

# Mössbauer Spectroscopy of Minerals

## I. Inadequacy of Lorentzian-line Doublets in Fitting Spectra Arising from Quadrupole Splitting Distributions

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**Abstract.** We compare two different approaches to fitting the Fe-57 Mössbauer spectra of paramagnetic state minerals: the widespread practice of using Lorentzian line doublets with adjustable  $\Gamma$  widths and a new method (Rancourt and Ping, 1991) based on quadrupole splitting distributions (QSDs). We argue that there is no physical justification for the former and that the latter is a theoretically correct approach. With the same number of free parameters, the QSD method performs better. The Lorentzian doublet method 1) significantly overestimates the background, 2) puts overly large wings or tails on the main absorption peaks, and 3) gives unphysically large values of  $\Gamma$ . Whereas Lorentzian doublets are often arbitrarily (and incorrectly) assigned to model sites in the average unit cell, QSDs represent the most information that can be distilled from the spectra and are caused by the various local and long-range structural and chemical environments acting concomitantly.

**Key words:** Mössbauer spectroscopy – quadrupole splitting distributions – Lorentzian – Voigt – spectral analysis

### Introduction

In all types of resonance emission or resonance absorption spectroscopy (atomic, vibrational, nuclear, Mössbauer, etc.), the spectroscopist ideally uses the lineshape predicted by theory given the relevant physical processes. Weisskoff and Wigner (1930) showed that, in the most common circumstances involving a single (or many identical and non-interacting) quantum emitter(s) (or absorber(s)), quantum mechanics predicts an emission (or absorption) line that has the Lorentzian shape:

$$L(\nu_0, h, \Gamma; \nu) = \frac{h\Gamma^2/4}{(\nu_0 - \nu)^2 + \Gamma^2/4} \quad (1)$$

Here,  $h$  is the height (or depth),  $\nu_0$  is the resonance position and  $\Gamma$  is the full width at half maximum. They

showed that  $\Gamma$  is related to the discrete state's exponential lifetime  $\tau$  as:

$$\Gamma = \hbar/\tau \quad (2)$$

where  $\hbar$  is Planck's constant divided by  $2\pi$ .

In  $^{57}\text{Fe}$  Mössbauer spectroscopy, the 14.4 keV state has  $\tau = 141$  ns giving  $\Gamma = 4.66 \times 10^{-9}$  eV or 0.0970 mm/s. In an absorption experiment using a thin absorber and a single-line thin source, one has  $\Gamma = 2 \times 0.0970 = 0.194$  mm/s.  $\Gamma$  is not an adjustable parameter. It has a known fixed value. If broader lines are observed, then additional physical processes (thickness effects, dynamic effects, inhomogeneous broadening, etc.) are at work.

The spectroscopist should make every attempt to identify the relevant physical processes in order to impose the corresponding theoretical constraints. Instead, it has become widespread practice to use arbitrary numbers of Lorentzian components with adjustable  $\Gamma$  values.

In this paper, we compare the latter approach with a more physical method based on quadrupole splitting distributions in which all the parameters have direct meaning. We find that, for the same numbers of adjustable parameters, the physical method gives significantly lower and near-ideal chi squared values in fitting Mössbauer spectra typical of those obtained with  $^{41}\text{Fe}^{3+}$ -,  $^{61}\text{Fe}^{3+}$ - and  $^{61}\text{Fe}^{2+}$ -bearing silicates.

The present paper is part I of a three part study. The accompanying papers are referred to as II (Rancourt, 1994) and III (Rancourt et al., 1994a). In II we address the problem of resolving cis and trans octahedral sites and show that it is not possible to obtain quantitative cis and trans  $\text{Fe}^{2+}$  populations by Mössbauer spectroscopy. Instead, one obtains continuous  $\text{Fe}^{2+}$  quadrupole splitting distributions (QSDs) that are caused by local distortions and atomic disorder rather than by the ideal point symmetries of the relevant unit cell sites. In III we obtain the  $\text{Fe}^{2+}$  QSDs for a series of type 2:1 layer silicates and elucidate their origin.

