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Simultaneous fitting of Mars Mössbauer data

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Abstract Mössbauer spectra acquired by the Mars Exploration Rovers (MERs) often have low statistics with overlapped component spectra, making it difficult to fit individual spectra for all hyperfine or other parameters. When a set of spectra is complementary in the sense that components are weak in one and strong in another, analyzing the spectra simultaneously (simfitting them) while equating or relating parameters among the spectra will reduce parameter correlations and can lead to convergence of otherwise unfittable spectra. We apply an author-written Windows-based Mössbauer data fitting program to three cases from the MER data set to demonstrate the capabilities and advantages of the simfit method.

Keywords Mössbauer · Data analysis · Mars · MER · Simultaneous fitting · Simfit

1 Introduction

Two Mössbauer spectrometers "MIMOS II" [1] located on the deployment arms of NASA's Mars Exploration Rovers (MERs) have been operating on the surface of Mars since January 2004. Spectra are acquired in up to 13 10-K wide temperature windows, ranging from <180 K to >290 K. MER-team analyses for the iron mineralogy of martian rocks and soils [2, 3] reveal the presence of water-processed minerals, with implications for potential past Martian habitats.

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Because of mission constraints, the statistical quality of MER Mössbauer spectra is frequently low compared to typical laboratory measurements, and it is often difficult to carry out a complete analysis of a single MER spectrum while freely varying all parameters. To obtain satisfactory fits, the MER team has typically taken two approaches: (1) summing similar spectra to increase statistical quality, such as over a range of temperatures or over similar rock and soil types; and (2) fitting hyperfine and other parameters where a site is strong, then holding the parameters constant while fitting other spectra for which the contribution of the site to the spectrum is weak.

Here we present some early results of a new approach to fitting MER Mössbauer data that takes direct advantage of the spectral complementarity resulting from the relatively small number of Fe-bearing mineral phases observed to date by MIMOS II on Mars—eight at each of the two martian sites [2, 3]. With this approach a set of spectra are fit simultaneously (simfit) to a single chi-squared (χ^2) convergence criterion while equating or otherwise relating parameter values from different spectra of the set to each other, thus enabling fits of calibrated but otherwise unprocessed spectra with few or no constraints on parameter values. Each individual spectrum is preserved in the fit, so that slight changes in spectra from one to another significantly reduce parameter correlations. This powerful analysis tool [4, 5] was first employed in Mössbauer spectroscopy over 40 years ago [6]. Before the current work, it had not yet been applied to spectra of Mars surface material.

After reviewing this early example, we present three applications to MER Mössbauer data where: (1) simfitting is required to obtain certain parameter values from the given data set; (2) multi-spectrum fitting is an improvement over single-spectrum fitting; and (3) the results of the two approaches are equivalent. The mathematics of the method was presented in [4, 5]. In the current implementation, we have constructed from scratch a Windows-based fitting program that employs programming techniques developed for extraction and calibration of MER data [7] released to the MER Analyst's Notebook (http://anserver1.eprsl.wustl.edu/) and Planetary Data System (PDS) Geosciences Node (http://pds-geosciences.wustl.edu/).

2 Early simfit example

The discovery of the Mössbauer effect provided direct access to multipole properties of the upper level of the Mössbauer transition, for example, the magnetic moment of the 99-keV first-excited state in ^{195}Pt. To determine a value for this parameter, Mössbauer measurements with three applied field configurations (Fig. 1) were made on ~2–3% platinum substitutionally alloyed with ultrapure iron [6]. Because of the short half life (620 ps) of the excited level, resolution of the spectral lines for this 3/2 to 1/2 transition is poor and individual spectral lines are highly overlapped. Hyperfine field and excited-state-moment are strongly correlated and fits to the individual spectra do not converge. However, a simultaneous fit of the three spectra while equating magnetic moment and hyperfine field for all spectra did converge, and an acceptable value (±7%) was obtained for this previously undetermined moment [6]. In another application [8] all the transmission integral parameters [9] of both source and absorber were determined by simultaneously fitting ^{151}Eu spectra of a set of absorbers with thicknesses ranging from 4 to 100 mg Eu/cm^2.

