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Mössbauer spectroscopy of tetrahedral Fe^{3+} in trioctahedral micas—Discussion

M. Darby Dyar
Department of Geological Sciences, University of Oregon, Eugene, Oregon 97403, U.S.A.

In a recent paper, Rancourt et al. (1992) challenged the interpretations of Dyar (1990) and other previous workers who have noted the presence of $^{[4]}\mathrm{Fe}^{3+}$ in mica minerals. Their stated purpose was to determine the spectral features of $^{[4]}\mathrm{Fe}^{3+}$ in trioctahedral micas, despite the fact that these parameters had already been determined both for naturally occurring and synthetic samples by Dyar and Burns (1986). Rancourt et al. (1992) observed parameters that duplicated the results of our work on samples where Al saturation is not present. It is easy to fit a doublet corresponding to $^{[4]}\mathrm{Fe}^{3+}$ in a spectrum where it is required by stoichiometry, is present in significant amounts, and is not overlapped by other peaks representing Fe in other sites. Dyar (1990) addressed the far more difficult problem of resolving contributions of Fe^{3+} in spectra of micas from Al-saturated metapelites, where contributions from $^{[6]}\mathrm{Fe}^{2+}_{\mathrm{M1}}$, $^{[6]}\mathrm{Fe}^{2+}_{\mathrm{M2}}$, $^{[6]}\mathrm{Fe}^{3+}_{\mathrm{M1}}$, $^{[6]}\mathrm{Fe}^{3+}_{\mathrm{M2}}$, and $^{[4]}\mathrm{Fe}^{3+}$ all overlap. In those spectra, Rancourt et al. (1992) suggested that the area of the spectrum assigned to a half of a doublet corresponding to a $^{[4]}\mathrm{Fe}^{3+}$ component is "most likely an artifact" of an Fe^{2+} peak. The work of Rancourt et al. overlooks numerous other relevant related studies and contains several problems that compromise its conclusions. The purpose of this paper is to clarify and discuss these problems so that the work of Rancourt et al. (1992) can be judged in perspective with other current Mössbauer studies.

The most significant drawback of Rancourt et al. (1992) is the fact that single-crystal Mössbauer spectroscopy is poorly suited to the study of micas. The quadrupole splitting (Δ) of a Mössbauer doublet arises from the interaction between the nuclear quadrupole moment and the electric field in which it occurs. Because the $I = \frac{3}{2}$ state of the $^{57}\mathrm{Fe}$ nucleus (in the case of Fe Mössbauer) is split into two levels, two nuclear transitions from the $I = \frac{1}{2}$ state are made possible. The transition probabilities are dependent upon the angle between the direction of the electric field gradient at the nucleus and the direction of propagation of the γ rays (Hawthorne, 1988). If the absorber (i.e., the sample) consists of randomly oriented absorbers (as in the work by Dyar, 1990, and others), both peaks of a quadrupole split doublet will ideally have the same intensities (i.e., their areas will be equal). In single-crystal spectra (such as those shown by Rancourt et al., 1992), peak intensities are unequal, and adjustments must be made to deal with the effects of orientation; the task of interpreting the areas of peaks with unequal intensities becomes quite complicated. The result is that smaller peaks in single-crystal spectra are easily overlooked. As Bancroft (1973) explained, "orientation of the crystallites or an anisotropic *f* factor can markedly alter the spectrum and lead to difficulties in interpretation, especially for small quadrupole splittings." A recent paper by Aldridge et al. (1991) showed this effect quite clearly: only three doublets could be resolved in a single-crystal Mössbauer spectrum of biotite, whereas a spectrum obtained from a powdered sample of the same specimen (prepared in the same fashion as those in Dyar et al., 1990) could be fitted with four doublets. Single-crystal Mössbauer spectroscopy is the wrong technique to use to look for doublets with small quadrupole splittings (Δ). For this reason, the majority of previous workers in the field of Mössbauer spectroscopy of micas, ranging from Bancroft and Brown (1975) to Annersten and Olesch (1978) to Dyar (1990) have all used spectra taken from powdered, randomly oriented absorbers.