## Choice of Samples

The  $^{57}\text{Fe}$  hyperfine parameters (center shift =  $\text{CS} = \delta$ ; quadrupole splitting =  $\text{QS} = \Delta$ ) in paramagnetic-state silicates are primarily determined by the valence state such that  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are easily resolved (Greenwood and Gibb, 1971). Typical values at room temperature (RT) are:  $\delta_{3+} \sim 0.2\text{--}0.4$  mm/s,  $\delta_{2+} \sim 1.0\text{--}1.2$  mm/s (all  $\delta$  values are with respect to metallic  $\alpha\text{-Fe}$  at RT),  $\Delta_{3+} \sim 0.4\text{--}1.5$  mm/s, and  $\Delta_{2+} \sim 1.5\text{--}3.0$  mm/s.

As a result of these values, the RT Mössbauer spectra of the great majority of silicates are very similar, with  $^{44}\text{Fe}^{3+}$  and  $^{61}\text{Fe}^{3+}$  being resolved in certain cases (Rancourt et al. 1992). For the present purpose we chose three Fe-rich trioctahedral micas with representative ranges of  $^{44}\text{Fe}^{3+}$ ,  $^{61}\text{Fe}^{3+}$  and  $^{61}\text{Fe}^{2+}$  populations:

- 1) Sample M-Bi is a low  $\text{Fe}^{3+}$ -content biotite (MOC 2661, Rancourt et al., 1993a) containing no tetrahedral  $\text{Fe}^{3+}$  (Rancourt et al., 1992).
- 2) Sample B-Bi is a relatively high  $\text{Fe}^{3+}$ -content biotite (S200, Bishop intrusive suite; Lalonde, 1989; Lalonde and Bernard, 1993) also containing no tetrahedral  $\text{Fe}^{3+}$  (Rancourt et al., 1994b).
- 3) Sample N-Ann is a natural annite that contains both tetrahedral and octahedral  $\text{Fe}^{3+}$  (M42126; Rancourt et al., 1992; Lalonde et al., 1994).

The RT Mössbauer spectra of these samples are typical of those observed for the great majority of micas, layer silicates, and  $^{44}\text{Fe}^{3+}$ ,  $^{61}\text{Fe}^{3+}$  and  $^{61}\text{Fe}^{2+}$ -bearing silicates in general (e.g., Dyar, 1987; Ericsson et al., 1977; Hawthorne, 1988; Coey, 1984; Rossman, 1983). Our purpose is not to reanalyse all previously published data but simply to illustrate the advantages of a different and more founded analysis by a careful examination of representative spectra.

## Experimental Methods

Transmission Fe-57 Mössbauer spectra were collected at RT ( $=22^\circ\text{C}$ ) using a  $\sim 10$  mCi Co-57 rhodium-matrix single-line thin source on a velocity range of  $\pm 4$  mm/s with a constant acceleration drive. Data was acquired on 1024 channels and folded to give a flat background (BG) and a zero velocity position corresponding to the CS of metallic  $\alpha\text{-Fe}$  at RT in the 512-channel calibrated spectrum.

Absorbers were prepared as follows. The B-Bi material was separated from the rock and divided into different size fractions up to the maximum size of  $\sim 2$  mm. The 100–300  $\mu\text{m}$  fraction was used to make a random-orientation (i.e. non-textured) absorber using a new method in which the granules are suspended in a viscous medium in a volume large enough to minimize inter-granule and granule-container contacts. In this way, the usual problems related to the packing of solid irregularly shaped materials in a gravitational field are avoided.

We tried many jels (vacuum greases, silicone bases, etc.) but found petroleum jelly to be the best. This organic jel is sufficiently viscous and has a relatively low non-resonant cross-section at 14.4 keV. An amount of sample corresponding to the ideal (or near-ideal) absorber thickness (Rancourt et al., 1993b) was mixed with petroleum jelly in a 5 mm thick and 0.5 inch inside diameter holder having clear tape windows. Enough petroleum jelly was used to fill the sample space volume.

We refer to such an absorber as a “thick viscous mount” (TVM). The method was thoroughly tested with known mica samples, using various sample amounts, using different size-fractions, and by making measurements using various orientations of the TVM. No texture effects are seen within experimental accuracy.

In using such a TVM method that allows random-orientation absorbers of relatively large flakes to be prepared, the reader should be aware that even with ideal randomness of orientation large euhedral flakes can lead to polarization effects in addition to the usual thickness effects. Each flake or granule should be thin (in the Mössbauer sense, Rancourt et al., 1993b) in all orientations to avoid this problem.

The absorbers for M-Bi and N-Ann were prepared in the same way except that these samples were originally large (5–50 mm) euhedral single crystal wafers. Selected wafers were crushed under acetone using mortar and pestle and then size separated. The 125–250  $\mu\text{m}$  fraction was used for the M-Bi absorber and the 0–180  $\mu\text{m}$  fraction was used for N-Ann.

