

TEMPERATURE DEPENDENCE OF THE MÖSSBAUER FRACTION IN MARS-ANALOG MINERALS.

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Introduction: Mössbauer spectrometers are being used on the martian Athena rovers to identify and quantify relative amounts of Fe-bearing minerals, as well as to determine their Fe³⁺/Fe²⁺ ratios, allowing more realistic modeling of martian mineralogy and evolution. But successful attainment of these values from the data acquired on the Mars surface is not possible using present data on the Mössbauer spectra of likely minerals. The accurate analysis of these data requires (among other data) knowledge of the fundamental Mössbauer parameters needed to correct Mössbauer peak areas. We present here the first results from a broader initiative to determine the intrinsic isomer, or center shift (δ_i), the characteristic Mössbauer temperature (θ_M), and the recoilless fraction (f) of a suite of Mars-analog minerals.

Background: The Mössbauer effect arises from the recoilless emission and resonant absorption of nuclear gamma rays in solids. Only a certain fraction of these emissions and absorptions take place without recoil, and this is the Mössbauer fraction, f . This Mössbauer or recoilless fraction 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:

$$f = \exp\left(\frac{-4\pi^2 \langle X^2 \rangle}{\lambda^2}\right)$$

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 $\langle X^2 \rangle$ 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.

It is often (erroneously) assumed that the area of the peaks in each Mössbauer doublet (or sextet) roughly corresponds to the amount of Fe actually present in that site and/or valence state. However, it has long been known that the area of a Mössbauer doublet is actually a function of peak width (Γ), sample saturation ($G(x)$), and the recoilless fraction f as just discussed. Bancroft [1,2] uses the following formulations for area ratios in a mineral where there is only a single site for Fe, and it may be occupied by either Fe³⁺ or Fe²⁺. The doublets corresponding to

Fe³⁺ and Fe²⁺ have areas equal to A^{3+} and A^{2+} ; N is the “true” amount of each species and C is the “correction factor”:

$$\frac{A^{3+}}{A^{2+}} = C \left(\frac{N^{3+}}{N^{2+}} \right)$$

where

$$C = \frac{\Gamma_A G(x_A) f_A}{\Gamma_B G(x_B) f_B}$$

Therefore the degree of correspondence between peak areas and actual Fe occupancy depends on three assumptions, namely that 1) the linewidths of the Fe²⁺ and Fe³⁺ peaks are the same (only reasonable in end-members, but most fitting routines allow linewidths to vary); 2) saturation corrections are unnecessary if samples are correctly prepared as thin absorbers (for transmission Mössbauer spectroscopy this is true – in reflection spectroscopy it is expected to contribute a roughly 2-5% error), and 3) the amount of recoil-free fraction for both Fe²⁺ and Fe³⁺ in those sites is the same (the subject of the present study). As noted above, recoilless fractions depend greatly on site geometries and valence state, and thus different values of f are likely in cases where two sites have radically different geometries. Whipple [3] has suggested that variations in C can influence the results of Mössbauer Fe³⁺/Fe²⁺ ratios by up to 30%; much of this error is due to variations in f .

The approach we chose to calculate f uses the temperature dependence of the center shift (δ), which can be written as $\delta(T) = \delta_i + \delta_{\text{SOD}}(T)$, where δ_i is the intrinsic isomer shift (not dependent on T), and $\delta_{\text{SOD}}(T)$ is the second order Doppler shift. To calculate f , Mössbauer spectra of the mineral of interest were acquired over a range of temperatures, from 15 to 295 K at from 10-30 K increments. Next, the Mössbauer temperature (θ_M) and the intrinsic center shift (δ_i) 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

$$f(T) = \exp\left\{ \frac{-3E_R}{2k_B\theta_M} \left[1 + 4 \left(\frac{T}{\theta_M} \right)^2 \int_0^{\theta_M/T} \frac{x dx}{e^x - 1} \right] \right\}$$

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

this method can be found in Herberle [4] and Grant [5].

Results are presented here for ferric iron in a synthetic hematite. Ferric iron in hematite gives rise to two sextets in its Mössbauer spectrum, each of which represents a magnetic sublattice. Below about 230 K (or less, for small particle sizes) the magnetic sublattices rotate spontaneously (Morin transition).

