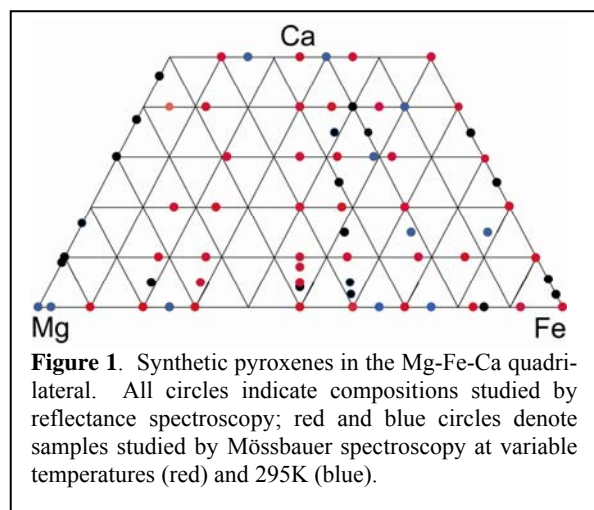# REFLECTANCE AND MÖSSBAUER SPECTROSCOPY OF SYNTHETIC PYROXENES: I. IMPLICATIONS FOR INTERPRETING COOLING RATES OF REMOTE-SENSED SURFACES.

M.D. Dyar[1], R.L. Klima[2], and C.M. Pieters[2]. [1]Department of Astronomy, Mount Holyoke College, South Hadley, MA 01075; mdyar@mtholyoke.edu. [2]Department of Geological Sciences, Brown University, Providence RI 02912.

Introduction: Interpretations of remote-sensed planetary surfaces often use pyroxene features to address questions about the magmatic evolution and cooling history of the pyroxene-bearing terrestrial bodies. Such inferences depend on detailed understanding of the relationships among pyroxene spectral features, mineral chemistry, and cooling rates. To evaluate the fundamental relationships among these variables, we have undertaken spectroscopic studies of synthetic pyroxenes that span the compositional range of the Mg-Fe-Ca quadrilateral (Figure 1).

Figure 1. Synthetic pyroxenes in the Mg-Fe-Ca quadrilateral. All circles indicate compositions studied by reflectance spectroscopy; red and blue circles denote samples studied by Mössbauer spectroscopy at variable temperatures (red) and 295K (blue).

The majority of spectroscopic studies of pyroxenes have focused on characterizing the positions of the strong spin-allowed crystal field absorption bands centered near 1 and 2 µm as a function of Ca and Fe content (Figure 2). Both the 1 and 2 µm bands of pyroxenes move regularly to longer wavelengths with increasing Fe and/or Ca contents. Despite these compositional trends, extracting geothermometric information from the measurement of the 1 and 2 µm band minimum has been shown to be impossible [1] because the contours of band position on the pyroxene quadrilateral are roughly orthogonal to geotherms.

However, pyroxene spectra also exhibit a weaker absorption band at 1.2 µm (light blue in Figure 2), which is best-defined in Ca-saturated pyroxenes. The 1.2 µm band in pyroxene provides information about the distribution of Fe^{2+} between the octahedral M1 and M2 sites; this can also be determined from Mössbauer spectroscopy [2]. Because the distribution of Fe^{2+} between cation sites is a function of the thermal history of a pyroxene, Fe-Mg ordering provides an additional constraint for assessing the cooling history of a pyroxene-bearing planetary body or surface unit observed by near-infrared remote sensing.

In this paper, we report on a subset of results of a large study relating the reflectance spectral characteristics of synthetic pyroxenes to accurately-determined Fe^{2+}, Mg, and Ca site occupancies measured by Mössbauer spectroscopy (corrected for differential recoil-free fractions from Fe^{2+} in the M1 and M2 sites), and discuss kinetics of cooling rates that pertain to their proper interpretation for spectra of meteorites and terrestrial bodies such as asteroids. The companion paper [3] applies these results to Mössbauer and reflectance spectra of 51 HED meteorites.

Experimental: Synthesis procedures are described in [4] with minor variations. Specific methods varied by composition, and were chosen to prevent nucleation of pyroxenoids and produce homogeneous pyroxenes. All samples were cooled to room temperature from 900-1500ºC in water, so cooling rates are estimated to be less than 1 minute. For most of our samples, this is fast enough to quench the equilibrium distribution of Fe^{2+} and Mg [5,6]. Compositions and space groups were confirmed by EMPA and XRD.