Finally, since the present work makes extensive use of the  $\chi^2$  statistical criterion, it was important to verify that the noise in our folded spectra was indeed Gaussian with the predicted  $\sigma = \sqrt{N}$ . This was found to be the case, implying that the known properties of  $\chi^2$  can be used rigorously. In particular, models that give  $\chi^2$  values outside the ideal predicted  $\chi^2$ -distribution can be ruled out (e.g., Rancourt, 1993).

## Fitting Methods, Lineshapes and Analysis Philosophy

A Lorentzian doublet consists of two Lorentzian lines of equal depth, of equal width, and separated by the quadrupole splitting  $\Delta$ :

$$D(\delta, \Delta, h, \Gamma; \nu) = BG - L(\delta - \Delta/2, h, \Gamma; \nu) - L(\delta + \Delta/2, h, \Gamma; \nu) \quad (3)$$

where  $\delta$ ,  $\Delta$ ,  $h$ ,  $\Gamma$  and  $BG$  are adjustable fitting parameters. As a result, using  $n$  Lorentzian doublets requires  $1 + 4n$  fitting parameters unless some are frozen at specified values. Such a fit is denoted  $nL$ . For example, a fit using three Lorentzian doublets is a “ $3L$  fit”.

The Voigt-based QSD method of Rancourt and Ping used here is described in detail elsewhere (Rancourt and Ping, 1991; Ping et al., 1991; Rancourt et al., 1994c). The method uses a certain number  $m$  of generalized sites that each have their own continuous QSD. Each normalized site-specific QSD is in turn taken to be made up of a certain number ( $n_1$  for site-1, etc.) of Gaussian components. The corresponding fitting lineshape is neither Gaussian nor Lorentzian but is a sum of Voigt lines. The corresponding fit is denoted  $n_1 - n_2 - \dots - n_m V$ .

Since in a QSD analysis  $\Gamma$  has a precise physical meaning, it is taken to be the same for all sites (and each component in each distribution) and is often fixed at the natural width value. In the absence of thickness effects, vibrational broadening, cosine smearing, etc.,  $\Gamma$  should always be fixed at the natural value. This is also appropriate in fitting non-thickness corrected raw spectra if the distribution broadening is large enough and the absorber thickness is not too great (Rancourt et al., 1993b). In the latter case with raw spectra, one may also treat  $\Gamma$  as an adjustable parameter as an approximate way to take thickness and/or instrumental broad-

ening into account, however, the validity of this procedure has not been studied or demonstrated. It is best to perform thickness corrections and freeze  $\Gamma$  at its natural value in fitting the thickness corrected spectra, as we have done in III. In the present paper, we occasionally allow the QSD analysis  $\Gamma$  to be a free parameter in fitting raw spectra, as a convenient way to vary the number of free parameters in comparing models (QSD lineshapes versus Lorentzian doublets) that are required to have the same numbers of free parameters.

Also, each site has distribution components whose center shifts are taken to be correlated to their QS values as  $\delta = \delta_0 + \delta_1 \Delta$ . Therefore, the QSD analysis requires at most  $2 + 2m + 3 \sum_{i=1}^m n_i$  fitting parameters: two spectrum-

specific parameters ( $BG, \Gamma$ ), two site-specific parameters ( $\delta_0, \delta_1$ ), and three component-specific parameters ( $h, \Delta, \sigma_A$ ).

Assuming  $\delta_1 \equiv 0$  for a given site is equivalent to assuming that all elemental components in the QSD pattern of that site have the same  $CS = \delta_0$ . This is often approximately true since local structural and chemical variations have a much smaller effect on  $\delta$  than on  $\Delta$  (Greenwood and Gibb, 1971).

In using Lorentzian doublets or QSD analysis, it is important to keep in mind that both suffer from a fundamental limitation of non-linear least squares minimization: the solution is often not a single point in parameter space but rather an entire region. That is,  $\chi^2$  minimiza-

tion does not usually produce unique solutions. One must admit the possibility of parameter trade-offs. This problem has been discussed in detail for annite (Rancourt et al., 1994c). It is less severe with QSD models because distribution component trade-offs give the same QSDs and are therefore of no concern. In addition, our QSD method (Rancourt and Ping, 1991) imposes as many practical a priori theoretical constraints as possible in order to minimize other trade-off problems.