Rancourt et al. (1992) reported only the statistical parameter χ^2 as a measure of the appropriateness of their fits. This parameter is known to be dependent on the magnitude of the base line of the spectra rather than on the quality of the model and data. Ruby's (1973) Misfit parameter is commonly used to "facilitate comparison between a single theory and several measurements of varying quality," unlike χ^2 it is "free from the unwelcome property of appearing to improve the goodness-of-fit with poorer data" (Ruby, 1973). Nor did Rancourt et al. (1992) give estimates of deviations on Mössbauer parameters or peak areas. Their Δ and isomer shift (δ) parameters are given with three significant digits after the decimal, when generally accepted errors on these parameters are no better than ±0.02 mm/s (Bancroft, 1973; Dyar, 1984). Neither error bars nor residuals are plotted on the spectra shown in Rancourt et al. (1992). Thus it is difficult to evaluate their results.

In Rancourt et al. (1992), data from previous work were overinterpreted by the omission of error bars and misinterpreted by the omission of appropriate data. Figures 6 and 7 showed plots of peak parameters and positions, respectively, from which they drew the conclusion that "two narrow fields" emerge. These plots were based only on data from Dyar (1987), which was a review paper; no other relevant literature published contemporaneously or subsequently was used. These plots are misleading because they contrast data based on three doublet fits (i.e., doublets assigned to $\mathrm{Fe}^{2+}_{\mathrm{M2}}$, $\mathrm{Fe}^{2+}_{\mathrm{M1}}$, and $^{[4]}\mathrm{Fe}^{3+}$) with data based on four doublet fits (i.e., also including a contribution from $^{[6]}\mathrm{Fe}^{3+}$). In the case of the Dyar (1990) data, they chose to plot only the tetrahedral peaks and to

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omit the octahedral peaks altogether. Of course the two models yield different sets of data and of course the models that fail to distinguish between $^{[6]}$Fe^{3+} and $^{[4]}$Fe^{3+} have higher Mössbauer parameters because a single Fe^{3+} doublet would have parameters averaging the contributions from tetrahedral and octahedral sites.

Rancourt et al. (1992) repeatedly refer to the contribution of "completely hidden doublets" corresponding to Fe^{3+}, which are an "artifact of improper analysis and interpretation." Dyar's (1990) interpretation was criticized for ignoring texture effects, thickness effects, and non-Lorentzian line shapes. In fact, Dyar (1990) clearly stated that samples were carefully mounted to obtain random orientation using the method of Clark et al. (1967), which was shown by Bancroft and Brown (1975) to give randomly oriented samples for micas. Optimal sample quantities were used in the powdered mounts to avoid thickness effects (as discussed by Ruby and Hichs, 1962; Lang, 1963; Bancroft, 1967; and others). Non-Lorentzian line shapes were modeled and found to be unnecessary (i.e., no statistical justification could be found for their use). These points are discussed in detail in Dyar and Burns (1986).

Figure 1 shows a typical spectrum of one of the biotite samples from Dyar (1990). The same spectrum is shown fitted with, in all three examples, two Fe^{2+} doublets corresponding to Fe^{2+} in M2 and M1 sites. Spectrum A adds a doublet corresponding to Fe^{3+} in octahedral coordination with unconstrained Fe^{2+} peak areas, with no $^{[4]}$Fe^{3+} (as preferred by Rancourt et al., 1992). Spectrum B shows the same sample fit with $^{[4]}$Fe^{3+} only, and spectrum C shows the data fit with doublets corresponding to both $^{[4]}$Fe^{3+} and $^{[6]}$Fe^{3+} (model used by Dyar, 1990). The line passing through most of the data points represents the sum of contributions from all modeled doublets shown in a given spectrum. Note that in spectrum A, a significant number of data points in the region around 0.25 mm/s is not represented by the model of Rancourt et al. (1992). This is the region of the spectrum where the "completely hidden doublets" referred to by Rancourt et al. (1992) lie; readers are asked to use their own judgment in evaluating this issue.

