On simfitting MER Mössbauer data to characterize Martian hematite

David G Agresti¹, Iris Fleischer², Göstar Klingelhöfer² and Richard V Morris³

¹ University of Alabama at Birmingham, Birmingham, AL 35294-1170, USA
² Institut für Anorganische und Analytische Chemie, Universität Mainz, Germany
³ NASA Johnson Space Center, Houston, Texas 77058, USA

E-mail : agresti@uab.edu ; fleischi@uni-mainz.de

Abstract. Mössbauer spectra of Eagle Crater outcrop rocks in Meridiani Planum were acquired by the Mars Exploration Rover (MER) Opportunity. Sixty spectra, containing ~20 to 60% hematite by area, were simultaneously fit (simfit) in a self-consistent manner to a single chi-squared minimum, where relations among parameters from different spectra were defined for both sol (Martian day) and acquisition temperature (200–280 K). Different spectral models were compared, hematite being modeled optimally with two sextets. Sextet S1 (~35% of total sextet area) has narrower linewidths, a larger magnetic hyperfine field, and a quadrupole shift that changes smoothly from positive to negative values as the temperature increases through the bulk Morin transition temperature. Sextet S2 has broader linewidths, a likely skewed line shape, a smaller hyperfine field, and a quadrupole shift that remains negative at all temperatures, implying the S2 phase is weakly ferromagnetic at all temperatures.

1. Introduction
Hematite ($\alpha$-Fe₂O₃) is paramagnetic above the Curie temperature ($T_C = 956$ K) and weakly ferromagnetic (wfm) below $T_C$, down to the Morin temperature $T_M$, where hematite undergoes a phase transition to an antiferromagnetic (afm) state [1, 2]. For well crystalline, chemically pure hematite, $T_M = 264$ K [3]. Wfm and afm phases can coexist over a range of temperatures $\Delta T_M$ (e.g. [4]). Small particle sizes, poor crystallinity, and cation substitution can reduce $T_M$ and broaden the temperature interval $\Delta T_M$ over which the transition occurs.

On Mars, backscatter Mössbauer spectra were acquired in 10-K-wide temperature windows between 180 K and 290 K with the Mössbauer spectrometers (MIMOS II) on board the two Mars Exploration Rovers (MERs) [5]. Here, we focus on the hematite component identified in spectra of outcrop rocks from Eagle Crater acquired by the MER rover Opportunity at Meridians Planum during sols 16–51 (Martian days after landing).

Analyses of Mössbauer spectra of Eagle Crater outcrop were reported in [6], for which single-sol spectra were summed over several temperature windows and fit individually, with the hematite component modeled as a single sextet. Given the possibility that afm and wfm phases may coexist in the temperature range over which these spectra were acquired, we investigated two-sextet models for hematite, fitting unsummed spectra from many sols and temperatures simultaneously (simfitting).

Compared with single-spectrum fits, multi-spectrum fits result in reduced correlations among parameters because parameters in different spectra are held in fixed relations (e.g. equal) during a fit. As a result, fitted parameter values are automatically consistent among all spectra in the simfit set.
whereas repeated single-spectrum fits might otherwise be required to arrive at compatible parameter values. Simfits were performed with MERFit [7] after spectrum extraction, velocity calibration, and fold-summing to ~256 data values with MERView [8]. Written in Lahey-Fujitsu Fortran, both programs are Windows-based, enabling data entry and control through specially designed dialog boxes, with graphical display of spectra that can change as parameter values are changed.

2. Two-dimensional simfitting

In a preliminary application [9], Mössbauer spectra from Eagle Crater outcrop were organized into equal-temperature groups. Each group was simfit separately, and sextet hyperfine parameters were held equal for all sols within the group, resulting in unique hyperfine values at each temperature. However, because a given sol appeared in several different simfit groups, there was no way to establish sol-related equalities. Consequently, temperature-independent quantities, such as most doublet hyperfine parameters and relative doublet areas for a given sol, were not uniquely determined in this "one-dimensional" simfitting procedure.

