ERROR ANALYSIS OF REMOTELY-ACQUIRED MÖSSBAUER SPECTRA. Martha W. Schaefer[1], M. Darby Dyar[2], David G. Agresti[3], and Bradley E. Schaefer[4], [1]Dept. of Geology and Geophysics, E235 Howe-Russell, Louisiana State University, Baton Rouge, LA 70803 USA, schaefer@geol.lsu.edu, [2]Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075 USA, mdyar@mtholyoke.edu, [3]Dept. of Physics, University of Alabama at Birmingham, Birmingham, AL 35294-1170 USA, agresti@uab,edu, [4]Dept. of Physics and Astronomy, Louisiana State University, Baton Rouge, LA 70803 USA, schaefer@lsu.edu.

Introduction: On the Mars Exploration Rovers, Mössbauer spectroscopy has recently been called upon to assist in the task of mineral identification, a job for which it is rarely used in terrestrial studies. For example, Mössbauer data were used to support the presence of olivine in Martian soil at Gusev [1] and jarosite in the outcrop at Meridiani [2]. The strength (and uniqueness) of these interpretations lies in the assumption that peak positions can be determined with high degrees of both accuracy and precision. We summarize here what we believe to be the major sources of error associated with peak positions in remotely-acquired spectra, and speculate on their magnitudes. Our discussion here is largely qualitative because necessary background information on MER calibration sources, geometries, etc., have not yet been released to the PDS; we anticipate that a more quantitative discussion can be presented by March 2005.

Major sources of error: There are a variety of both statistical and systematic errors that must be included in any analysis of MER Mössbauer data.

Counting statistics. Typical terrestrial Mössbauer transmission spectra have backgrounds of 10^6 counts or more, and thus an associated rms error in channel intensity of 0.1%. Individual MER spectra may have backgrounds of only 10^4 to a few times 10^5, with an associated error of as much as 1%. These errors may be lessened if it can be shown that summation of spectra over multiple temperature windows is scientifically valid. It is unfortunate that reports published to data do not show any error bars based on even standard error counting statistics, which would give a more realistic idea of the data quality.

Effects of using non-standard calibration targets. In terrestrial Mössbauer spectroscopy, it is the convention to use the well-understood six-line spectrum of room-temperature iron foil as a calibration standard, to convert counts per channel to counts per velocity bin. Because it is impractical to fix a Martian calibration standard at 295K, and because it was decided to use a combination of iron, hematite, and magnetite [3] as the calibration standard for the MER spectrometers, the calibration process is somewhat more complicated. The peak positions of all the reference materials on each MER must be known to a high degree of precision at the range of Martian surface temperatures, and those data must be made available to the PDS. The PDS must also state the degree of error associated with those peak positions because any errors in the peak positions determined for the standard materials in the laboratory will be propagated through to the spectra measured in the field. In the case of the iron oxides, Mössbauer parameters are sensitive to exact composition and particle size, so the pre-launch calibration spectra are needed from the materials used on the MER spacecraft, or additional error will be introduced. Thus, the community is dependent on as-yet-unreleased calibration data from the MER science team in order to assess the errors associated with calibration.

Effects of variable temperature during spectra accumulation. The Mössbauer parameters of materials are variable with temperature to a greater or lesser degree. In the most extreme cases, some materials undergo a magnetic transition and their spectra can change from that of a simple doublet at higher temperatures to a magnetically-split sextet at lower temperatures, and show a complicated transitional form at intermediate temperatures. The consequences of summing spectra over multiple temperature windows, which are relatively minor for the MER-A data released to date, are discussed in [4].

Effects of non-linear velocity scale on peak positions. This effect is not generally important for well-maintained terrestrial spectrometers, because drive linearity can be easily monitored and adjusted in the laboratory. This is, unfortunately, not the case when the spectrometer is located a great distance away. The non-linear character of the MER spectrometers can be seen in the drive error signal (Figure 1). The effects of this nonlinearity are dramatically illustrated when the calibration spectra are folded around the midpoint of the channel range (Figure 2). Note that smaller error signal (Figure 1) corresponds to a smaller shift in peak position (Figure 2), and similarly for the larger. If the non-linearity of the velocity is not correctly accounted for in the calibration of the spectra, the shape of the spectra when plotted against velocity may be severely distorted. Peak positions can be incorrect by an

amount up to the maximum velocity error (which may be as large as several percent of the velocity range of the spectrometer, 0.1-0.4 mm/sec), and may be broadened also. Such large errors in the velocity scale, up to twice the peak widths, would render the Mössbauer spectra essentially useless.
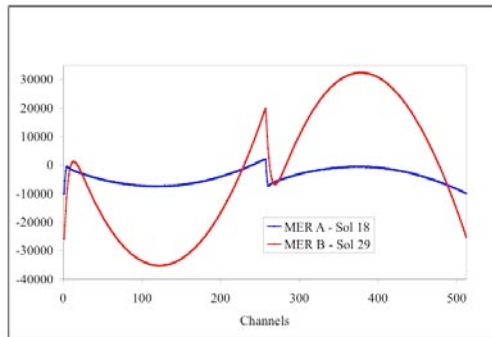

