Mössbauer spectroscopy of tetrahedral Fe\textsuperscript{3+} in triocathedral micas—Reply

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The stated purpose of our original paper (Rancourt et al., 1992) was to show that certain observed spectral features in the room-temperature and liquid-N\textsubscript{2}-temperature Mössbauer spectra of triocathedral micas unambiguously indicate the presence of [\textsuperscript{56}Fe\textsuperscript{3+}] independently of any assumed line-shape fitting model. We established this by showing that several spectra have distinct sharp shoulders, on the high-energy side of the low-energy line in the [\textsuperscript{56}Fe\textsuperscript{2+}] absorption doublet, that are different from any of the known [\textsuperscript{56}Fe\textsuperscript{3+}] and [\textsuperscript{56}Fe\textsuperscript{2+}] spectral features. This occurred in samples that were expected to contain [\textsuperscript{56}Fe\textsuperscript{3+}] based on formula recalculations and in one sample that was known to contain [\textsuperscript{56}Fe\textsuperscript{3+}] on the basis of its optical reverse pleochroism (Hogarth et al., 1970).

After comparison with all of the studies that had been reviewed by Dyar (1987), we (1) concluded that the presence of our observed shoulder implies the presence of [\textsuperscript{56}Fe\textsuperscript{3+}], and (2) argued that the absence of such a visible shoulder implies the absence (to within the detection limit) of [\textsuperscript{56}Fe\textsuperscript{3+}]. Contrary to Dyar’s claims, this is the main thrust of our paper. We also criticized Dyar’s (1990) work, and that has led to the present discussion (Dyar, 1993).

Dyar (1993) did not refute or address point 1 but rejected point 2 in that she would have us believe in [\textsuperscript{56}Fe\textsuperscript{3+}] contributions that correspond to completely hidden doublets that do not give rise to visible spectral features. Dyar rejected our criticism of her work (Dyar, 1990) and made ancillary comments on our methods.

We (Rancourt et al., 1992) were compelled to criticize Dyar’s work on biotite samples from metapelites (Dyar, 1990) for two reasons. Firstly, despite her statements to the contrary, it is in clear disagreement with both the great majority of studies that report [\textsuperscript{56}Fe\textsuperscript{3+}] in triocathedral micas (see Table 4 and Fig. 7 of Rancourt et al., 1992) and our own results, including data for phlogopite and annite end-members. Secondly, her conclusion concerning [\textsuperscript{56}Fe\textsuperscript{3+}] (which, by her own account, should not be present in her biotite samples, given the present understanding of the crystal chemistry of micas) depends entirely on a small spectral component that is not seen directly in the spectra, may result from the particular spectral analysis, and could easily be an artifact arising from the simple mechanism that we have proposed (Rancourt et al., 1992) and which Dyar has not considered or discussed.

Dyar’s (1993) discussion paper contained many incorrect statements concerning our paper and errors relating to fundamental aspects of Mössbauer spectroscopy. We now address some of these for the benefit of the non-expert reader.

**Powder vs. Single-Crystal Mössbauer Spectroscopy**

Dyar stated that hidden doublets such as her [\textsuperscript{56}Fe\textsuperscript{3+}] contributions are generally not resolved in single-crystal Mössbauer work but can more easily be “seen” in powder spectra. She stated that this is due to the orientational dependence of doublet line intensities. She also stated that “single-crystal Mössbauer spectroscopy is poorly suited to the study of micas.” That is the same as saying that powder XRD is better suited to structural studies than single-crystal work because Rietveld analysis can be applied.

In fact, single-crystal (or mosaic or textured absorber) studies offer a powerful method for testing the existence of hidden contributions because the total species-specific spectral areas do not depend on orientation. As a function of orientation, the hidden area does not change, whereas the high- and low-energy lines in the main Fe\textsuperscript{2+} absorption doublet exchange intensity according to well-known laws (e.g., Hargraves et al., 1990). Such methods need to be developed and should be encouraged. The fact that so far most spectroscopists have used powder absorbers to simplify the analysis does not diminish the vast potential for single-crystal Mössbauer spectroscopy. Much more information is contained in several single-crystal spectra obtained at different orientations of the same sample than in one powder spectrum.

**Electric Field Gradients at Fe\textsuperscript{3+} Sites**

In discussing the physical cause of electric field gradients and corresponding quadrupole splittings (QS), it is important to distinguish Fe\textsuperscript{3+} from Fe\textsuperscript{2+}. (Dyar does not.) In Fe\textsuperscript{2+} the main contribution is from the local Fe\textsuperscript{2+} valence electrons, whereas in Fe\textsuperscript{3+} the entire contribution arises from a long-range lattice sum because the Fe\textsuperscript{3+} ion is spherically symmetric.

The QS of Fe\textsuperscript{3+} cannot be discussed in terms of local distortions alone (as is done by Dyar) because the lattice sum is primarily determined by the crystal structure and long-range charge distribution. That is why it is wrong for Dyar to appeal to the variety of Fe\textsuperscript{3+} QS seen when comparing minerals such as chlorite, nontronite, and serpentinite, to justify her anomalously small biotite values (Δ = 0.25 mm/s).

For the same reasons, true and brittle triocathedral micas should have significantly different lattice sums and corresponding [\textsuperscript{56}Fe\textsuperscript{3+}] QS. We found that true triocathedral micas have Δ ≈ 0.5 mm/s and that brittle triocathedral micas have Δ ≈ 0.7 mm/s. It surprised us that
Dyar did not recognize this in her review (Dyar, 1987). We do not believe that $^{57}$Fe$^{3+}$ QS in biotite, even biotite from metapelites, can be as small as $\Delta = 0.25$ mm/s. Several of Dyar’s doublets ($\sim 10$ samples) have $\Delta = 0.15$ mm/s.