For the present paper, we do not overly concern ourselves with the trade-off problem since we only ensure that we are in the lowest valley of the  $\chi^2$  surface for the particular model. We do not describe the region in parameter space that contains all points corresponding to equally low (in the statistical sense) values of  $\chi^2$ . The aim is to compare different fitting models having the same numbers of adjustable parameters, not to obtain full Mössbauer characterizations.

Also, it is appropriate to discuss how the choice of a particular model (number of Lorentzian doublets or of distribution components, etc.) is made. With simple stoichiometric compounds it is appropriate to assign one elemental spectral component (i.e. doublet) for each crystallographic site occupied by Fe. In materials with atomic disorder (e.g. solid solutions), however, it is not appropriate to make such an assignment because local distortions and local compositions can have a larger effect on the hyperfine parameters than the position (or site) in the average unit cell.

This is the case in most paramagnetic minerals where,

**Table 1.** Fit parameters for different models

Sample	Fit	Site	$\delta_0$ (or $\delta$ ) (mm/s)	$\delta_1$	$\Delta$ (mm/s)	$\sigma_A$ (mm/s)	$\Gamma$ (mm/s)	Area (%)	BG MC/ch	No. par.	$\chi^2_{red}$
M-Bi	1-1-1V	[3+]	0.413	0.0 <sup>†</sup>	0.848	0.474	0.2 <sup>†</sup>	10.60	0.54157	13	1.50
		[2+]-1	1.117	0.0 <sup>†</sup>	2.536	0.197	0.2 <sup>†</sup>	45.92			
		[2+]-2	1.120	0.0 <sup>†</sup>	2.163	0.359	0.2 <sup>†</sup>	43.48			
M-Bi	3L	[3+]	0.513	-	0.626	-	0.402	8.62	0.54253	13	4.37
		[2+]-1	1.118	-	2.592	-	0.277	36.75			
		[2+]-2	1.108	-	2.231	-	0.408	54.63			
B-Bi	1-1-1-1V	[3+]-1	0.358	0.0 <sup>†</sup>	0.822	0.261	0.2 <sup>†</sup>	16.41	0.89743	17	1.62
		[3+]-2	0.427	0.0 <sup>†</sup>	1.463	0.575	0.2 <sup>†</sup>	9.03			
		[2+]-1	1.113	0.0 <sup>†</sup>	2.629	0.156	0.2 <sup>†</sup>	40.67			
		[2+]-2	1.156	0.0 <sup>†</sup>	2.181	0.437	0.2 <sup>†</sup>	33.89			
B-Bi	4L	[3+]-1	0.355	-	0.823	-	0.414	18.94	0.89876	17	3.63
		[3+]-2	0.393	-	1.367	-	0.268	3.23			
		[2+]-1	1.120	-	2.628	-	0.293	39.63			
		[2+]-2	1.146	-	2.145	-	0.496	38.20			
N-Ann	1-1-3V	<3+>	0.194	0.0 <sup>†</sup>	0.448	0.093	0.261	7.10	0.39709	21	1.20
		[3+]	0.526	0.0 <sup>†</sup>	0.725	0.370	0.261	10.42			
		[2+]-1	1.224	-0.0402	2.605	0.073	0.261	28.95			
		[2+]-2	1.224	-0.0402	2.309	0.262	0.261	42.10			
		[2+]-3	1.224	-0.0402	1.793	0.614	0.261	11.43			
N-Ann	5L	<3+>	0.154	-	0.549	-	0.250	6.07	0.39760	21	1.90
		[3+]	0.550	-	0.617	-	0.583	12.72			
		[2+]-1	1.120	-	2.632	-	0.269	31.16			
		[2+]-2	1.141	-	2.339	-	0.298	25.43			
		[2+]-3	1.131	-	2.030	-	0.438	24.62			

<sup>†</sup> These values frozen during fit

once the ionic state ( $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ) is resolved, each such state gives a continuous QSD arising from all effects. The latter QSDs are the experimental results that need to be interpreted in terms of all possible causes acting concomitantly. For each ionic species, the Mössbauer measurement gives a QSD that contains much information but of a more complex nature than is often assumed. This is the philosophy in using QSD analysis. The next challenge is to discover the precise causes of QSDs by systematic experimental and theoretical studies so that the true information content of spectra can be exploited. The present series of papers represents a first step in this direction.