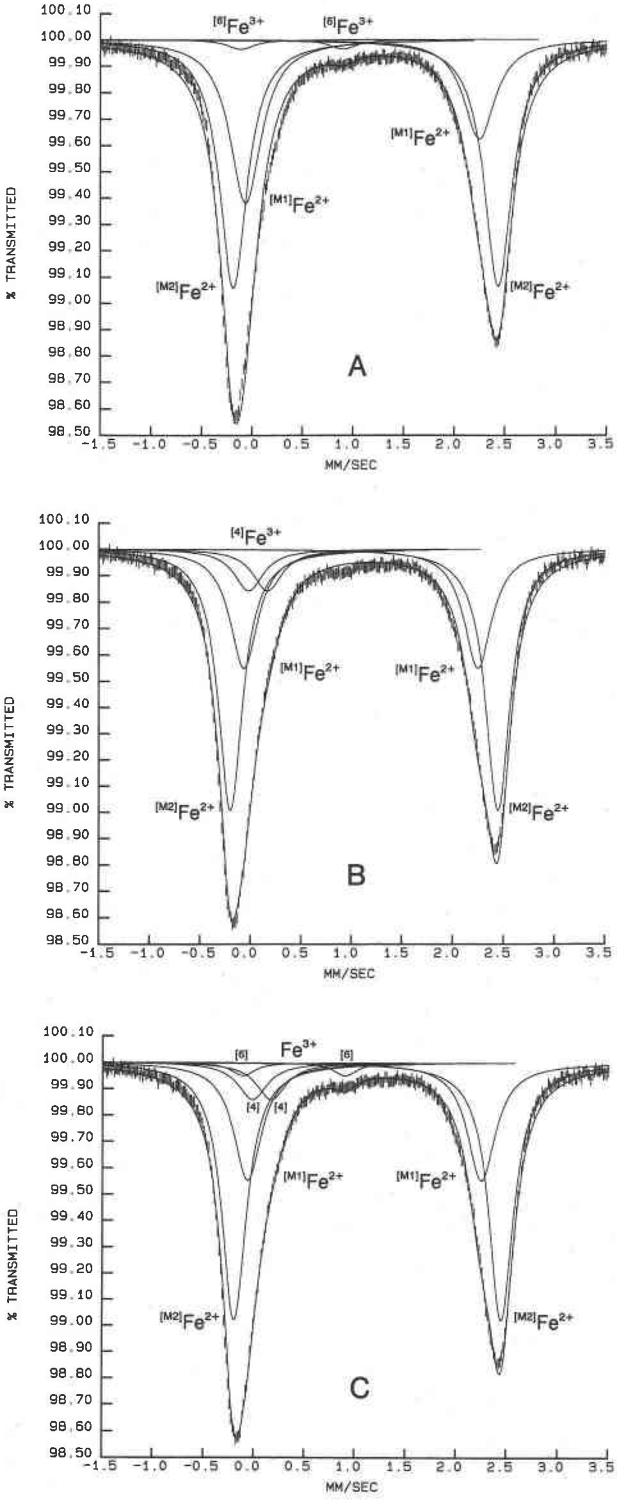

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Fig. 1. Mössbauer spectrum of Maine biotite sample O-K-8′ (see Dyar et al., 1990, for detailed background information, including methods, error bars, and counting statistics). Three fits to this spectrum are shown to illustrate three different models for interpreting the data; Misfit values (Ruby, 1973) are 0.195 ± 0.020%, 0.056 ± 0.011%, and 0.045 ± 0.010% in models **A**, **B**, and **C**, respectively. The top fit (**A**) shows the spectrum fit with contributions from Fe^{2+} in octahedral coordination (peaks located at −0.19, −0.06, 2.24, and 2.44 mm/s, as shown in all three models) and from Fe^{3+} in octahedral coordination only (model suggested by Rancourt et al., 1992). Fe^{2+} peak areas are unconstrained. Peaks areas are 31, 23, 1, 1, 14, and 30%. The 10% extra area in the lower velocity peaks represents either an artifact of Fe^{2+} or the contribution of $^{[4]}$Fe^{3+}. Note that the envelope of the fit, which indicates the sum of all peaks in a given model, does not pass through a number of data points in the region around 0.25 mm/s. Part (**B**) shows the Fe^{2+} doublets joined by a doublet representing $^{[4]}$Fe^{3+} only; this model does not adequately represent data in the region around 1.0 mm/s. Part (**C**) shows both Fe^{2+} doublets with $^{[4]}$Fe^{3+} and $^{[6]}$Fe^{3+} added.