Reflectance and Mössbauer spectra were measured using methods described in [7,8]. Results from the latter show that Fe^{3+} is not observed in any sample.

In addition, Mössbauer peak areas were corrected for differential recoil-free fraction (f), calculated using the Debye approximation as described in [9], based on temperature-series data (red circles in Figure 1). We quantify f by using the temperature dependence of the center shift (δ). The Mössbauer temperature (an approximation of the Debye temperature, θ_D) and the center shift (δ) are calculated based on a fit of the Debye integral approximation to the experimental data. The f value for each site is calculated from:
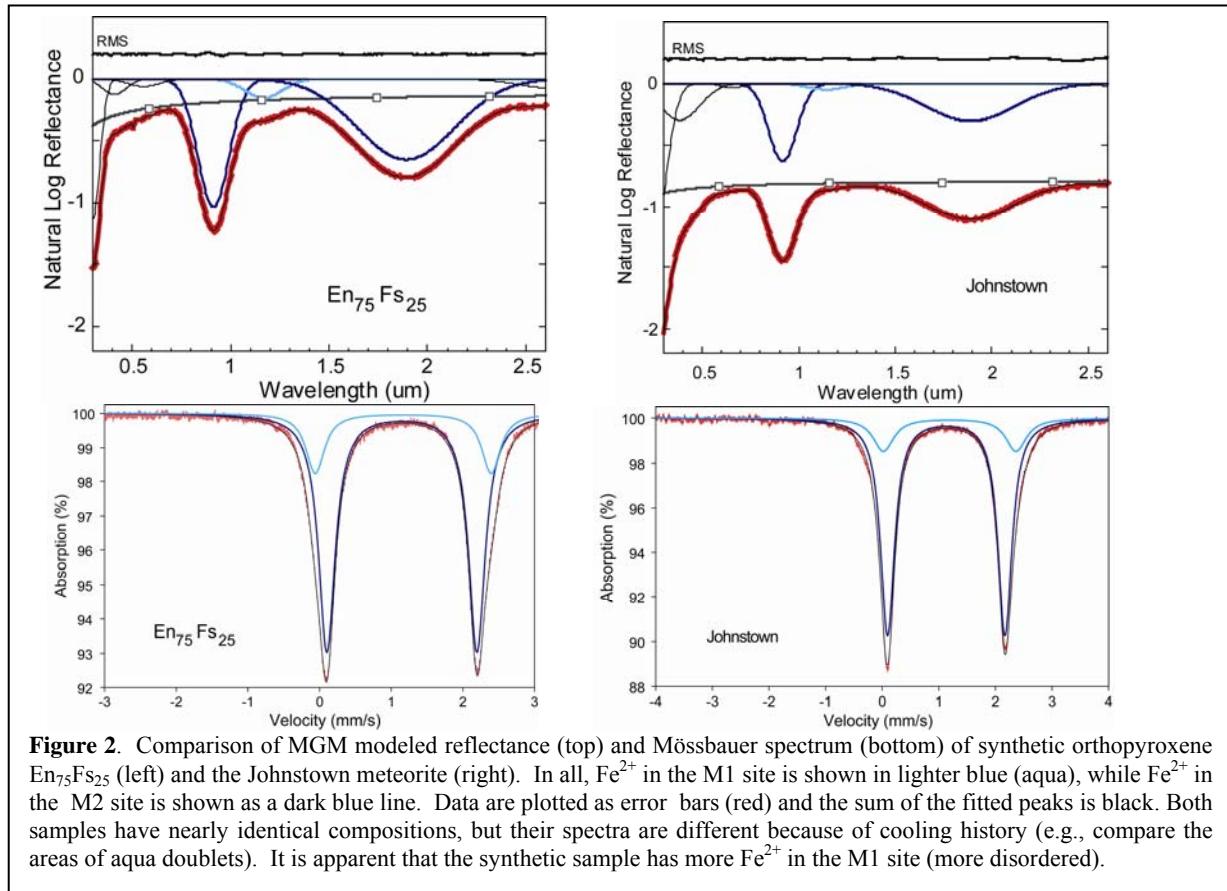
$$f = \exp\left[-6E_R/k\theta_D\left[\tfrac{1}{4}+T/\theta_D\right]^2\int(xdx)/(e^x-1)\right]],$$

where E_R is the recoil energy, related to the transition energy, E_γ by $E_R = E_\gamma^2/2Mc^2$.