Finally, it is possible that some minerals with chemical and/or structural disorder will not show resolvable distribution broadening. This may occur with certain crystal structures giving Fe sites with local distortions that are not sensitive to the particular disorder. To demonstrate the absence of distribution broadening in such cases, one must show that natural  $\Gamma$  width Lorentzian doublets assigned to the particular Fe-bearing sites give statistically ideal fits to high quality thickness corrected spectra. We have not encountered any such cases. That is, we have always found in QSD analysis that  $\sigma > 0$  in materials with known chemical disorder.

## Results and Discussion

Each sample (M-Bi, B-Bi and N-Ann) was fitted using Voigt-based QSD analysis and a Lorentzian line doublet model. Both models for a given sample were chosen to have the same number of free parameters; between 13 and 21 depending on the complexity of the spectrum. We have analysed many spectra ( $\sim 100$  samples) in this way. The chosen examples are representative of the general behaviour.

Sample M-Bi has the simplest RT Mössbauer spectrum which, in the QSD analysis, is modelled by an  $^{61}\text{Fe}^{3+}$  QSD (denoted [3+] in Table 1) having a single Gaussian component and two  $^{61}\text{Fe}^{2+}$  QSDs (denoted [2+]–1 and [2+]–2 in Table 1) each having one Gaussian component. Here, we take  $\delta_1 = 0$  for all sites and  $\Gamma \equiv 0.2$  mm/s for all lines such that the corresponding 1–1–1V fit has 13 free parameters. The Lorentzian doublet fit is a 3L fit and also has 13 free parameters.

The resulting fit parameters for both models are given in Table 1. These 3L and 1–1–1V fits for sample M-Bi are compared in Fig. 1. The main differences between the two fits are as follows.

Firstly, it is clear from the residuals (Fig. 1) and the values of reduced  $\chi^2$  (1.5 versus 4.4; Table 1) that the 1–1–1V fit is far superior to the 3L fit. As in most cases, the Lorentzian doublet fit significantly overestimates the BG, puts exaggerated wings or tails on the main absorption peaks, and has unphysically large values of  $\Gamma$  often beyond twice the natural width. As is also usually the case, the partitionment of spectral area between the sites (here [3+], [2+]–2, and [2+]–1) is significantly different in the two models (Table 1).

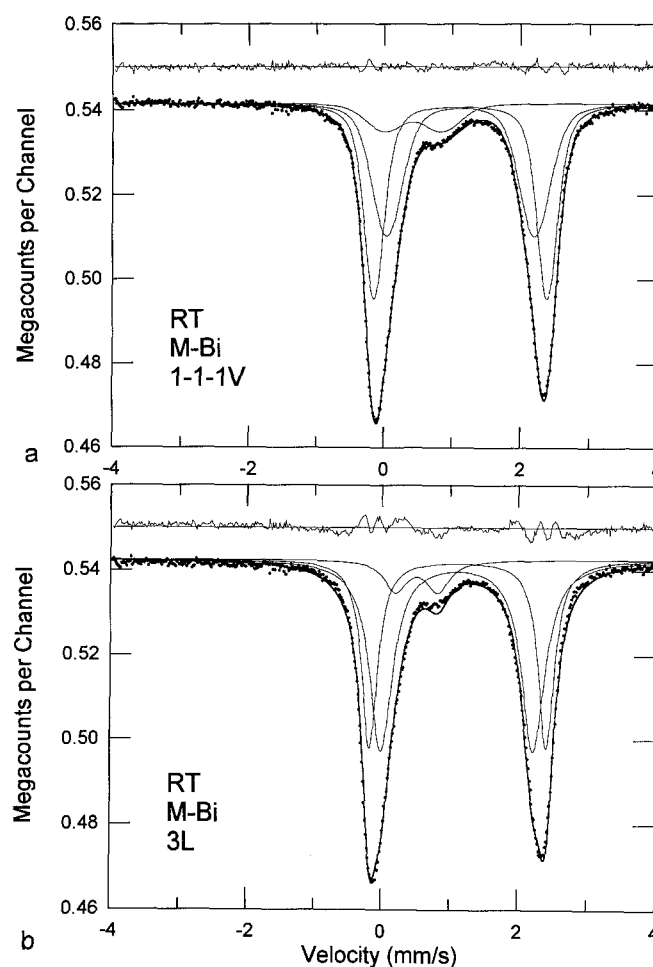


Fig. 1. **a** Voigt-based QSD fit (1–1–1V fit, Table 1) of the RT random orientation absorber Mössbauer spectrum of biotite sample M-Bi. **b** Lorentzian doublet fit (3L fit, Table 1) of the same spectrum

Finally, relatively small differences in the usual hyperfine parameters ( $\delta$  and  $A$ ) also occur. For the M-Bi sample, the largest change is in the  $\text{Fe}^{3+}$  QS that goes from 0.85 to 0.63 mm/s in going from the 1–1–1V to the 3L analysis. Such smaller effects can only be adequately discussed, however, in the context of a full parameter trade-off study for both models which is beyond the scope of the present paper.

