

**MÖSSBAUER SPECTROSCOPY OF CLAY MINERALS AT VARIABLE TEMPERATURES.** M.D. Dyar<sup>1</sup>, E.C. Sklute<sup>1</sup>, M.W. Schaefer<sup>2</sup>, and J.L. Bishop<sup>3</sup>. <sup>1</sup>Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075, USA mdyar@mtholyoke.edu. <sup>2</sup>Dept. of Geology and Geophysics, E-235 Howe-Russell, Louisiana State University, Baton Rouge, LA 70803, USA. <sup>3</sup>SETI Institute/NASA-Ames Research Ctr, Mountain View, CA, 94043.

**Introduction:** Clay minerals are ubiquitous constituents in soils on Earth, are infrequently found in meteorites, and may also occur on planetary surfaces in the presence of water. However, little is known about the fundamental Mössbauer parameters that are characteristic of clay minerals. In particular, knowledge of the differential recoil-free fractions ( $f$ ) for Fe atoms in different sites in these minerals is critical to correctly interpreting  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios as well as mineral modes. Multi-temperature spectra of well-characterized single mineral samples at multiple temperatures are required for determinations of  $f$ . Thus, we present here  $\ddot{o}$ for six layer silicates with a range of layer types. This work is part of a larger study to characterize and interrelate the spectroscopic characteristics of these minerals using emittance, reflectance, and Mössbauer spectroscopies (see [1]). We are also using this study to examine the variations in fitting results that are obtained with various different software packages available for processing Mössbauer data.

**Background:** This group of minerals was chosen for our detailed studies because they contain a range of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  contents and have already been well-characterized by previous workers [2-7] (Table 1).

**Table 1. Mineral Species Studied**

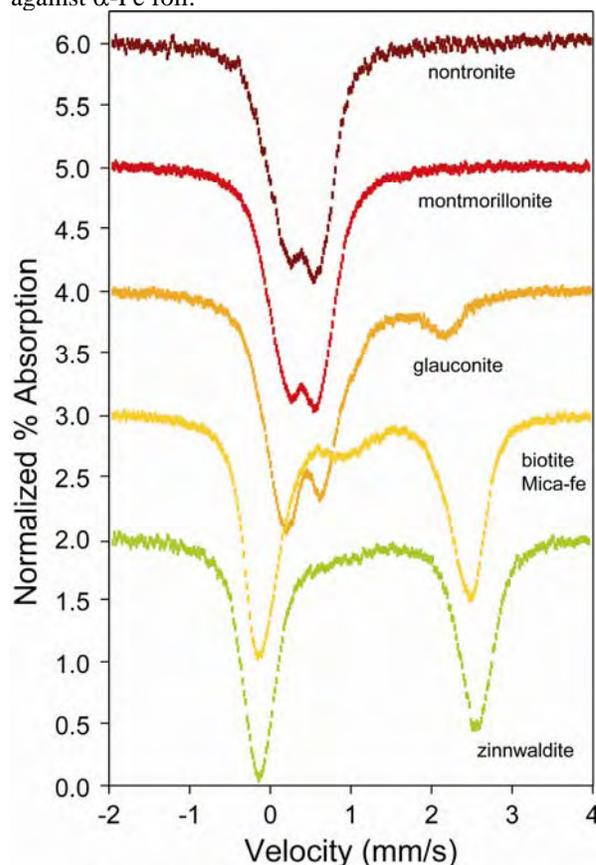
Mineral	Locality	Citation
celadonite*	Mojave desert, CA	[2]
clinocllore	West Chester, PA	[3]
zinnwaldite ZW-C	Cinovec, Czech Republic	[4]
biotite Mica-Fe	CRPG standard	[5]
glauconite	Hurricane Mtn.	[6]
nontronite JB175	Sampor, Slovakia	[7]
montmorillonite JB170 SWa-1	Washington, CMS Source Clays	[7]

\*[1] already determined the  $f$  values for this sample, but we are including it in this study for purposes of cross-comparison.

