SIMFITTING: A NEW APPROACH TO MER MÖSSBAUER DATA ANALYSIS. D. G. Agresti and P. A. Gerakines, Dept. of Physics, U. of Alabama at Birmingham, Birmingham, AL 35294-1170 (agresti@uab.edu).

Introduction: In order to enhance the analysis methodology for data acquired by the Mössbauer spectrometers on the two Mars Exploration Rovers (MERs), we have developed a Windows-based simultaneous fitting (simfitting) program for Mars Mössbauer data in which several spectra are fit at the same time to a single least-squares (χ^2) convergence criterion while individual spectral identities are maintained in the fit. The technique was first employed in Mössbauer spectroscopy over 40 years ago to analyze ^{195}Pt spectra for which the desired parameters could not be obtained by fits to individual spectra [1]. The mathematics of the method was presented in [2-3]. Before the current work, it had not yet been applied to spectra of Mars surface material.

MER Mössbauer spectra are superpositions of doublets and sextets resulting from constituent minerals present in different proportions in a sample. Because of mission constraints, MER spectra are frequently of relatively low statistical quality. This often leads to strong correlations among fitting parameters and an inability to carry out a complete analysis of a single MER spectrum while freely varying all parameters, i.e., those for hyperfine interactions, line widths, line shape, spectral area, etc. In such cases, the MER team has derived parameter values by fitting spectra where a site is strong, then held them constant while fitting other spectra where the contribution of the site is weak.

The advantage of fitting several spectra simultaneously is that a given phase can be required to have the same hyperfine and other defining parameters for all spectra of the set. For spectra that are of poor statistical quality or highly overlapped, and where the contribution of each phase is prominent in at least one of the spectra, this has the effect of reducing parameter correlations and enabling a convergent fit. The parameter values are determined in a self-consistent, self-contained manner, and the need to import parameter values into the set is reduced or eliminated.

MER Mössbauer measurements are identified by rover (MER-A Spirit or MER-B Opportunity; analyses were reported in [4] and [5], respectively), sol (martian day), and temperature window during acquisition. For the present work, spectra were extracted and calibrated by *MERView* [6] and fit individually, as far as possible, using model and initial parameter values of [4-5]. Simultaneous fits were then carried out, relaxing as many parameter constraints as proved reasonable, then compared with MER-team results.

To illustrate the possibilities, we present three examples of simfitted sets of MER Mössbauer spectra, for which: 1) simfitting eliminates the need for most externally derived parameter values; 2) multi-spectrum fitting reduces parameter uncertainty over single-spectrum fitting; and 3) the results of the two approaches are equivalent.

Example 1: Simfitting yields self-contained hyperfine parameter values: We analyzed a set of six complementary Mössbauer spectra acquired in and around Eagle Crater, where hematite-rich "blueberries" are found in abundance: B052–B056 and B060 [5].

The spectra were fit individually by the MER team as a sum of subspectra of olivine (Ol), pyroxene (Px), nanophase oxide (npOx), hematite (Hm), and the double-sextet magnetite (Mt1, Mt2). Fitting parameters were center shift (CS), quadrupole splitting/shift (QS), magnetic hyperfine field (B_{hf}), Lorentzian line width (W = FWHM), and relative areas of each doublet or sextet. Spectral areas were allowed to vary for all subspectra, since they relate to phase abundance. Otherwise, parameters were held to predetermined values, except for Ol, Hm in B052 and Ol, Px, npOx in B060.

To carry out the simfit, both single- and multi-spectrum constraints were applied. For each spectrum, doublet widths and areas were paired equal. Hematite sextet widths were broadened as W+2δ, W+δ, W, W, W+δ, W+2δ, while sextet areas varied as 3:x:1:1:x:3, with W, δ, and x variable in the simfit. The six widths of each magnetite sextet were set equal, while the areas varied in the ratio, 3:2:1:1:2:3. Multi-spectrum constraints imposed the requirement that the parameters, CS, QS, B_{hf}, and line widths of each site be kept the same for all spectra. Spectral areas of the three doublets and three sextets in the fitting model, as well as the baselines, were varied freely from spectrum to spectrum, except that the ratio, Area(Mt1)/Area(Mt2), was constrained to be equal for all six spectra.

As a result, the spectral parameters for Ol, Px, npOx, and Hm were determined by simfit among the six spectra, B052–B056, B060, without reference to any data outside this restricted set. The exception was magnetite, whose contribution was so weak in all six spectra (3.2–11.4% of total area) that its hyperfine parameters could not be determined in the simfit; they were fixed to the values given in [5]. Because sextet line widths were not reported, widths for Mt1 (0.50 mm/s) and Mt2 (0.55 mm/s) were determined by fit to A379 Peace_Justice2 (see [4]) and also held constant. Representative simfit spectra are displayed in Figure 1.

