

EFFECTS OF VARIABLE TEMPERATURE ON MÖSSBAUER DATA ACQUISITION: LABORATORY-BASED AND MER A RESULTS. Y. Rothstein¹, E.C. Sklute¹, M.D. Dyar¹, and M.W. Schaefer². ¹Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075, yrothste@mtholyoke.edu; ²Dept. of Geology and Geophysics, E235 Howe-Russell, Louisiana State University, Baton Rouge, LA 70803.

Introduction: Mössbauer spectrometers on the Spirit and Opportunity rovers have played a valuable role in identifying mineralogy at both the Gusev and Meridiani landing sites [1,2]. Key to the application of Mössbauer results is the issue of how accurately the peak positions, on which the mineral identifications are based, can be determined. Remote Mössbauer spectroscopy has by necessity some unusual experimental constraints that may influence the confidence with which peak positions can be fit. We present here an analysis of the effects of variable temperature and short duration run times on spectral resolution.

Background: Because of the diurnal temperature variations on Mars, the MER Mössbauer spectrometers were set up to acquire data in 13 separate memory areas that correspond to 11 temperature intervals [1]. Depending on the timing of the temperature changes and on the duration of the experiment, each of these temperature intervals contains a variable number of counts (e.g. roughly 10,000-300,000 for MER A). In most cases, the signal to noise ratio was so large that individual temperature intervals could not be uniquely fit. So, the MER science team adopted the practice of summing Mossbauer data over the 200-280K temperature intervals, as well as folding the data to effectively double the number of counts. The resultant data files had sufficient counts to allow fitting of the data using Lorentzian line shapes [1].

The MER team noted several problems with their approach. Even in the summed spectra, components of magnetic sextets were so low in intensity that they were “not optimal” [1], and it was necessary to constrain peak areas in the 3:2:1:1:2:3 proportion. For spectra with two sextets, peak width and centers had to be constrained based upon the spectrum of A042_Mimi_Shoe (which had the most intense two-sextet spectrum) and that of the magnetite calibration target on board. For spectra with a single sextet, targets were added together. These methods are well-described in [1].

Methods: To independently assess these issues, we undertook careful study of the effects of low count rates, using three different approaches:

1) In our laboratory, we simulated the effects of summing MER spectra by running a römerite at four discrete temperatures for 12 hours each, To obtain typical laboratory spectra with ~3 million baseline

counts before folding. We then summed the spectra and fit the composite.

2) Again in our laboratory, we simulated low count rates by acquiring short runs at discrete temperature intervals. For this purpose we used a synthetic olivine (Fo₇₀). The olivine was run for 50,000 baseline counts (about 7 minutes each) at each of five temperatures (210-250K). These five data files were summed. Then, the sample was run for 250,000 counts (~35 minutes) at the midpoint of that temperature range, which was 230K.

3) We fit all the MER A data currently available on the PDS using quadrupole splitting distributions [3], comparing fits to data from individual temperature increments to fits of summed MER A data. We here compare the results of our fits to the MER A data with those reported in [1].

Table 1. Mössbauer Parameters, Laboratory Data

Römerite 1	^[M1-M3] Fe ²⁺ (parameters in mm/s)				
	Γ	δ	Δ	Area	χ ²
210	0.24	1.335	3.041	67.52	2.5842
230	0.24	1.325	3.008	66.90	3.6875
250	0.24	1.310	2.968	66.94	3.9457
270	0.24	1.297	2.918	66.27	4.7755
Summed	0.24	1.317	2.989	66.66	20.037
Römerite 2	^[M] Fe ³⁺ (parameters in mm/s)				
	Γ	δ	Δ	Area	
210	0.27	0.368	0.616	32.48	2.5842
230	0.27	0.359	0.606	33.10	3.6875
250	0.25	0.350	0.603	33.06	3.9457
270	0.26	0.340	0.606	33.73	4.7755
Summed	0.27	0.353	0.586	33.34	20.037
Olivine	^[M1-M3] Fe ²⁺ (parameters in mm/s)				
	Γ	δ	Δ	Area	χ ²
210	0.26	1.215	3.104	100	0.600
220	0.26	1.209	3.097	100	0.559
230	0.26	1.207	3.092	100	0.647
240	0.26	1.199	3.080	100	0.644
250	0.26	1.194	3.039	100	0.644
Added	0.26	1.205	3.089	100	0.650
230 long	0.26	1.205	3.084	100	0.743

Results of laboratory simulations: Figs. 1 and 2 show stacked plots of laboratory data that were used to simulate MER acquisitions.

The römerite was fit to two doublets, one for Fe²⁺ and one for Fe³⁺. As seen in Table 1 and Figure 1, under these ideal circumstances (i.e., high counts), summing the four temperature intervals gives identical results to fitting the temperature interval at the middle

of the range. Note in Table 1 that the χ^2 value for the fit of the summed data is larger because the error bars are small and the peaks are broadened.