Figure 1. Examples of differential signal for MER-A (Sol 18) and MER-B (Sol 29). This drive error signal shows the difference between the actual and expected velocities of the spectrometer (assumed linear) [5].
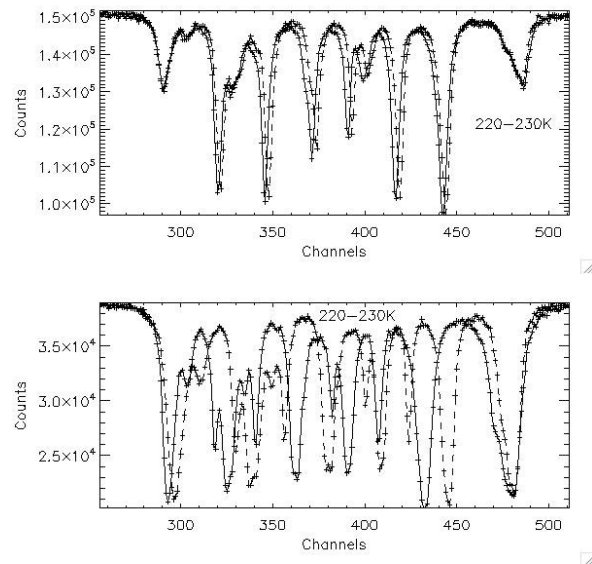

Figure 2. Upper figure shows MER-A calibration spectrum from Sol 18, with data from low channel numbers (dotted lines) folded onto data from higher channel numbers. For a spectrometer with a linear velocity range, peak positions overlay exactly. Lower figure is same exercise for MER-B calibration spectrum from Sol 29.

Ideally, the MER spectrometers should be calibrated by using the drive error signal and the calibration targets in conjunction. We suggest, and will be testing, a technique as a starting point as follows: Let c = channel, v(c) = velocity, e(c) = error signal. The relationship between velocity and channel may be modeled as: $v(c) = V*[(c - c_0) +$

$p*[e(c) - e_0]]$, where V provides a velocity scaling, c_0 and e_0 are zero offsets, and p reflects the strength of the error signal. This formula may be rewritten as $v(c) = V*c - V_0 + E*e(c)$. Now, v(c) is linear in the parameters V, V_0, and E, which should be determinable by a linear least-squares fit to the iron line positions only. More precise values may be obtained by using the entire calibration spectrum. The accuracy of the calibration obtained in this way may be checked by converting the calibration spectra from channels to velocity, and performing the same sort of folding as is seen in Figure 2. The validity of this approach can be confirmed by a good overlap of peaks from the two halves.

Calibration is additionally complicated because, as the source ages, emission line shapes change (broaden), especially for the high specific-activity sources on the MERs, and this affects any model of the reference spectrum. When broad peaks overlap in a spectrum the apparent peak positions are shifted and a precise determination of those positions requires that the peak shape be modeled correctly. The drive error signal, however, is not affected by this, because it is obtained electronically.

Geometry effects. Mössbauer spectra lines do not always have the simple, ideal Lorentzian shapes employed by the MER team in its initial published analyses [1, 2]. Line shapes can be influenced by many things, including: (1) source, sample, and detectors are all extended objects; (2) source radiation reaching the sample is distributed over a wide angle to increase counting statistics; (3) the radiation penetrates deeply into the sample, leading to saturation effects; and (4) multiple processes in the sample, resonant and non-resonant, including gamma-rays, x-rays, and electrons, are involved. An analysis where complex, multicomponent spectra are fit while employing incorrect assumptions about the line shape may lead to incorrect line positions and incorrect mineral distributions. The effects are more noticeable for high-statistics spectra, but accounting for them may also be required to provide reliable constraints on potential spectral models where counting statistics is low, as is typical for the individual MER spectra.

References: [1] Morris R.V. et al. (2004) *Science*, 305, 833-836. [2] Klingelhöfer G. et al. (2004) *Science*, 306, 1740-1745. [3] Klingelhöfer G., Morris R.V. and Squyres, S., private communication (2004). [4] Rothstein et al. (2005) *LPS XXXVI*, [5] EDR Software Interface Specification (SIS) Document, SIS-SCI009-MER, JPL D-22849, 07-31-2004.