

## Practical application of Mössbauer goodness-of-fit parameters for evaluation of real experimental results: A reply

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Waychunas (1986) has commented on possible misinterpretations of Mössbauer results with specific reference to my 1984 paper, "Precision and interlaboratory reproducibility of measurements of the Mössbauer effect in minerals." In order to properly address the remarks of Waychunas (1986), it is helpful to review the main points of the original paper and then to discuss specifically the criticisms leveled toward it.

The study by Dyar (1984) sought to provide answers to three fundamental questions: (1) What are the reproducibility and standard errors of Mössbauer measurements? (2) How can experimental conditions be optimized? (3) How can results from different laboratories be compared? The study showed that the standard deviation of multiple measurements on a single apparatus is better than 0.016 mm/s for isomer shift, 0.060 mm/s for quadrupole splitting, and 1.02% on individual peak-area data. The standard deviation of interlaboratory measurements on the same minerals is slightly better because only optimal run conditions were used: 0.006 mm/s for isomer shift, 0.023 mm/s for quadrupole splitting, and 1.44% on individual peak-area data. These results constitute the main thrust of the Dyar (1984) paper and represent (as will be discussed later) the main drawback to the work of Waychunas. His (1986) paper discusses two points that are not main conclusions: the "failure" of Dyar (1984) to consider the effects of varied signal-to-noise ratio (S/N) on the tabulated statistical parameters and the omission by Dyar (1984) of any consideration of the uncertainty or error in the MISFIT for each of the fits given.

The primary thrust of the Waychunas (1986) paper is to point out that random noise in a spectrum (simulated by his variance of the signal-to-noise ratio) may be responsible for the observed variation in statistical parameters seen by Dyar (1984). He has elegantly demonstrated that random noise can be simulated and can cause variations in the statistical parameters of a Mössbauer fit. Waychunas has performed a service by quantifying signal-to-noise effects and improving our understanding of how statistical parameters may be affected by data quality. My earlier study (Dyar, 1984) did not and could not examine signal-to-noise ratio independently because it was an *experimental* study; it is useful now to have the synthetic spectral results because they provide a comparison. How-

ever, I fundamentally disagree with the conclusion of Waychunas (1986) that signal-to-noise variations can explain all the statistical variance observed in Dyar (1984) for the following reasons:

1. The 1984 paper deals with the much more complicated problem of how much experimentally observed noise (i.e., the random noise studied by Waychunas *plus* other potentially systematic noise) is observed under varying experimental conditions. A Mössbauer experiment is never influenced only by random noise, but by a combination of random and systematic factors that are indistinguishable. Waychunas has misleadingly stated that I attributed the poor statistics of increasingly long runs to spectrometer drift; in fact what I have assigned them to are "small instrumental problems, such as the cosine smearing factor, baseline inconsistencies, source problems, non-linear drives, etc." (not to mention doors slamming, trucks passing, temperature changes). In short, it is questionable to assume that his theoretically simulated noise is comparable to what is observed in the laboratory. In fact, his simulation does not even reproduce the trends observed in real data. For example, data in my 1984 paper show that  $\chi^2$  reaches a minimum as MISFIT approaches zero in spectra with one million baseline counts; the simulation of that experiment by Waychunas holds  $\chi^2$  constant and shows MISFIT decreasing with increasing baseline counts. Clearly the simulated data (representing only varied signal-to-noise ratio) is *not* adequate to explain the trends in the experimental work. In order to really understand the sources of error and noise in a Mössbauer spectrum, his type of statistical analysis should be performed on real experimental data; the eighty-odd data files collected for the Dyar (1984) paper are still accessible and could be contributed toward such an endeavor.

2. The conclusions of Dyar (1984) are *not* based strictly on statistical parameters, but also on the physical parameter of gamma-ray absorption (a factor that is clearly *not* affected by fitting procedures or goodness-of-fit parameters). "Percentage transmitted" data given in Tables 3, 4, and 5 in the original paper show that gamma-ray absorbance *is* affected by sample concentration and run duration. The synthetic simulations done by Waychunas do not reproduce these trends: another justification for performing his analysis on *real* data.