Rancourt et al. (1992) believed that the results given in Dyar (1990) are "clearly and systematically different from all previously reported values." This statement refers to a difference in quadrupole splittings (Δ) and reflects a lack of familiarity with the literature in this field on the subject of $^{[4]}Fe^{3+}$. Dyar (1990) observed parameters for $^{[4]}Fe^{3+}$ of $\delta = 0.15 \pm 0.05$ mm/s and $\Delta = 0.25 \pm 0.03$ mm/s. Other workers who have found similar results for related structures include Longworth et al. (1987): $\delta = 0.12$ mm/s and $\Delta = 0.27$ mm/s (biotite); Homonnay et al. (1988): $\delta = 0.25$ and 0.03 mm/s with $\Delta = 0.62$ and 0.49 mm/s (mantle phlogopite); de Parseval et al. (1991): $\delta = 0.12$ mm/s and $\Delta = 0.39$ mm/s (chlorite); Luca (1991a): $\delta = 0.12$–0.24 mm/s and $\Delta = 0.46$–0.64 mm/s (nontronite and vermiculite); Luca (1991b): $\delta = -0.12$–0.25 mm/s and $\Delta = 0.53$–1.82 mm/s (dehydrated nontronite); Luca and MacLachlan (1992): $\delta = 0.15$–0.24 mm/s and $\Delta = 0.44$–0.57 mm/s (nontronite); Mizutani et al. (1991): $\delta = 0.23$ and 0.25 mm/s and $\Delta = 0.34$ and 0.83 mm/s (1:1 and 2:1 phyllosilicates); Malysheva et al. (1976): $\delta = 0.14$ mm/s and $\Delta = 0.26$ mm/s (serpentine); Rozenson et al. (1979): $\delta = 0.21$ mm/s and $\Delta = 0.42$ mm/s (serpentine); Blaauw et al. (1979) and Stroink et al. (1980): $\delta = 0.20$ mm/s, $\Delta = 0.34$ mm/s (serpentine). Homonnay et al. (1988) further commented that their data "unambiguously support the conclusions of Dyar (1987) that Fe^{3+} can substitute for tetrahedral Al, even if there is excess Al."

This disagreement in interpretation is also a function of the authors' fields of expertise. Physicists generally work on materials with small ranges of structures and compositions, for which variations in quadrupole splitting are small. Geological materials (i.e., naturally occurring minerals), however, pose an entirely different set of problems, and Δ values for Fe^{3+} cover a broad range of values from 0.2 up to 2.0 mm/s in epidote (Dollase, 1973). In this context the difference between the average Δ values of 0.25 mm/s observed by Dyar (1990) and 0.40–0.55 mm/s observed by Rancourt et al. (1992) is small, especially since their Δ values are probably averages that, when properly resolved with powder spectra, would yield a pair of doublets with higher and lower Δ values. Furthermore, significant compositional and paragenetic differences exist between igneous and metamorphic biotite (e.g., Foster, 1960). The use of igneous samples to make a point about the minor compositional variations in metapelite samples is not unlike a comparison between apples and oranges.

