was initiated to provide a solid foundation for developing such a method.

Pyroxenes Analysis of the pyroxene group is most critical to spectral studies due to their relative abundance among the rock-forming minerals throughout the solar system. In addition, the spectral character of pyroxenes is well described and systematic [3,4,5]. The spectra of pyroxenes are dominated by Fe$^{2+}$ absorption bands centered near 1.0 and 2.0 μm. In reflectance spectra, the centers of these bands vary with Fe and Ca concentration from 0.90 to 1.05 μm and 1.80 to 2.30 μm, respectively [3]. These absorptions are primarily caused by spin-allowed electron transition of Fe$^{2+}$ in highly distorted octahedral (M2) sites [6]. Pyroxenes often also included Cr$^{3+}$ in the M1 sites, which cause absorptions in the 0.62 to 0.65 μm region [4].

The Gaussian Model Absorption features observed at visible and near-infrared wavelengths arise from a variety of electronic and vibrational processes [3,4,6,7]. The observed absorption energies of these processes are thought to be randomly distributed around a discrete energy. The Central Limit Theorem of Statistics states that given sufficient sampling, all random distributions will approach Gaussian distributions. As such, absorption features have often been considered to be Gaussian in shape [8,9,10]. Although sometimes successful [11,12], early experimentations in modeling reflectance absorption features with Gaussians have not been actively pursued, largely due to the inability of the computers to efficiently handle the mathematics.

New Software A relatively fast Gaussian fitting routine has been adapted for use on a Micro Vax II, based on the algorithm developed by Kaper [13]. Absorption features are modeled in natural log reflectance and energy (cm$^{-1}$) space. The accuracy of fit is determined by a non-linear least squares analysis. This routine, operating under the capabilities of a Micro Vax II, can simultaneously fit thirteen Gaussians, which necessitates a reduction of a 39-by-39 matrix, in less than 30 seconds.

Data Acquisition Hand picked mineral separates of low-calcium (websterite) and high-calcium (Hawaiian xenolith) pyroxenes were crushed and wet-sieved to particle size separates. Initial analyses have been performed for particles of less than 45 μm. Spectra of these pyroxenes and mass fraction pyroxene mixtures were obtained from 0.325 to 2.60 μm at 5 nm sampling resolution (θ=30°, η=0°) using the RELAB bidirectional spectrometer. The spectra are calibrated to absolute reflectance using a Halon standard [14].

Method of Gaussian Analysis Each spectrum is first fit with a straight line continuum in energy space. It should be noted that in the absence of such a continuum, the routine would attempt to approximate the continuum with a Gaussian by broadening and decreasing one of the Gaussian distributions to an extreme. Using an initial estimate of the Gaussian parameters, the centers, widths and depths are adjusted until a negligible improvement in the fit is produced. Additional Gaussians are then added based on examination of the residual. After both the number and properties of all the Gaussians have been determined, final adjustments to the fit are made by optimizing the continuum parameters.

Results The orthopyroxene was best fit with a continuum and seven discrete Gaussian distributions (Fig 1). Both the 1.0 μm and 2.0 μm absorption features required two Gaussians in order to produce an acceptable fit. Additional Gaussians were needed in the the ultraviolet and visible regions. Finally, a relatively weak and broad Gaussian was necessary to accommodate H$_2$O absorption at longer wavelengths. Even though the detailed spin-forbidden features in the 0.3 to 0.6 μm region were not modeled, an RMS error of 0.0042 was obtained.

The clinopyroxene was best fit with nine discrete Gaussians (Fig. 2). As with the low-calcium pyroxene, two Gaussians were required in the 2.0 μm feature (although there was apparently no need for an H$_2$O band), as well as one in the ultraviolet and one in the visible. The 1.0 μm Fe$^{2+}$ feature required three Gaussians while two additional Gaussians were necessary at shorter wavelengths to accommodate the probable Cr$^{3+}$ features. Here again, the fit is excellent with an RMS of 0.0037.

The 75/25 and 25/75 Opx/Cpx mass fraction mixtures were fit using Gaussians centered at the wavelengths of those determined for the end members (Fig. 3 and 4). Since the end members have three band centers in common, each was fit with a continuum and thirteen Gaussians. The results for the 75/25 and 25/75 Opx/Cpx mixtures yields RMS errors of 0.0068 and 0.0057 respectively.
Discussion The results imply that many of the absorption features in reflectance spectra that have been treated as single phenomenon are in fact composed of multiple distributions, as expected from detailed transmission studies [15]. In addition, this mathematical analysis clearly requires the inclusion of a continuum in order to produce a good fit. Finally, these preliminary results indicate that, with further examination of the quantitative systematics of pyroxene mixtures and their chemistry, Gaussian analysis can readily provide an objective approach to the classification of pyroxene absorption features.

Figure 1. (Bottom to top) The bidirectional reflectance spectra of orthopyroxene, the seven discrete Gaussians that comprise the fit and the residual error of that fit (offset 10% for clarity).

Figure 2. (Bottom to top) The bidirectional reflectance spectra of clinopyroxene, the nine discrete Gaussians that comprise the fit and the residual error of that fit (offset 10% for clarity).

Figure 3. (Bottom to top) The bidirectional reflectance spectra of 75% Opx 25% Cpx, the thirteen discrete Gaussians that comprise the fit and the residual error of that fit (offset 10% for clarity).

Figure 4. (Bottom to top) The bidirectional reflectance spectra of 25% Opx 75% Cpx, the thirteen discrete Gaussians that comprise the fit and the residual error of that fit (offset 10% for clarity).

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