3. It is important to note that my conclusions (as based on *combined* evaluation of gamma-ray absorbance, MISFIT,  $\Delta$  MISFIT, and  $\chi^2$ ) are well corroborated by theoretical con-

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siderations. In a Mössbauer experiment, the line width of a spectrum,  $\Gamma$ , increases because  $\Gamma_{\text{experimental}} = \Gamma_{\text{absorber}} + \Gamma_{\text{source}} + nK$ , where  $n$  is in  $\text{mg}/\text{cm}^2$  and  $K$  is a constant based on the maximum nuclear cross section at resonance ( $2.35 \times 10^{-18} \text{ cm}^2$  for Fe) (Bancroft, 1973). For  $^{57}\text{Fe}$ , as long as a sample contains less than  $10 \text{ mg}/\text{cm}^2$  of Fe, any deviation from Lorentzian line shape cannot be detected (Bancroft, 1973); at higher concentrations, saturation effects become a problem. In this light it cannot be merely "fortuitous" that my experiments confirm that a sample concentration of  $7 \text{ mg}/\text{cm}^2$  gives the most desirable combination of gamma-ray absorbance,  $\chi^2$ , and MISFIT for the silicates studied. The value of  $2 \text{ mg}/\text{cm}^2$  for sulfide samples was based on preliminary data (as stated in the original paper); that value is still very close to the  $10 \text{ mg}/\text{cm}^2$  Fe value beneath which line-shape variations become negligible. These results strongly support the use of statistical parameters together to evaluate Mössbauer fits.

Waychunas was also critical of the lack of  $\Delta \text{ MISFIT}$  values in the original Dyar (1984) paper. Those values were given in Document AM-84-256, which is available from the Business Office of the Mineralogical Society of America. Waychunas implied that MISFIT is of little use without  $\Delta \text{ MISFIT}$ , which is not the case. If I were evaluating data of highly variable quality, or several fits to a single data set, then it would of course be essential for me to list  $\Delta \text{ MISFIT}$  values for each fit. However, I *did* utilize  $\Delta \text{ MISFIT}$  because I had already tested several fits on each of the data sets in Dyar (1984); the tabulated results represent the lowest values of  $\Delta \text{ MISFIT}$ . For this reason and owing to space considerations,  $\Delta \text{ MISFIT}$  values were not printed in the original article.

In summary, the fundamental problem with Mössbauer goodness-of-fit parameters can be simply stated. Waychunas (1986) has successfully shown that in the *ideal* case, with only random noise, statistics on Mössbauer spectra improve with longer runs. The data in Dyar (1984) show that in the *experimental* case, statistics of Mössbauer spectra degrade with longer runs. Why don't the experiments reproduce the theory? The state-of-the-art spectrometers in use today (at least, in the seven labs surveyed in the original study) produce spectra that do not live up to the sophistication of the statistical parameters that are used to evaluate them. Waychunas optimistically tabulated only *statistics* in his paper; results are not given. This

Table 1. Statistics for fits with varying run durations

	3 h	60 h	Standard deviation
Isomer shift (1) (mm/s)	1.144	1.139	0.006
Isomer shift (2) (mm/s)	1.060	1.061	0.006
Quadrupole splitting (1) (mm/s)	2.818	2.792	0.023
Quadrupole splitting (2) (mm/s)	1.553	1.538	0.010
Gamma-ray absorption (%)	7.28	6.45	
$\chi^2$	493	947	
MISFIT (%)	-0.034	0.058	
$\Delta \text{ MISFIT}$ (%)	-0.055	0.006	

is misleading because it glosses over the real limitation of the Mössbauer technique: the fact that although statistical parameters may vary, the *results* of the different fits are often the same within experimental error. As an example, data from Dyar (1984) are given in Table 1; note that the same sample run for 3- and 60-h periods gives the same "answer" within the standard deviations of the technique, but with widely varying statistics. In this case, the goodness-of-fit parameters are encouraging us to discriminate between spectra that are experimentally identical! The experimental error resulting from the accumulation of a Mössbauer spectrum greatly exceeds the counting error described by Waychunas. This does not mean that the Mössbauer technique is a poor one; it simply reinforces the need for accurate estimates of experimental error. At the present time, we do not necessarily need better statistics for evaluating Mössbauer spectra; instead, we need better spectrometers!

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