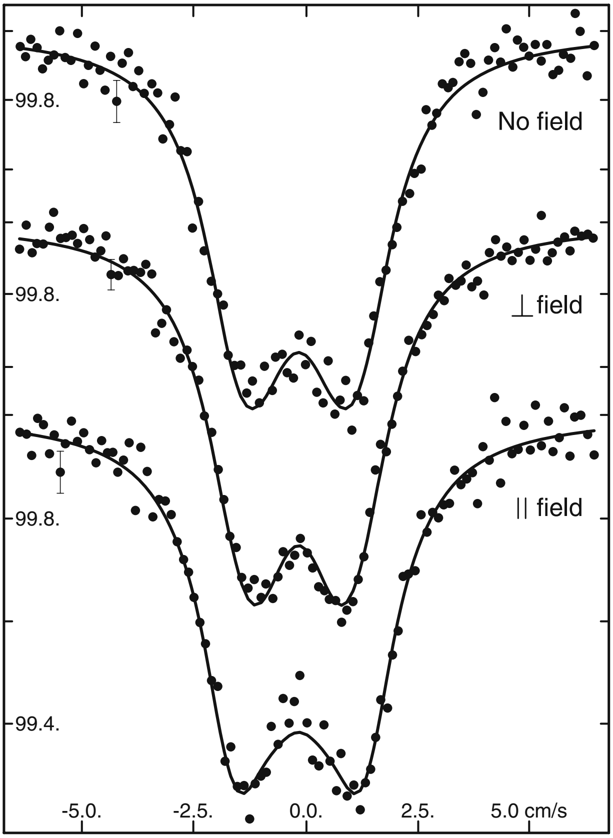

Fig. 1 Spectra of ^{195}Pt in Fe, fit simultaneously. Area ratios for component peaks are fixed at 3:2:1, 3:4:1, and 3:0:1, as appropriate for a 1/2–3/2 transition, reading from *top to bottom*, with no external magnetic field and with fields applied perpendicular and parallel to the source-absorber direction

3 MER examples

MER Mössbauer measurements are identified by rover (MER-A Spirit or MER-B Opportunity), sol (martian day), and temperature window during acquisition. To overcome weak statistics, the MER team often summed spectra over temperature, and occasionally over similar sample type as well. The resulting spectra were modeled as superpositions of Lorentzian doublets and sextets and fitted for hyperfine parameters, line widths, and component areas. Frequently parameters of weaker components were held constant because they could not be determined in a single-spectrum fit.

For the present work we selected several sets of complementary measurements from the lists in [2, 3], either because of similar mineral content or because they were taken at different temperatures. Spectra were extracted and calibrated by *MERView* [7] and fit individually, as far as possible, using model and initial parameter values of [2, 3]. Simultaneous fits were carried out, relaxing as many parameter constraints as proved reasonable, then compared with MER-team results.

Parameter constraints and relations among parameters are at the heart of the simfitting process. Examples of single-spectrum constraints, which for the present work apply identically to all spectra of a simfit set, include: equating line widths or areas of

Table 1 Site constraints used by Morris et al. [3] for Lorentzian fits of the spectra, B052–B060

	Ol	Px	npOx	Hm	Mt1,2	Temps
B052	var[a]	fix[b]	fix	var	fix	250–270
B053	fix	fix	fix	fix	fix	260–270
B054	fix	fix	fix	fix	fix	240–260
B055	fix	fix	fix	fix	fix	230–240
B056	fix	fix	fix	fix	fix	250–260
B060	var	var	var	fix	fix	230–270[c]

To improve statistics, spectra were summed over the temperature range shown in the last column

[a] Site parameters varied freely

[b] Site parameters (CS, QS, B_{hf}, W) held constant

[c] Temperature summation range for current work

the two components of a doublet (“paired” widths or areas); relating sextet widths as $W + 2\delta$, $W + \delta$, W, W, $W + \delta$, $W + 2\delta$, appropriate for broadening due to a simple hyperfine field distribution; and requiring sextet areas to be in the ratio, 3:2:1:1:2:3, or relating them. For simfits, multi-spectrum constraints are defined to take advantage of similarities among spectra in order to reduce parameter correlations. For example, if a single MER spectrum is modeled with four doublets and fit with 17 variable parameters (CS, QS, W, Area for each doublet, see below, plus baseline), then fitting five such spectra, presumably with different mineral proportions, involves 85 variable parameters. Assuming baseline and site areas remain variable for each spectrum, a simfit where all sites have the same hyperfine parameters and widths reduces this number to just 37 for the same data. If each doublet component is prominent in at least one spectrum while possibly obscured in others, the likelihood of a successful fit is greatly increased and parameter uncertainties are reduced.