It is worthwhile, however, to review the possible reasons for the high distortion evidenced by the low Δ parameters. As explained in great detail in Dyar (1990), micas from metapelites are known to have extensive trivalent and quadruvalent substitutions in the octahedral sheets, which are charge-balanced by vacancies. More recent work (Dyar et al., 1991) has also shown that H contents of micas are variable, and, moreover, that interlayer occupancy by H_2O or H_3O^+ is likely. The effects of exchangeable cations and dehydration have been thoroughly studied in the related mineral nontronite, showing that as interlayer H_2O is removed, the tetrahedral sites distort (e.g., Luca, 1991b). Such distortion is shown (in their samples) to result in a wide range of Mössbauer peak positions and parameters for $^{[4]}Fe^{3+}$. In clay minerals in general, structural distortion of tetrahedral sites occupied by Fe^{3+} can be caused by many different crystal chemical factors, representing both local and long-range distortions, such as (1) $>2+$ occupancy of adjacent octahedral sites (which share an O atom with the tetrahedra), (2) vacancies in adjacent octahedral sites, (3) H^+ or even OH^- vacancies in the octahedral sheet, (4) distortion of tetrahedra by vacancy or H-species substitution in the interlayer sites, (5) changes in layer-stacking order-disorder (Luca, 1991b), and (6) direct electronic interaction of cations in the interlayer sites (Luca, 1991b). Real, naturally occurring minerals are complex, and it is unfair to abandon the most plausible interpretation of Mössbauer spectra, as Rancourt et al. (1992) would have us do, because we cannot identify which of the mechanisms is responsible for tetrahedral distortion and related substitution of Fe^{3+}. It is also worth pointing out that Ti^{4+}, ascribed by Rancourt et al. (1992) to tetrahedral coordination, is generally assumed to be in octahedral coordination in biotite (Guidotti, 1984).

Finally, Rancourt et al. (1992) did not cite the substantial body of literature written in the Russian language on this topic (e.g., Ushakova, 1971; Usenko et al., 1972; Khomenko et al., 1989). Most recently, Dudko et al. (1991) analyzed 160 biotite samples from garnet-bearing metapelites and independently confirmed Dyar's (1990) results by reporting almost identical data. For example, they noted a mean of 8.2% Fe^{3+} with a standard deviation of 3.7% in their garnet metapelite biotite; Dyar (1990) reported a mean of 7.8% Fe^{3+} in tetrahedral sites and a standard deviation of 2.5%. Dudko et al. (1991) concluded that the Fe^{3+} contents of their biotite samples were "practically independent of facies conditions of metamorphism," in agreement with the conclusion of Dyar (1990) that "Fe^{3+}/Σ Fe remains constant within analytical errors . . . as long as the oxide mineral phase does not change." Dudko et al. (1991) also observed a difference in oxidation between samples coexisting with garnet and those coexisting with magnetite. However, the results of Dudko et al. (1991), which were confirmed by 22 wet chemical analyses, do not agree with those of Dyar (1990) if her $^{[4]}Fe^{3+}$ peaks are interpreted to be Fe^{2+} artifacts.

In short, the questions raised by Rancourt et al. (1992) focus on a single issue: the presence and interpretation of an area of absorption in the spectra located around 0.25 mm/s. On the basis of their single-crystal Mössbauer spectra (which are unsuited to resolve such a small peak), they claimed that no real absorption occurs in that area, and that the feature fitted by Dyar (1990) and other previous workers (and subsequent workers, e.g., de Parseval et al., 1991) is an artifact of an Fe^{2+} peak. Their conclusion is inconsistent with a large body of work, only some of which is cited herein, which confirms the presence of

$^{[4]}Fe^{3+}$ in clay minerals and the effects of composition on its Mössbauer parameters. Furthermore, Mössbauer Fe^{3+} data of Dyar (1990) and of the past workers tabulated in Dyar (1987), dating back as far as Bancroft and Brown (1975), and the Ukrainian research (Dudko et al., 1991) all are in agreement with wet chemical data. If the interpretations of past workers are, as claimed by Rancourt et al. (1992), "artifact[s] of improper analysis and interpretation," then we have the larger problem on our hands of reconciling wet chemical results that indicate the presence of Fe^{3+} with the new interpretation of Mössbauer spectra that suggests that Fe^{3+} is not present. Acceptance of the model suggested by Rancourt et al. would lead to the conclusion that Mössbauer and wet chemical data are irreconcilable, which I believe to be untenable.

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