

Temperature dependence of the quadrupole splitting of olivine and pyroxene from the Plains of Gusev Crater on Mars

David G. Agresti

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Abstract In the present work, we report application of simultaneous fitting procedures to Mössbauer data acquired on the Plains of Gusev Crater by the MIMOS II spectrometer on board the Mars Exploration Rover Spirit. Based on a quantitative measure of spectrum quality, the 34 best of the ~ 126 spectra acquired on the Plains are grouped together for a single simultaneous fit with a common least-squares criterion. Fitted values for the quadrupole splitting (QS) of olivine (Ol) from 200 K to 260 K are shown to lie between reported trend lines for Fo50 and Fo30 olivine, with a temperature gradient of $(-11.2 \pm 1.2) \times 10^{-4}$ mm/s/K, a nearly five-fold improvement in precision over the previously reported value, enabling extrapolation to $QS(\text{Ol}) = (2.93 \pm 0.01)$ mm/s at 295 K. QS of pyroxene fit as a single doublet exhibits a temperature gradient of $(-7.3 \pm 2.3) \times 10^{-4}$ mm/s/K.

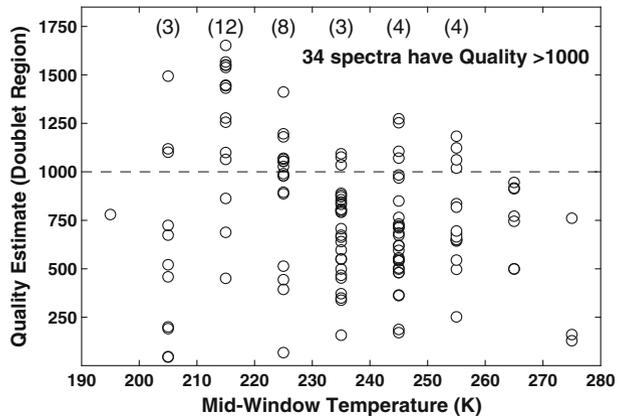
Keywords Mössbauer · Mars-mineralogy · Simultaneous fitting · Olivine · Pyroxene

1 Introduction

After reaching Mars in 2004, the Mars Exploration Rover Spirit (MER-A) traversed the Plains of Gusev Crater for approximately 150 martian days (sols), where its MIMOS II Mössbauer (MB) spectrometer [1] acquired spectra in 10-K wide temperature intervals. Iron mineralogy was determined by fitting individual MB spectra of rock and soil targets, typically summed over temperature [2]. Unequivocal temperature dependence was reported only for the quadrupole splitting (QS) of olivine (Ol), for which a gradient of $-(9.7 \pm 5.0) \times 10^{-4}$ mm/s/K was derived (see Fig. 5 of [2]).

D. G. Agresti (✉)
Department of Physics, University of Alabama at Birmingham,
Birmingham, AL 35294, USA
e-mail: agresti@uab.edu

Fig. 1 Quality estimates for the “doublet region” of the ~ 126 Mössbauer spectra taken on different sols at different temperatures during MER’s traverse of the Plains of Gusev Crater. The number of spectra (sols) in each temperature interval is shown in parentheses at the top of the figure



In an ongoing effort [3–5], we have been fitting MER MB spectra simultaneously (simfitting) in order to enhance their information yield. Initially we derived a value for the QS(OL) gradient of a single target with improved precision [3]. Later we demonstrated the presence of two distinct phases in Meridiani hematite [4, 5]. In this report the focus is on the doublet components of the ~ 126 Plains spectra.

2 Data in the simfit set

To optimize simfitting, the quality of each of the ~ 126 Plains spectra was defined as $Quality = \sum_i (S/N)_i$, the sum over channels of signal-to-noise, $S/N_i = (Y_i - B)/\sqrt{Y_i}$, where Y_i = counts and B = baseline. The spectra were calibrated with *MERView* [6], fold-summed, and velocity referenced to α -Fe. For the *Quality* calculation, only velocities within the interval, $(-2.5, 3.75)$ mm/s, the “doublet region,” were included in the sum. The results are displayed in Fig. 1. Only the 34 spectra with *Quality* > 1,000 were fit simultaneously, using the MER-data fitting program, *MERFit* [3].

3 The spectral model

For the simft, each spectrum was modeled as a superposition of three doublets for OL, pyroxene (Px), and nanophase oxide (npOx), and three sextets for magnetite (Mt1, Mt2) and hematite (Hm) (as in [2]). An example spectrum, together with its simfit model, is shown in Fig. 2. Because the sextets are weak in the doublet region (Mt < 2% and Hm < 1% total area), only their areas were varied in the simfit, while Area(Mt1)/Area(Mt2) was held to 1.54 [3]; other sextet values, listed in [2, 3], were held fixed during the simfit. Subspectral area ratios (doublets and sextets) were held equal for a given target, independent of temperature (fixed composition). For each doublet, width and center shift (CS) were the same for all spectra (i.e. independent of temperature), while QS was held equal for spectra at the same temperature.