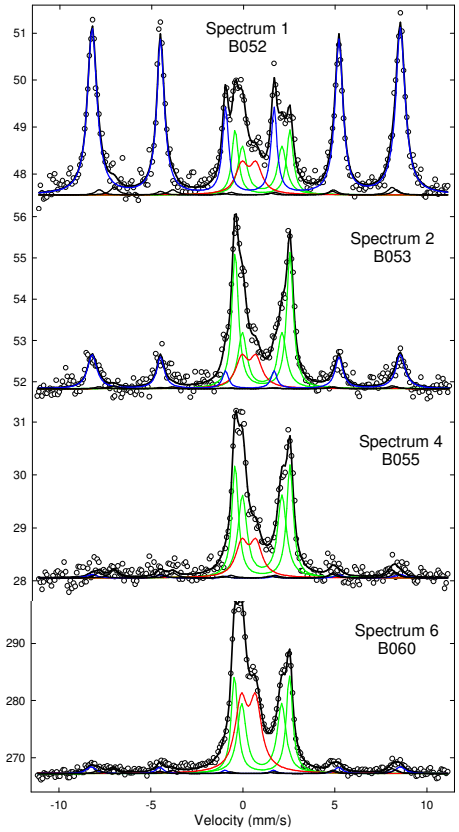

Figure 1. Counts data (o) with full function and site model subspectra (lines) for representative simfit spectra of the set B052–B056, B060. Hm (blue) is strong in spectrum 1–2; Ol, Px (green) in 2–4; npOx (red) in 6; and two weak sextets most clearly seen in 1 comprise the (Mt1, Mt2) contribution. The ordinate is kilocounts.

Simfit parameter values generally agree with those of [5] to within the precision cited there, except for npOx, where the deviations of CS and QS are ~3σ. Relative site areas derived for each sol are also in reasonable agreement; interestingly, and possibly fortuitously, the simfit result for Area(Mt1)/Area(Mt2) = 1.54, precisely what is reported for A379 in [4].

Example 2: Simfitting reduces statistical error: We investigated the temperature dependence of the quadrupole splitting in martian olivine. Morris et al. [4] derive a gradient of $-(0.97\pm0.50)\times10^{-3}$ mm/s/K based on QS values from many different samples (cf. Figure 5f in [4]). MER-A sample A050 LagunaHollow_WallMIonly was measured over 210-280 K with good statistics and thus provides a good test for deriving QS temperature dependence from a single sample. Its spectrum closely resembles Spectrum 4 of Figure 1.

We first fit all seven spectra individually as a superposition of Ol, Px, npOx, and (Mt1, Mt2), then performed a simfit of the same data. Single- and multi-spectrum constraints were as for B052–B060, except that QS (Ol) was allowed to vary freely for all spectra.

The results are shown in Figure 2. The temperature gradient, $-(1.21\pm0.43)\times10^{-3}$ mm/s/K, derived from the single-spectrum fits is in good agreement with the published value, while that derived from the simfit *to this one sample*, $-(1.47\pm0.24)\times10^{-3}$ mm/s/K, is significantly more precise. Deviations from the straight line fits to the QS values show a two-fold reduction in parameter uncertainty, from ±0.02 mm/s for the single-spectrum fits to ±0.01 mm/s for the simfit.

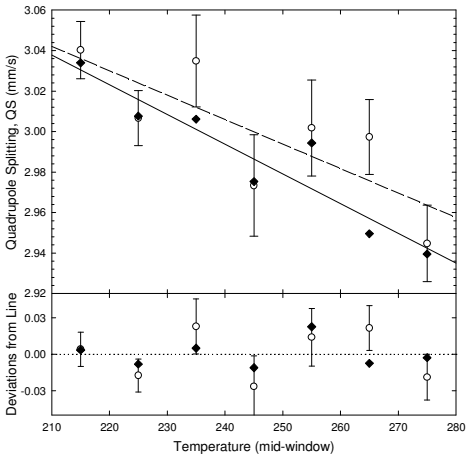

Figure 2. Variation of fitted quadrupole splitting for olivine in sample A050. Shown (top) are QS from six single-spectrum fits (open circles with error bars) and from simfits to the same data set (filled diamonds). The fitted linear fit trend lines are also shown. Deviations from the trend lines (bottom) demonstrate improved precision for the simfit values.

Example 3: Simfitting results are equivalent: We compared single-spectrum fits with simfits for MER-B sample B348 SpongeBob_Squidward, also known as Heat Shield rock, an iron meteorite, for which spectra were acquired at eight temperature intervals from 200–280 K. The spectrum consists of a dominant sextet (94%) with a weak central doublet (6%). For both types of fit, B_{hf} was varied freely at each temperature. The values derived for B_{hf} are indistinguishable because the defining peaks, 1, 2, 5, 6, are strong and isolated, and simfitting makes no improvement. A more detailed discussion is presented in [7].

We acknowledge financial support under NASA Grant No. NNX06AD93G.

References: [1] Agresti D. et al. (1967) *Phys. Rev.*, *155*, 1339–1341. [2] Agresti D. et al. (1969) *Nucl. Instr. Meth.*, *72*, 235–236. [3] Bent M.F. et al. (1969) *Computer Phys. Commun.*, *1*, 67–87. [4]. Morris R.V. et al. (2006) *JGR*, *111*, *E02S13*, 1–28. [5] Morris R. V. et al. (2006) *JGR*, *111*, *E12S15*, 1–27. [6] Agresti D.G. et al. (2006) *Hyp. Interact.*, *170*, 67–74. [7] Agresti D.G. & Gerakines P.A. (2008) *Hyp. Interact.*, submitted.