The peak positions in a Mössbauer spectrum are described in terms of the isomer shift ( $\delta$ , which arises from the difference in  $s$ -electron density between the source and the absorber) and quadrupole splitting ( $\Delta$ , which arises from the interaction between the nuclear quadrupole moment and the electric field gradient at the nucleus), when the magnetic moment is zero. The combination of  $\delta$  and  $\Delta$  is sufficient to assess the valence state and coordination polyhedron surrounding each Fe atom in a structure. The temperature dependence of the Mössbauer parameters will vary from spe-

cies to species depending on the polyhedral geometry and the nearest and next nearest neighbors of the Fe sites. Neither the temperature dependence nor the recoil-free fraction can be determined empirically or theoretically; they must be measured.

**Methods:** Samples for this project (Table 1) were made available to us in pure form. Samples were mixed with sucrose under acetone to prevent oxidation and preferred orientation of the flat mineral grains. Sample thicknesses were 1 mg Fe/cm<sup>2</sup>, except in the case of clinocllore which was run at 5 mg Fe/cm<sup>2</sup>. Variable temperature Mössbauer spectra were acquired under low He gas pressure at 17 temperatures ranging from 4-295K. A source of 100-70 mCi <sup>57</sup>Co in Rh was used on a WEB Research Co. model W302 spectrometer equipped with a Janus closed-cycle 4K He refrigerator. Run times ranged from 6-24 hours, and results were corrected for Compton absorption and calibrated against  $\alpha$ -Fe foil.



**Figure 1.** Mössbauer spectra of clay minerals acquired at 225K, a typical surface temperature for the MERs.

Spectra were fit using several different lineshapes and models as implemented in three software packages: WMOSS from WEB Research Co. in Minnesota, Recoil, from the University of Ottawa in Canada, and an in-house program from the University of Ghent in Belgium (the Wivel-Mørup program).

**Recoil-free fraction calculations:** The Mössbauer or recoilless fraction ( $f$ ) is the fraction of nuclear events that take place without exciting the lattice; i.e., they produce no change in the quantum state of the lattice. This fraction of the recoil energy that cannot be transferred to exciting a lattice vibration can be quantified as:  $f = \exp [(-4\pi^2\langle X^2 \rangle)/\lambda^2]$ , where  $\langle X^2 \rangle$  is the mean square vibrational amplitude of the absorbing/transmitting nucleus in the solid, and  $\lambda$  is the wavelength of the  $\gamma$  photon. The value of  $\langle X^2 \rangle$  (typically in the range of  $10^{-4} \text{ \AA}^2$ ) varies for different chemical compounds depending on the site geometry and valence state of the Fe atom. Therefore,  $f$  also varies for different valence states of iron in different types of sites.

The area of a Mössbauer doublet (pair of peaks) is actually a function of peak width  $\Gamma$ , sample saturation  $G(x)$ , and the Mössbauer recoil-free fraction  $f$ . The doublets corresponding to  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  have areas equal to  $A^{3+}$  and  $A^{2+}$ ;  $N$  is the "true" amount of each species and  $C$  is the "correction factor," as in:

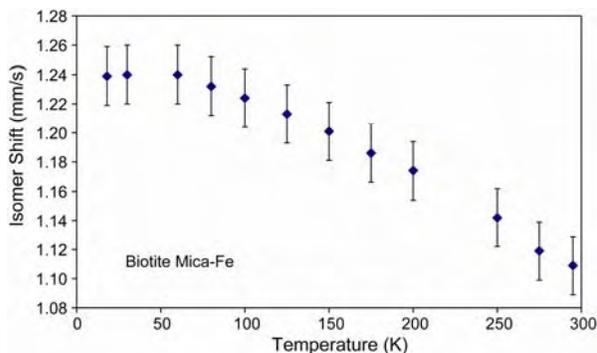
$$\frac{A^{3+}}{A^{2+}} = C \frac{N^{3+}}{N^{2+}}, \text{ where } C = \frac{\Gamma_{3+} G(X_{3+}) f_{3+}}{\Gamma_{2+} G(X_{2+}) f_{2+}}.$$

