

FUNDAMENTAL MÖSSBAUER PARAMETERS OF HYDROUS IRON SULFATES. Y. Rothstein¹, M.D. Dyar¹, M.W. Schaefer², M.D. Lane³, and J.L. Bishop⁴. ¹Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075, yrothste@mtholyoke.edu; ²Dept. of Geology and Geophysics, E235 Howe-Russell, Louisiana State University, Baton Rouge, LA 70803. ³Planetary Science Institute, Tucson, AZ 85719; ⁴SETI Institute/NASA-Ames Research Ctr, Mountain View, CA, 94043.

Introduction: Hydrous iron sulfates, which form as alteration products of sulfides, are rare on Earth. On Mars, the low temperature and pH found in the martian permafrost create ideal conditions for the formation of this group of minerals [1], which includes such phases as coquimbite ($\text{Fe}_2(\text{SO}_4) \cdot 9\text{H}_2\text{O}$) and amaranthite ($\text{FeSO}_4(\text{OH}) \cdot 3\text{H}_2\text{O}$). Viking, Mars Pathfinder, MER and OMEGA data [e.g., [2]] have all indicated the presence of high sulfur contents on the surface of Mars, but the mineralogy of the sulfur-rich phases has not been well constrained. Recent work by [3] suggests that hydrous iron sulfates might satisfy the Martian thermal emission, vis-near IR, and Mössbauer spectra. These data suggest that sulfide and sulfate minerals might be significant contributors to all types of spectra acquired on the Martian surface.

However, little is known about the fundamental Mössbauer parameters that are characteristic of hydrous sulfates. Prior to our study, only a handful of spectra had been previously reported, all acquired at room temperature. 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 fundamental Mössbauer parameters for four key hydrous sulfates, with a fifth mineral tochilinite, included for comparison.

Background: This group of largely Fe^{2+} minerals was chosen for our detailed studies because their Mössbauer spectra closely resemble those of the mineral olivine, which has been reported at Gusev site [4].

The peak positions in a Mössbauer spectrum are described in terms of the isomer shift (δ , which arises from the difference in s -electron density between the source and the absorber) and quadrupole splitting (Δ , 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 δ and Δ is sufficient to assess the valence state and coordination polyhedron surrounding each Fe atom in a structure. Many phases have Fe^{2+} in octahedral coordination, but only a few (nesosilicates, hydrous sulfates) are characterized by the large quadrupole splitting that is a reflection of their more regular

site geometry relative to other silicates. The temperature dependence of the Mössbauer parameters will vary from species 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 first hand-picked to purify them, a step that was vitally important because many of these phases occur in intergrowths with other minerals. Separates were then analyzed by XRD to confirm their purity and make unequivocal phase identifications. All samples were kept in dry air in a dessicator when not being analyzed. Variable temperature Mössbauer spectra were acquired under low He gas pressure at 16 temperatures ranging from 12-295K. A source of 100-70 mCi ^{57}Co in Rh was used on a WEB Research Co. model W100 spectrometer equipped with a Janus closed-cycle He refrigerator. Run times ranged from 12-48 hours, and results were calibrated against α -Fe foil.

Table 1. Mineral Species Studied

Mineral Species	Nominal Formula
szomolnokite	$\text{Fe}[\text{SO}_4] \cdot \text{H}_2\text{O}$
rozenite	$\text{Fe}[\text{SO}_4] \cdot 4\text{H}_2\text{O}$
melanterite	$\text{Fe}[\text{SO}_4] \cdot 7\text{H}_2\text{O}$
römerite	$\text{Fe}^{2+}\text{Fe}_2^{3+}[\text{SO}_4]_4 \cdot 14\text{H}_2\text{O}$
tochilinite	$(\text{Fe}, \square)\text{S} \cdot \sim 0.85(\text{Mg}, \text{Fe})(\text{OH})_2$

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 λ is the wavelength of the γ photon. The value of $\langle X^2 \rangle$ (typically in the range of 10^{-4} \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 Γ , sample saturation $G(x)$, and the Mössbauer recoil-free fraction f . The

doublets corresponding to Fe^{3+} and 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 (δ), which can be written as $\delta(T) = \delta_{1+} + \delta_{\text{SOD}}(T)$. 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, θ_D) and the center shift (δ) 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:

$f = \exp[-6E_R/k\theta_D^{1/4} + T/\theta_D]^2 \int (xdx)/(e^x - 1)]$, where E_R is the recoil energy, related to the transition energy, E_γ by $E_R = E_\gamma^2/2Mc^2$.