For olivine, (Fig. 2) we found virtually the same results, even with poorer data. Fits to the summed data again match those of data acquired at the central temperature range, especially when the number of counts was the same. Thus, we conclude that summing Mössbauer data over a range of temperatures actually gives a good representation of a single spectrum acquired at the average temperature of the acquisitions.

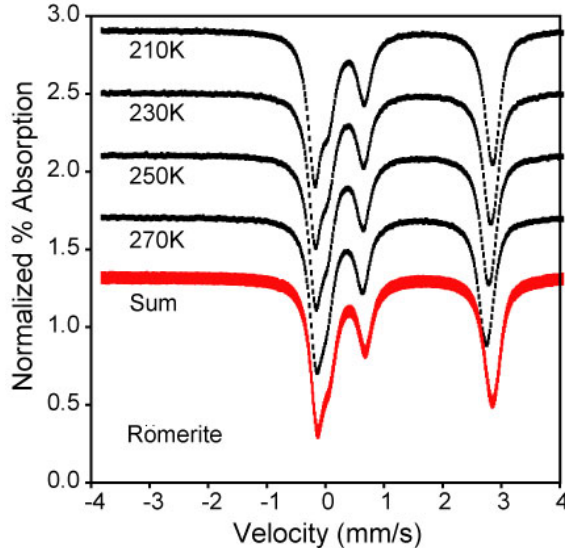


Fig. 1. Romerite spectra acquired at different temperatures, and summed.

Results of Fits to MER A Data: We were able to obtain fits that satisfied our convergence criteria for at least one temperature interval from a majority of the MER A data sets released to date. Based upon these results, we make the following observations:

1. Every spectrum can be fit without constraints on peak positions. All the spectra converged on fits with a single sextet (average isomer shift = 0.30 mm/s, average quadrupole splitting = 0.122 mm/s, and average hyperfine field = 48.8 T) that can be assigned to magnetite. We found no evidence for any sextet with hematite-like parameters, even for the Mazatzal spectra in which the MER team reported hematite.

2. For the paramagnetic peaks, we consistently fit two Fe^{2+} and one or two Fe^{3+} doublets *without position constraints*, depending on temperature. All spectra gave nearly identical parameters for Fe^{2+} doublets with isomer shifts = 1.14-1.24 mm/s and quadrupole splittings in two groups: 2.80-3.05 mm/s and 1.90-2.10 mm/s. The MER team attributes these doublets to olivine and pyroxene, respectively, but we believe that there may be many minerals with these parameters that should be considered [4].

A wide range of parameters was obtained for the paramagnetic Fe^{3+} doublets, but generally, quadrupole splittings suggest octahedral rather than tetrahedral Fe^{3+} . We concur with the MER science team that these doublets are not “mineralogically specific” [1]; they probably represent superimposed contributions from Fe^{3+} in multiple phases.

3. All spectra fit were identical within reasonable error bars [5], although spectra of Mimi_Shoe, Desert Soil, and Mazatzal (except post-RAT1) had a slightly larger percentage of Fe as Fe^{3+} .

4. In both our experimental data and the MER A data, we found it necessary to fix the minimum peak widths to ensure that they were above the 0.19 mm/s theoretical linewidth.

5. In the MER A data, we compared fits of individual temperature bin spectra with fits of their sum. Isomer shift and quadrupole splitting values across multiple temperature bins do not change systematically. We believe that the signal to noise ratio in these data is so low that we are not obtaining unique fits.

6. Summing the MER A data and fitting the resultant spectrum does appear to give the average values of isomer shift and quadrupole splitting for all the temperature bins collected.

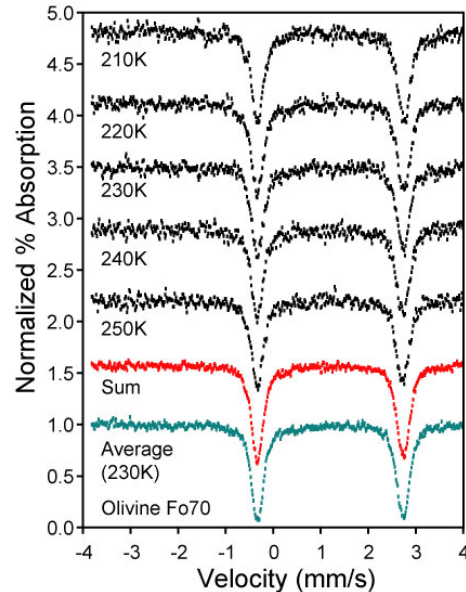


Fig. 2. Synthetic olivine (Fo_{70}) spectra acquired at different temperatures.

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