Next, consider a biotite that has a large enough  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio for two subspectral components to be required for its  $\text{Fe}^{3+}$  absorption. Sample B-Bi is such a biotite whose RT spectrum was fitted using 1–1–1–1V and 4L models. These fits are shown in Fig. 2 and the corresponding parameters are given in Table 1. The Voigt-based QSD analysis again used  $\delta_1 \equiv 0$  for all sites and  $\Gamma \equiv 0.2$  mm/s for all lines. Both models required 17 free parameters.

The Voigt-based QSD fit is again far superior to the Lorentzian doublet fit ( $\chi_{\text{red}}^2 = 1.6$  versus 3.6) and the same major differences noted above occur. Here, one of the  $\text{Fe}^{2+}$  line widths in the 4L fit is as large as 0.50 mm/s. Also, the  $\text{Fe}^{3+}/\text{Fe}$  spectral area ratio decreases by 13% on going to the 4L fit.

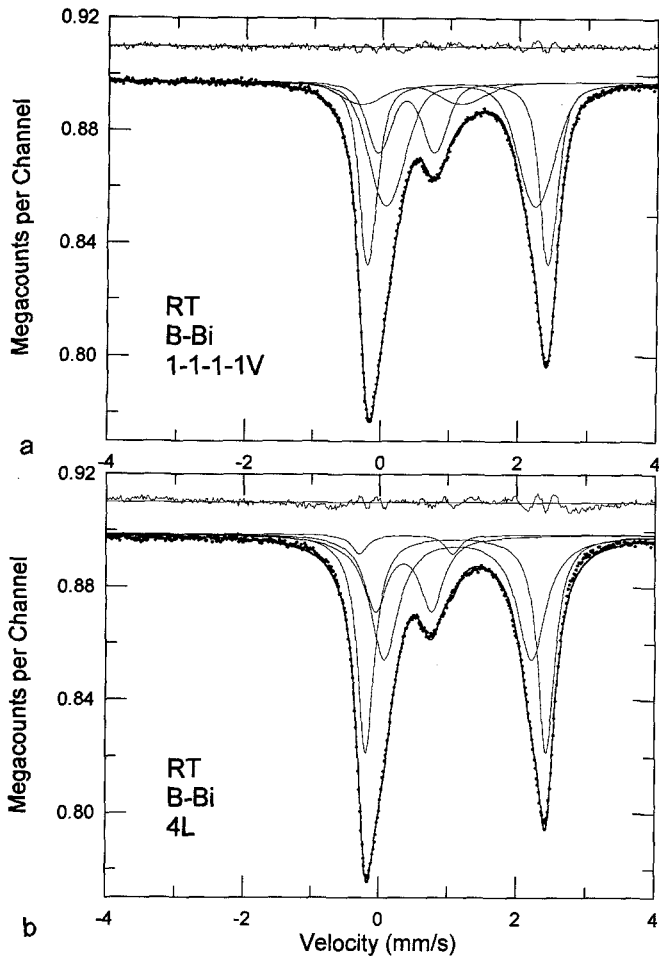


Fig. 2. a Voigt-based QSD fit (1-1-1-1V fit, Table 1) of the RT random orientation absorber Mössbauer spectrum of biotite sample B-Bi. b Lorentzian doublet fit (4L fit, Table 1) of the same spectrum

Finally, consider the RT Mössbauer spectrum of N-Ann. This is the most Fe-rich natural annite ever studied by Mössbauer spectroscopy (see Lalonde et al. (1994) for an in-depth study of Saint-Hilaire Fe-rich micas). As in synthetic annite (Rancourt et al. 1994c), its complicated spectrum has spectral components arising from both tetrahedral  $\text{Fe}^{3+}$  (denoted  $\langle 3+ \rangle$  in Table 1) and octahedral  $\text{Fe}^{3+}$  and an  $\text{Fe}^{2+}$  QSD requiring three Gaussian components.