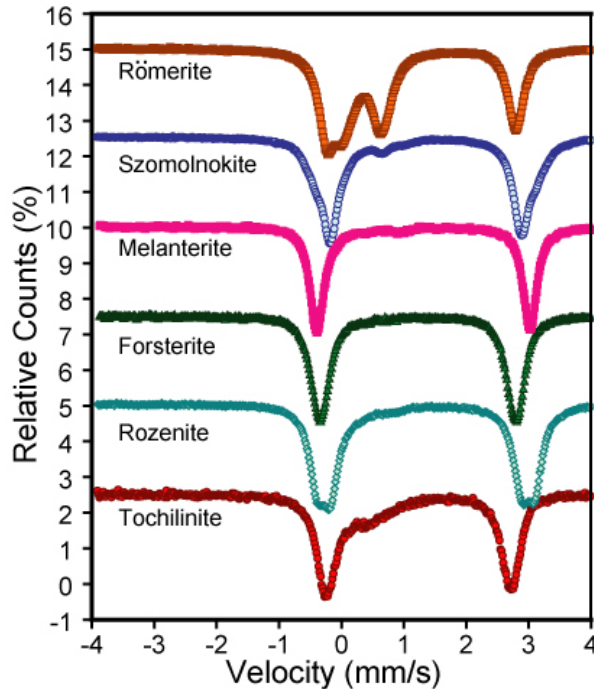


Figure 1. 220K Mössbauer spectra of olivine (forsterite) and hydrous sulfate group minerals.

Results: Typical Mössbauer spectra of our minerals are shown in Figure 1 at 220K (a temperature typical of the MER sites). All 16 spectra (at variable temperatures) of each mineral were fit and their Mössbauer parameters calculated; isomer shifts for Fe^{2+} doublets are shown in Figure 2. Finally, values for f were calculated at each temperature for use in future studies of these minerals (Figure 3).

Conclusions: The range of measured Mössbauer parameters for Fe^{2+} in many of these phases ($\delta = 1.15-$

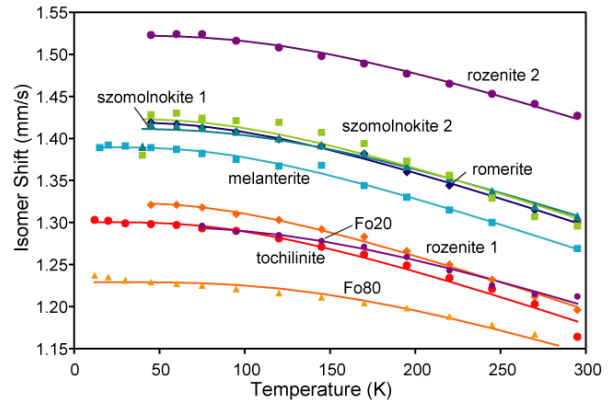


Figure 2. Experimental data (symbols) and modeled approximations (solid lines) for Fe^{2+} -bearing hydrous sulfates and two synthetic olivine compositions, Fo20 and Fo80.

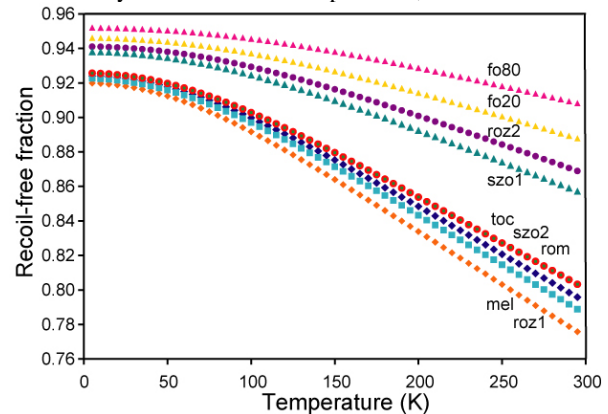


Figure 3. Recoil-free fractions for Fe^{2+} as a function of temperature.

1.30 mm/s and $\Delta = 2.80-3.00$ mm/s) is very similar to that for the mineral group olivine ($\delta = 1.13-1.17$ mm/s and $\Delta = 2.80-3.05$ mm/s). It is apparent that hydrous sulfates and sulfides can have spectra that are nearly identical to the forsterite. Thus, caution must be used when drawing conclusions about specific mineralogies on the basis of Mössbauer data alone, particularly when the large error bars associated with MER Mössbauer data are considered [5]. It is likely that hydrous iron sulfates and olivine group minerals may have indistinguishable Mössbauer spectra under these circumstances.

Acknowledgments: We are grateful for support from NASA grants NNG04GG12G, and NAG5-12687.

References: [1] R.G. Burns (1987) *J. Geophys. Res.* 92, E570-574. [2] B.C. Clark et al. (1982) *J. Geophys. Res.* 87, 10059-10067; H.Y. McSween et al. (1999) *J. Geophys. Res.*, 104, 8679-8715; G. Bonello et al. (2004) *Planet. Space Sci.* 52, 133-140. [3] M.D. Lane et al. (2004) *GRL*, 31, L19702; [4] R.V. Morris et al. (2004) *Science*, 305, 833-836. [5] M.W. Schaefer et al. (2005) *LPS XXXVI*, Abstract #2047.