4 Example 1: Simfitting is required to obtain values from a limited data set

Mössbauer spectra were acquired by MER-B on sols 52–56 and 60 in and around Eagle Crater, where hematite-rich “blueberries” are found in abundance [3]. Spectra B052 to B060 (cf. Fig. 2) show a progression from hematitic to basaltic character. Raw data from one or more temperature windows were summed to increase statistics (Table 1, last column) and fit individually by the MER team as a superposition of doublet subspectra of olivine (Ol), pyroxene (Px), nanophase oxide (npOx), a hematite sextet (Hm), and the double-sextet magnetite (Mt1, Mt2). The hyperfine parameters, center shift (CS), quadrupole splitting/shift (QS), and magnetic hyperfine field (B_{hf}), as well as Lorentzian line width (W = FWHM), were fixed as needed to values determined from single-spectrum fits to spectra acquired at other locations where the corresponding feature was prominent (shown by ‘fix’ in Table 1).

The contribution of magnetite to the six spectra, B052 through B060, was so weak (3.2–11.4% of total area) relative to statistics and the other components that its hyperfine parameters were held in the simfit to the values given in [3]. 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 [2]) and also held constant.

For the simfit, spectra acquired at each sol were converted to a common velocity scale by interpolation and summed over the temperature ranges indicated in Table 1.

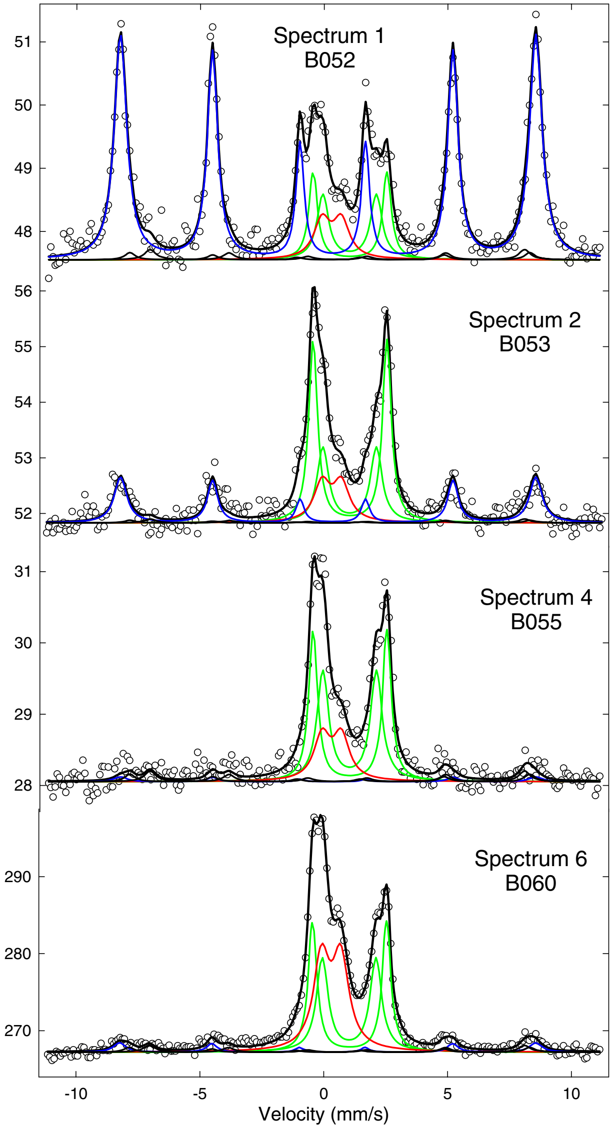

Fig. 2 Counts data (*open circle*) with full function and site model subspectra for representative simfit spectra of the set B052–B060. The ordinate is kilocounts for each spectrum

Single-spectrum constraints were: for doublets, paired widths and areas; for sextets, field-distribution width broadening (see earlier) for hematite; and areas ratios, 3:x:1:1:x:3 for hematite and 3:2:1:1:2:3 for magnetite. The parameters, CS, QS, B_{hf}, and W (line width) for each site were kept the same for all spectra. Baseline and spectral areas of the six sites varied from spectrum to spectrum, while the ratio, Area(Mt2)/Area(Mt1) was constrained to be the same for all spectra.