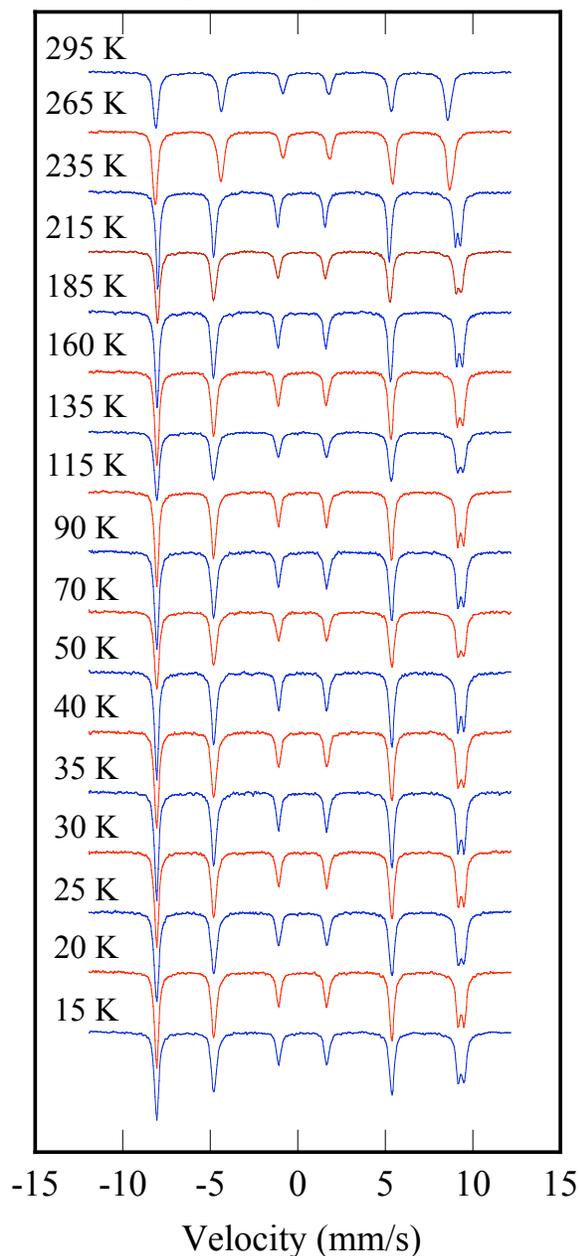


Figure 1. Mössbauer spectra of synthetic hematite at a range of temperatures from 15–295 K.

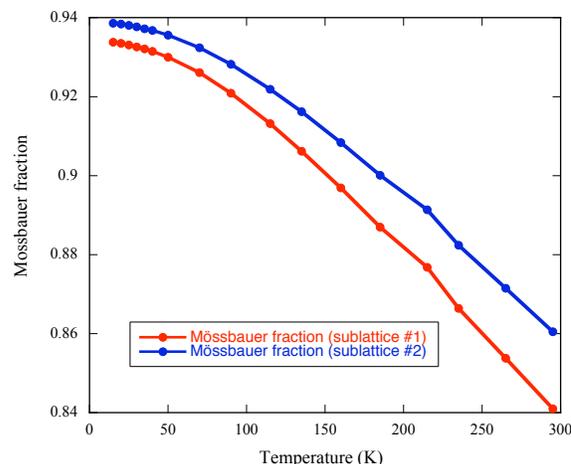


Figure 2. Mössbauer fraction vs. isomer shift of ferric iron in two magnetic sublattices in hematite. The Morin transition is probably causing the feature near 215 K.

The results presented here agree well with the data of De Grave and Van Alboom [6]. For an average of 10 synthetic hematites, they found f_{80} of 0.914 and 0.931, f_{RT} of 0.811 and 0.860, and θ_M of 460 and 540. We found θ_M of 500 and 540, and our corresponding f values may be drawn from Figure 2.

Conclusions: The temperature dependence of the Mössbauer fraction is significant, as the hematite sample presented here demonstrates. Interpretation of remotely-acquired Mars surface Mössbauer spectra will require this determination for every mineral suspected to be present. Work is underway by our group to provide these fundamental data.

References: [1] Bancroft, G. M. (1969) *Chem. Geol.*, 5, 255-258. [2] Bancroft, G.M. (1973) *Mössbauer Spectroscopy. An Introduction for Inorganic Chemists and Geochemists*. McGraw Hill, New York. [3] Whipple, E.R. (1968) *Quantitative Mössbauer spectra and chemistry of iron*. Earth and Atmospheric Science, 187 pp. Massachusetts Institute of Technology, Cambridge. [4] Herberle, J. (1971) in *Mössbauer Effect Methodology*, Plenum, New York, 299-308. [5] Grant, C. A. (1995) *Sources of experimental and analytical error in measurements of the Mössbauer effect in amphibole*, University of Oregon, 213 pp. [6] De Grave, E. and Van Alboom, A. (1991) *Phys. Chem. Minerals*, 18, 337-342.