Fig. 2 Example spectrum showing the three doublets and three sextets used in the fit. The *open circles* are the fold-summed counts and the solid blue line is the fit spectrum

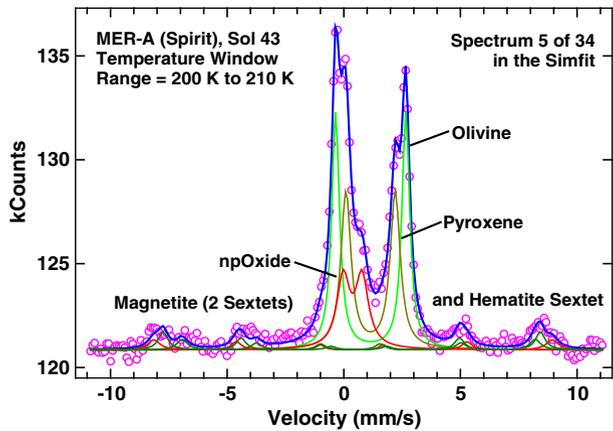
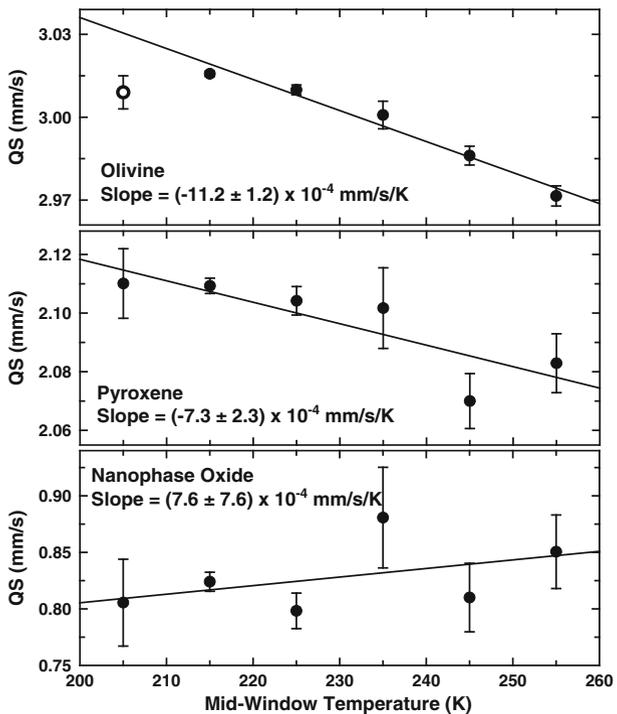
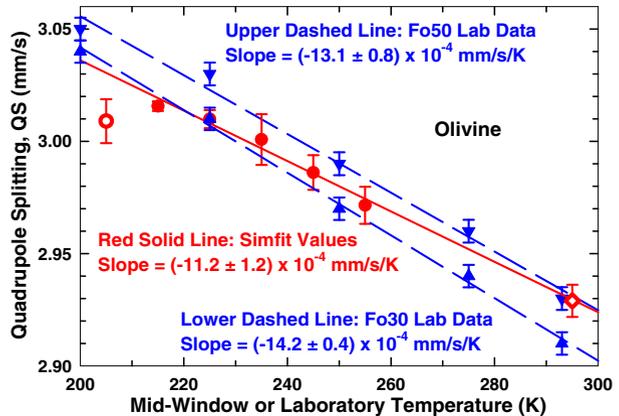


Fig. 3 Simfit values for quadrupole splitting (QS) in olivine, pyroxene, and nanophase oxide at each temperature, with computed error bars based on the linear fit and relative spectrum quality. The apparent outlier value for olivine at 205 K was not used in the linear fit



For MER MB spectra, it is expected that CS will not depend on temperature (see e.g. [2]) because sample and reference α -Fe foil are at the same temperature; however, an initial simfit did show such dependence for CS(OI) and CS(Px). Following this, laboratory spectra [7] were fit for CS (relative to α -Fe at 295 K) and $[CS - CS(\alpha\text{-Fe})]$ was computed for several olivines and pyroxenes at several temperatures. In each case, this difference varied <0.01 mm/s over the range from 200 K to 295 K.

Fig. 4 A comparison of simfit QS values (red filled circles) with laboratory data (up and down blue triangles) for two synthetic olivines, Fo50 and Fo30 [8]. The open red filled circle at the left was not used in the linear fit. The open red diamond at the lower right is the extrapolation of the fitted line to a value of (2.93 ± 0.01) mm/s at 295 K



4 The results

The QS variation with temperature for Ol, Px, and npOx is shown in Fig. 3. For Ol, the precision in the gradient is improved by a factor of nearly 5. For Px, a gradient is observed with reasonable precision. No such gradient can be claimed for npOx.

5 Conclusions

Simfitted QS(Ol) from MER data may be compared with laboratory measurements using a rather thorough study of synthetic olivines from near forsterite (Fo) to fayalite (Fa) [8]. This work lists QS values for one-doublet fits of spectra acquired from 293 K to 200 K and below. In Fig. 4 we see that the MER QS(Ol) simfit values are well bracketed between the QS trend lines for Fo₅₀ and Fo₃₀. This result, derived from MER-MB data alone, is consistent with a previous estimate of Fo₄₂ – Fo₄₉ for olivine of 4 Plains rocks (see Table 3 of [9]).

A comparison of the simfit QS(Px) temperature trend with laboratory data was not successful, perhaps because the pyroxene spectra of [7] are poorly fit with a single doublet, especially at lower temperatures. A two-doublet model (M1, M2 sites) for pyroxene will be tried. No explanation is at hand for the temperature dependence of CS(Ol) and CS(Px), when they are allowed to vary with temperature in the simfit.

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