Figure 2 displays the results visually for representative spectra. In spectrum 1 and 2 Hm is prominent; spectra 2–4 feature Ol and Px, but in different proportions; npOx is strong in spectrum 6; and magnetite is above statistics in spectrum 6, but still too weak (6.1% total area) to stand on its own in the simfit. Simfit values, listed

Table 2 Comparison of simfitting results with those of Morris et al. [3], who quote parameter errors at ±0.02 mm/s and ±0.8 T

	CS (mm/s)	QS (mm/s)	B_{hf} (T)	W (mm/s)
Fe2D1 (Ol)				
Ref. [3]	[1.15]	[3.00]		[0.41]
B052	1.15	3.03		0.39
B060	1.15	3.02		0.41
Simfit	1.15	2.98		0.43
Fe2D2 (Px)				
Ref. [3]	[1.14]	[2.12]		[0.57]
B060	1.16	2.14		0.59
Simfit	1.14	2.16		0.58
Fe3D1 (npOx)				
Ref. [3]	[0.37]	[0.85]		[0.66]
B052	[0.37]	[0.85]		[0.77]
B060	0.36	0.85		0.73
Simfit	0.41	0.78		0.79
Fe3S2 (Hm)				
Ref. [3]	[0.37]	[−0.16]	[51.7]	[?]
B052	0.36	−0.19	52.2	[?]
Simfit	0.36	−0.19	52.0	~ 0.51[b]
Fe3S1 (Mt1)				
Simfit[a]	[0.31]	[0.06]	[50.1]	[0.50]
Fe2.5S1 (Mt2)				
Simfit[a]	[0.64]	[0.00]	[46.9]	[0.55]

Fixed values are in brackets and apply to all sols for a given site, except as indicated (cf. Table 1)

[a] As in Ref. [3], except width is not given there

[b] Hm widths, inner to outer = 0.40, 0.51, 0.62

in Table 2, generally agree with those of [3], except for npOx, where the deviation is $\leq 3\sigma$. Relative site areas derived for each sol are also in reasonable agreement; the simfit result for Area(Mt1)/Area(Mt2) = 1.54, equal to the value reported for A379 in [2].

5 Example 2: Simfitting reduces parameter uncertainty

We investigated the temperature dependence of the quadrupole splitting in martian olivine. Morris et al. [2] derive a gradient of $-(0.97 \pm 0.50) \times 10^{-3}$ mm/s/K based on QS values from many different samples (cf. Fig. 5 f in [2]). Sample A050 was measured over 210–280 K with good statistics and thus provides a good test for deriving QS temperature dependence from a single sample. The six spectra of A050 closely resemble Spectrum 4 of Fig. 2. We first fit all spectra (raw data, no summing done) individually as a superposition of olivine, pyroxene, npOx, and magnetite, then performed a simfit of the same data. Single- and multi-spectrum constraints were as for B052–B060 above, except that QS(Ol) was allowed to vary for all spectra.

The results are displayed in Fig. 3. Deviations from 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 values. The temperature gradient