Here we use "two-dimensional" simfitting capability, where parameter relations are established for both environmental dimensions, sol and temperature, in the same simfit. We analyzed 60 Eagle Crater outcrop spectra with a single two-dimensional simfit. We assume all samples contain the same hematite and use the simfit results to compare four distinct temperature-dependent, two-sextet models for this hematite. The other Fe-bearing phases are modeled identically for all 60 spectra. Exactly one completed simfit is required to establish all parameter values for a given spectral model for all sols and temperatures of the entire 60-spectrum set.

3. The 60-spectrum simfit

The 60 spectra included in the simfit set are listed in Table 1 by sol (row) and mid-window temperature (column). Also tabulated are the total number of spectra (N) for a given sol (right column) and temperature (bottom row). Spectrum numbers (1-60) are used by MERFit to identify spectra over which particular parameters are related.

3.1. Spectral models

Spectra were modeled with four symmetric Lorentzian doublets, one each for olivine, pyroxene, an unidentified ferric doublet phase Fe3D3 [6], and jarosite, and two Lorentzian sextets (skewed for some models) for hematite. Four models were defined, as listed in Table 2, differing in the treatment of line shape (skew) and width of the second sextet S2. Separate two-dimensional simfits were carried out for each model.

An example from a simfit with model S1e2kd (see Table 2) is shown in Figure 1, which also illustrates the effect of skew. The absolute value of the skew parameter is the same for all six peaks of the sextet, being positive for peaks 1–3 and negative for peaks 4–6.
3.2. Parameter constraints

Simfitting employs single-spectrum constraints to define the details of a spectral model, the model and single-spectrum constraints being the same for all spectra of the simfit set. Multi-spectrum constraints are used to establish relationships among same-named parameters in different spectra.

Single-spectrum constraints used here: Doublet widths and areas were paired equal. Center shift CS (referenced to $\alpha$-Fe) and quadrupole splitting QS for the weaker olivine and pyroxene were fixed to values given in [6]. Center shift CS, quadrupole shift QS, and hyperfine field $B_{hf}$ were varied independently for each sextet, and peak areas were fixed in the ratio 3:2:1:1:2:3. The nature of sextet width constraints is shown in Table 2. When present, a single skew parameter refers to all six peaks (see example, Figure 1). We used $g(3/2)/g(1/2) = -0.572$ [10].

Multi-spectrum constraints used here: Doublet parameters except areas were held equal for all spectra. Doublet area ratios were held equal for all spectra of a given sol. Sextet parameters and area ratios were held equal for a given temperature.

4. Simfitting results

In Figure 2 we compare sextet hyperfine parameters QS and $B_{hf}$ for hematite derived by two-sextet simfitting of Eagle Crater outcrop spectra with the one-sextet model of Burn Outcrop Class rocks [6]. The one-sextet model leads to a cluster of points (open circles) whose spread in values results in part from the different temperature ranges for each spectrum [6] and, as discussed next, the presence of a second hematite sextet. Using simultaneous fitting we obtained unique values of QS and $B_{hf}$ at each temperature for each sextet of the two-sextet model. The data points for sextet S2 (triangles) overlap those for the single-sextet model, which is expected because sextet S2 is ~65% of total sextet area. For sextet S1 (~35% of total sextet area) the points (crosses) are clearly distinct from those for S2. As shown in Figure 3, S1 has a diffuse Morin transition because there are both positive and negative
values of QS, while S2 lacks a Morin transition because its QS is always negative. Figure 4 shows values for the magnetic hyperfine field $B_{hf}$ as a function of temperature for the two-sextet model.