The value of f is then used to correct the doublet areas, in this case A^{M1} and A^{M2}; N is the "true" amount of Fe^{2+} in each site:

$$\frac{A^{M1}}{A^{M2}} = \frac{\Gamma^{M1}G(x)^{M1}f^{M1}}{\Gamma^{M1}G(x)^{M1}f^{M2}}\frac{N^{M1}}{N^{M2}}.$$

Note that both peak width (Γ) and sample saturation $G(x)$ must also be considered. The Γ component is

Figure 2. Comparison of MGM modeled reflectance (top) and Mössbauer spectrum (bottom) of synthetic orthopyroxene En$_{75}$Fs$_{25}$ (left) and the Johnstown meteorite (right). In all, Fe^{2+} in the M1 site is shown in lighter blue (aqua), while Fe^{2+} in the M2 site is shown as a dark blue line. Data are plotted as error bars (red) and the sum of the fitted peaks is black. Both samples have nearly identical compositions, but their spectra are different because of cooling history (e.g., compare the areas of aqua doublets). It is apparent that the synthetic sample has more Fe^{2+} in the M1 site (more disordered).

easily constrained by forcing peak widths to vary in pairs. Thickness effects ($G(x)$) can be empirically corrected. Thus Fe^{2+} occupancy in M1 and M2 can be accurately determined, then related to MGM results and applied to kinetic equations for order/disorder.

Interpretation of cooling rates. The kinetics of cation disorder between sites in pyroxenes (especially orthopyroxenes) has been well-studied [5,6]. Equilibrium distributions of Fe^{2+} and Mg in the M1 and M2 sites as a function of temperature are described by:

$$\ln K_D = 0.391(\pm0.131) - \frac{2205(\pm141)}{T(K)} \text{ for } X_{Fs} \text{ up to}$$

~0.6, where $K_D = \dfrac{X_{Fe}^{M1} X_{Mg}^{M2}}{X_{Fe}^{M2} X_{Mg}^{M1}}$ [4]. However, the

value of K_D used in this formulation was derived from Mössbauer data for which $f(^{M1}Fe^{2+}) = f(^{M2}Fe^{2+})$ was assumed. Our work now shows that the differenece between these values is significant and *is composition-dependent*, so a new series of composition-specific equations for K_D are being derived.

As an example, consider the Johnstown diogenite, which has a composition of roughly Wo$_3$En$_{74}$Fs$_{23}$ (Figure 2) [10]. From our synthetic samples, we calculate that at 295K, f^{M1} =0.705 and f^{M2} = 0.724. The resul-

tant 3% change in K_D will propogate through the cooling rate calculations and change the ordering paths. Note that pyroxenes in other areas of the quadrilateral have larger differences between f^{M1} and f^{M2}.

Conclusions. Availability of accurate, composition-specific values for f will allow better interpretation of order-disorder relationships in pyroxenes, and improve our understanding of exchange kinetics and cooling histories of pyroxene-bearing rocks. These revisions may help rectify anomalous cooling rates calculated for the Johnstown meteorite [10] and permit more reliable estimates of cooling histories for HED meteorites.

References: [1] Cloutin and Gaffey (1991) *JGR-Planets*, 96, 22809-22826. [2] Besancon et al. (1991) *LPSC XXII*, 95-96; Burns et al. (1991) *NASA #N92-10823*, 253-355. [3] Klima R. (2008) this volume. [4] Turnock et al. (1973) *Amer. Mineral.*, 58, 50-59. [5] Wang et al. (2005) Fe-Mg disorder in orthopyroxenes. *GCA*, 69, 5777-5788. [6] Kroll et al. (1997) *Eur. J. Mineral.*, 9, 705-733. [7] Dyar et al. (2007) *Amer. Mineral.*, 92, 424-428. [8] Klima et al. (2007) *MAPS*, 42, 235-253. [9] Dyar et al. (2006) *Ann Revs. EPS*, 34, 83-125. [10] Heinemann et al. (2000) *Eur. J. Mineral.*, 12, 163-176.