We quantify  $f$  by using the temperature dependence of the center shift ( $\delta$ ), which can be written as  $\delta(T) = \delta_I + \delta_{\text{SOD}}(T)$ . To calculate  $f$ , Mössbauer spectra of the mineral of interest are acquired over a range of temperatures. Next, the Mössbauer temperature (an approximation of the Debye temperature,  $\theta_D$ ) and the center shift ( $\delta$ ) are calculated based on a fit of the Debye integral approximation to the experimental data. Finally, the recoil-free fraction for each site is calculated using the relation:

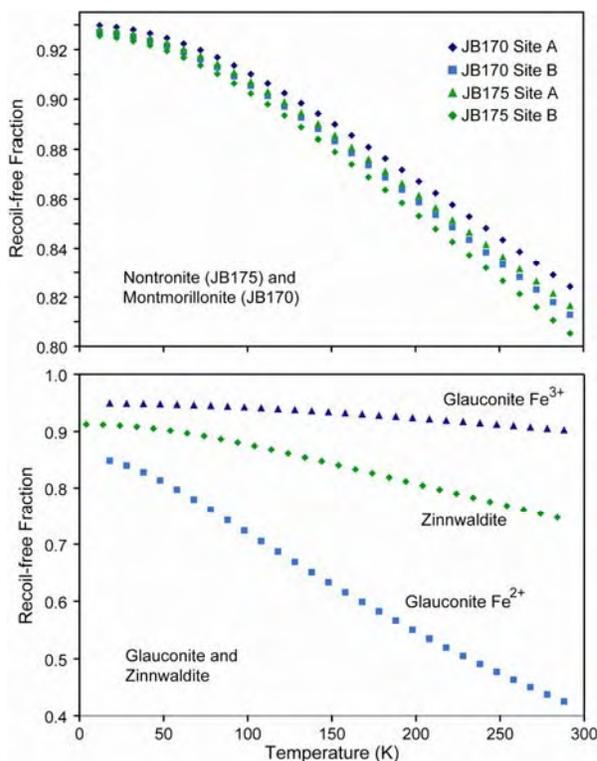
$$f = \exp [-6E_R/k\theta_D^{1/4} + T/\theta_D]^2 [(x dx)/(e^x - 1)],$$

where  $E_R$  is the recoil energy, related to the transition energy,  $E_\gamma$  by  $E_R = E_\gamma^2/2Mc^2$ . To do these calculations, we used software provided by E. DeGrave (University of Ghent).

**Results:** Typical Mössbauer spectra of our minerals are shown in Figure 1 at 225K (a temperature typical of the MER sites). All 17 spectra (at variable temperatures) of each mineral were fit and their Mössbauer parameters calculated; as an example, isomer shifts for one of the  $\text{Fe}^{2+}$  doublets in Biotite Mica-Fe are shown in Figure 2. Finally, values for  $f$  were calculated at each temperature for use in future studies of these minerals (examples given in Figure 3).



**Figure 2.** Plot of isomer shift vs. temperature for one of the  $\text{Fe}^{2+}$  doublets in the biotite mica-Fe sample. These points are fit to the Debye integral approximation, and the results are used to calculate values of  $f$  at each temperature for each doublet as explained in the text.



**Figure 3.** Recoil-free fractions for the two smectites (top) and two of the micas (bottom).

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**References:** [1] Bishop, J.L., et al. (2007) this volume. [2] Bowen, L.H. et al. (1989) *Phys. Chem. Mins.*, 16, 697-703. [3] Smyth, J.R. et al. (1997) *Clays Clay Mins.*, 45(4) 544-550. [4] Govindaraju, K. et al. (1994) *Geostand. Newsl.*, 18(1), 1-42. [5] LaLonde, A.E. et al. (1998) *Hyperf. Inter.*, 117, 175-204. [6] Francis, C.A. (in preparation) *Amer. Mineral.* [7] Bishop, J., et al. (2002) *Clay Minerals*, 37, 617-628.