We note that this question of $^{57}$Fe$^{3+}$ QS can be resolved by relatively simple theoretical calculations that involve evaluating the relevant lattice sums. This has, for example, been done for $^{57}$Fe$^{3+}$ in biotite (Mineeva, 1978). On the basis of preliminary calculations (unpublished), we are confident that detailed lattice sum calculations will corroborate our true and brittle mica $\Delta$ values and will demonstrate that $\Delta = 0.25$ mm/s values are not possible in specimens whose structures and compositions are such that they can be called biotite.

The main point, however, is that Dyar’s anomalously small $^{57}$Fe$^{3+}$ $\Delta$ values do not need to be explained because they characterize doublets whose existence has not been demonstrated by Dyar. Interpretations based on the existence of such contributions that do not give rise to visible spectral features and that are buried under more intense lines should not be believed because in these situations many fits are statistically equivalent, such that one can at best only conclude that the preferred model is not inconsistent with the data: one must admit that the chosen model cannot be distinguished from several other models.

**The Meaning and Usefulness of $\chi^2$**

Dyar (1993) criticized us for reporting only $\chi^2$ values and not Misfit values, yet in presenting her fits (Fig. 1 of Dyar, 1993) she reported only Misfit values and did not show residuals, instead relying primarily on the appearance of the fit. In the preferred fit shown by Dyar (Fig. 1C, Dyar, 1993), the line does not pass through all the points. There are systematic residuals in several broad velocity ranges that are significant enough to correspond to a statistically unacceptable value of $\chi^2$. If there are not, then I would ask how Dyar is calculating $\chi^2$.

The $\chi^2$ parameter is the most widely used criterion for evaluating comparisons between measured data and fitting models. It has several useful and rigorous properties. With a correct model, $\chi^2$ values for several identically performed experiments on the same sample are distributed on a Gaussian whose position and width are known. When the particular $\chi^2$ value falls within this distribution, the model may be right. However, when it does not, the model can be unambiguously rejected.

We used $\chi^2$ in this way to show that models that did not allow our visible $^{57}$Fe$^{3+}$ shoulder to have its own absorption line could be rejected. This was the main purpose in presenting fits to our data. We did not attempt to get spectral areas or site populations. That was not the purpose of our paper. Another reason for fitting was that it gave accurate positions for the underlying absorption line that causes the observed characteristic shoulder.

Using the same $\chi^2$ criterion, we found (and continue to find) that models that use Lorentzian lines can be ruled out. Lorentzian lines are fine for some purposes, but they are physically incorrect for all applications with minerals that have distributions of QS (see below).

Finally, noisy data such as Dyar’s (1990) do give lower $\chi^2$ values. This simply reflects the relatively large inability of noisy data to resolve different fitting models. It does not remove any of the known properties of the $\chi^2$ criterion. The answer is not to use Misfit but to obtain better statistics.

**Lorentzian Lines vs. QS Distributions**

Identical electronic environments of the probe $^{57}$Fe nucleus give rise to elemental Lorentzian contributions (elemental doublets) in the absence of artifacts such as thickness effects. Different electronic environments give rise to elemental doublets with different QSs. This is the case in minerals such as mica that have site to site variations in local chemistry, near-neighbor positions, etc. The result is that the total absorption line shape is the sum of a great many elemental contributions. Sums of Lorentzians are not Lorentzians, and the only physically correct way to analyze the observed absorption spectra is to acknowledge quadrupole-splitting distributions (QSD).

Rancourt and Ping (1991) have developed new and powerful methods for fitting with actual QSDs. These advances (Rancourt and Ping, 1991; Rancourt, 1989; Ping et al., 1991) show that the intrinsically suited basic line shape for cases with QSDs is the Voigt line shape. This conclusion is based on physical considerations and follows from the fact that true QSDs are well represented by sums of Gaussians.

In all our work involving various natural and synthetic minerals, transition metal oxides, quasi-crystals, synthetic intercalated layered materials, and metallic alloys, we find that for a given number of adjustable parameters, models using Voigt lines give statistically acceptable fits where Lorentzian lines do not. The Lorentzian line fits have persistent systematic residuals that can only be removed by adding extra lines.

**Minimal Fitting vs. Physical Model Fits**

Those who criticize our methods (Rancourt, 1989; Rancourt and Ping, 1991) should understand that, having shown the correctness of Voigt lines, we use these in two very different ways, depending on whether we wish to test a particular physical fitting model or to determine the amount of information contained in the data by fitting the smallest number of Voigt lines that gives a statistically acceptable fit.

In Rancourt et al. (1992), we used the latter approach to show that the visible shoulder caused by the high-energy line of the $^{57}$Fe$^{3+}$ doublet required its own Voigt line and that the low-energy line of the same doublet did not. We did not, as stated by Dyar, “suggest that the area of the spectrum assigned to a half of a doublet corresponding to a $^{57}$Fe$^{3+}$ component is ‘most likely’ an artifact of an Fe$^{3+}$ peak.”

In another such claim, Dyar found our conclusion con-
cerning her new hidden $^{56}$Fe$^{3+}$ doublets to be "inconsistent with a large body of work . . . which confirms the presence of $^{56}$Fe$^{3+}$ in clay minerals." We do not deny the existence of $^{56}$Fe$^{3+}$ in clay minerals. In fact, we are the first to point to compelling visible evidence for the presence of $^{56}$Fe$^{3+}$ and to show that the visible spectral feature in question can be made much more evident by obtaining data at liquid N$_2$ temperature.

REFERENCES CITED


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