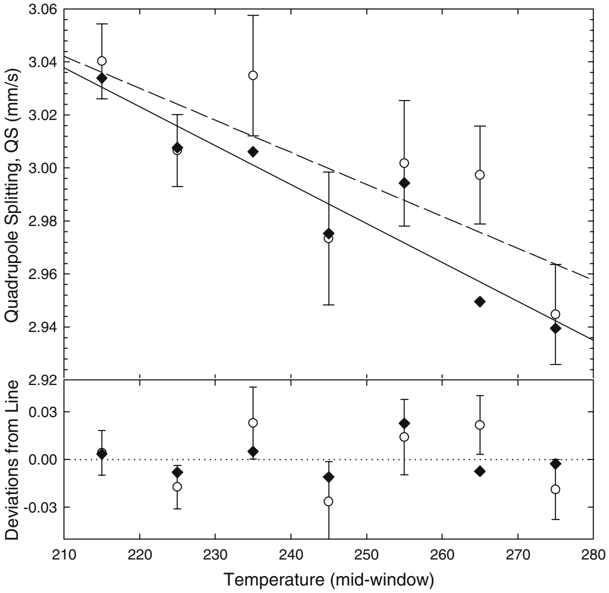

Fig. 3 Variation with temperature of fitted quadrupole splitting for olivine in sample A050. Shown (*top*) are QS from six single-spectrum fits (*open circles with error bars*) and from a simfit of the same data set (*filled diamonds*). The *fitted linear trend lines* are also shown. Deviations from the trend lines (*bottom*) demonstrate reduced uncertainty for the simfit values

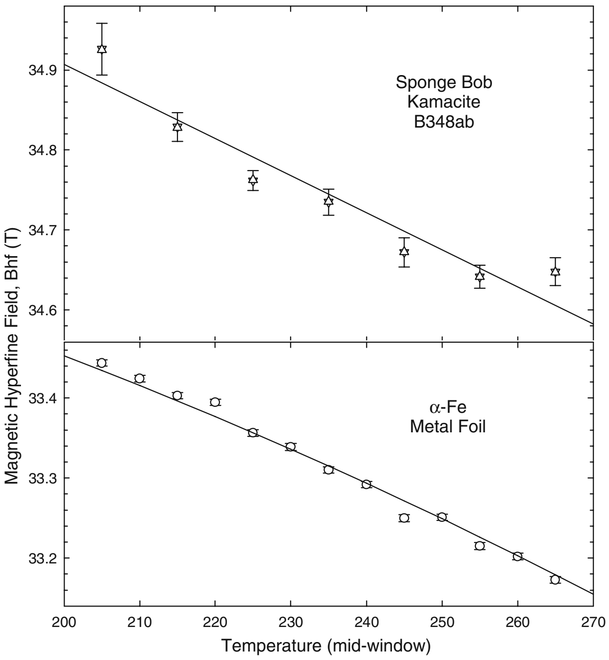

Fig. 4 Comparison of single-fit values (*triangle*, with *error bars*) for B_{hf} as function of temperature with simfit values (*inverted triangle*); these are essentially indistinguishable. For reference, a similar plot for α-Fe [7] is shown in the *lower panel*

derived from the single-spectrum fits, $-(1.21 \pm 0.43) \times 10^{-3}$, is in good agreement with the published value, while the value from the simfit, $-(1.47 \pm 0.24) \times 10^{-3}$ mm/s/K, has significantly reduced uncertainty.

6 Example 3: Simfit results are equivalent

We compared single-spectrum fits with a simfit for MER-B sample B348, known as Heat Shield rock, an iron meteorite [3]. The spectra consist of a dominant sextet (94%) with a weak central doublet (6%). Two sequences (200–280 K) accumulated by the MER were summed at each temperature for the present fits, for which sextet widths and areas were constrained as for hematite of B052–B060 above, with B_{hf} varied freely for each spectrum in the simfit. Peaks 1 and 6 were modeled with a "pseudo-Voigt" line shape (Lorentzian + Gaussian), reducing χ^2 by half compared to a Lorentzian line shape. The temperature dependence of B_{hf} for the two types of fit (Fig. 4) is identical because the defining peaks, 1, 2, 5, 6, are strong and isolated; simfitting makes no improvement. For comparison a similar plot for α-Fe [7] is also shown. Although the temperature trends are similar, the larger field for Heat Shield rock is evidence for kamacite, an iron-nickel alloy [3].

7 Conclusion

We have shown that simultaneous fitting of Mars Mössbauer data can improve MER-team data analyses by removing the need to hold certain parameters constant. By equating or relating variable parameters of complementary spectra, convergence becomes more likely and parameter errors are frequently reduced. We have shown three cases from the MER data set in which simfitting: (1) is required; (2) reduces uncertainties; and (3) makes no difference. Simfitting can enhance data yield for multi-component spectra with relatively poor statistics, and is thus recommended for routine use in analyzing the MER Mössbauer data set. We acknowledge financial support under NASA Grant No. NNX06AD93G.

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