Generally, for all models: 1) QS(S1) decreases quasi-linearly with temperature, changing sign at $T \sim 255$ K (Figure 3); 2) QS(S2) < 0 at all temperatures, and is nearly constant; 3) $B_{hf}(S1) > -52.5$ T > $B_{hf}(S2)$ (Figures 2 and 4), both decreasing slightly with temperature; 4) $B_{hf}(S2)$ is ~1 T larger for skew models, likely reflecting outward shifting of peak area; 5) CS(S1) ≈ CS(S2) at all temperatures; 6) S2 linewidths > S1 linewidths, with no clear temperature dependence; 7) models with skew converge to smaller chi-squared values than models without skew; 8) Skew increases strongly with temperature, from ~0.34 to 0.60 for S1e2ke and from ~0.32 to 0.46 for S1e2kd (based on fitted linear trend lines); and 9) sextets S1 and S2 are ~35% and 65% of total sextet area, respectively.

It is instructive to contrast single-spectrum and multi-spectrum fitting from a statistical point of view. Fitting one spectrum with model S1e2kd, and the given single-spectrum constraints, implies 24 free parameters for the 256-value data matrix. Simultaneous fitting of 60 such spectra with no multi-spectrum constraints would use 1,440 independent parameters to fit 15,360 values. Multi-spectrum constraints leave 98 doublet (90 area + 8 non-area) and 148 sextet parameters (68 area + 80 non-area), for a total of 246 independent parameters to fit the same 15,360 data values.

5. Conclusions
Simultaneous fitting is an effective method to fit a large number of MER spectra in a systematic way because summing of spectra to enhance statistics is avoided, fewer parameters are held fixed, sol-related quantities are unique, and deriving parameter values as a function of temperature is enabled. The method applied to 60 Mössbauer spectra from Eagle Crater outcrop demonstrates that modeling the hematite component with two independent hematite sextets provides additional information and statistically better fits compared to a one-sextet model [6] or a two-sextet model with identical linewidths for both sextets [11]. Sextet S1 has narrower lines, larger $B_{hf}$, and a QS that changes sign at $T \sim 255$ K, resulting from a diffuse Morin transition (bulk $T_M \sim 264$ K). Sextet S2 has broader, likely skewed lines, a smaller $B_{hf}$, and QS < 0 at all temperatures (i.e. weakly ferromagnetic with no Morin transition). The results are consistent, for example, with sextet S1 corresponding to a population of hematite particles with larger mean particle diameter than the population corresponding to sextet S2.

Acknowledgments

MERFit development was supported by NASA grant NNX06AD93G to DGA, who has benefited from discussions on hematite with R. Vandenberghe. IF and GK acknowledge support from the German Space Agency (DLR) and the University of Mainz. RVM acknowledges support from the NASA Mars Exploration Program.

References
[1] Cornell R M and Schwertmann U 1996, The Iron Oxides (VCH Publishers), 120–123.
[2] de Grave E and Vandenberghe R E 1990, Phys Chem Minerals 17, 344–352.
[3] Amin N and Arajs S 1987, Phys. Rev. B 35, 4810–4811.
[4] Murad E and Cashion J 2004, Mössbauer Spectroscopy of Environmental Materials and their Industrial Utilization (Kluwer Academic Publishers, Boston), 237–238.
[5] Klingelhöfer G et al. 2003 J. Geophys. Res. 108, 8067.
[6] Morris R V et al. 2006 J. Geophys. Res. 111, E12S15.
[7] Agresti D G and Gerakines P A 2009 Hyp. Interact. 188, 113–120.
[8] Agresti D G, Dyar M D and Schaefer M W 2006, Hyp. Interact. 170, 67–74.
[9] Fleischer I, Agresti D G and Klingelhöfer G 2009 Lunar Planet. Sci. 40, Abstract #1803.
[10] Guetlich P, Link R F and Trautwein A 1978, Mössbauer Spectroscopy and Transition Metal Chemistry (Springer-Verlag, New York).
[11] Van Cromphaut C, de Resende V G, de Grave E, van Alboom A, Vandenberghe R E and Klingelhöfer G 2007, Geochim. Cosmochim. Acta 71, 4814–4822.