The 1-1-3V fit to the RT spectrum of N-Ann had  $\delta_1 \equiv 0$  for both  $\text{Fe}^{3+}$  sites and a free  $\delta_1$  for the  $\text{Fe}^{2+}$  site.  $\Gamma$  was the same for all lines but was left as an adjustable parameter in this case. This is an approximate way of taking sample thickness broadening into account. As a result, the 1-1-3V fit had the same number of free parameters (21) as the 5L fit to which it is compared.

The fits are shown in Fig. 3 and the parameters are given in Table 1. Whereas the 1-1-3V fit is near-ideal ( $\chi_{\text{red}}^2 = 1.2$ ), the 5L fit has a reduced  $\chi^2$  value that is nearly twice the ideal value. The same major differences noted above for samples M-Bi and B-Bi again occur. These are general characteristics of the difference between Voigt-based QSD fits and Lorentzian-based doublet fits.

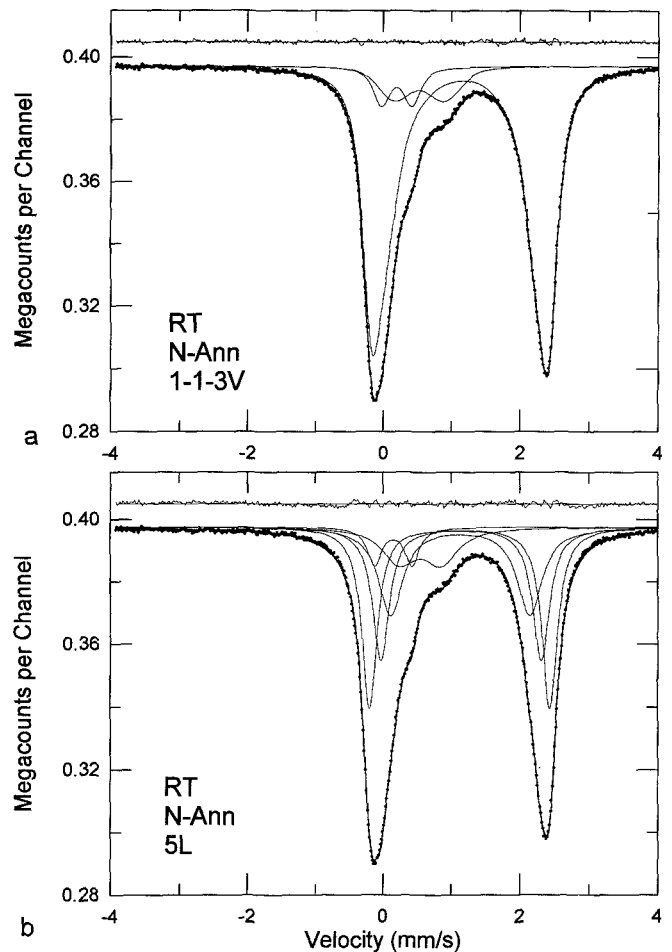


Fig. 3. a Voigt-based QSD fit (1-1-3V fit, Table 1) of the RT random orientation absorber Mössbauer spectrum of annite sample N-Ann. b Lorentzian doublet fit (5L fit, Table 1) of the same spectrum

Lorentzian-based fits of spectra that are distribution broadened always: 1) overestimate the BG, 2) put overly large wings or tails on the main absorption peaks, and 3) give unphysically large values of  $\Gamma$ .

These differences are of course not seen with spectra having poor statistics but any model will work with noisy enough spectra. Also, the differences can be removed by increasing the number of doublets in Lorentzian-based analyses because one thus moves towards a QSD situation but with serious shortcomings. Firstly, there is a strong temptation to ascribe meaning to doublets added in this way. For example, in Fig. 3b three Lorentzian doublets of comparable areas are used to model the  $\text{Fe}^{2+}$  contribution. There is no obvious structural or ideal site interpretation for this situation however one might be tempted to invent one, given the various intrinsic defects that occur in annite... Secondly, as Lorentzian doublets are added, the mathematical fitting problem itself becomes highly unstable with unchecked trade-offs between the parameters that describe the overlapping doublets.

QSD analysis is designed to avoid such stability problems and to extract unique QSDs. Such distributions

represent as much information as can be distilled from the Mössbauer spectra. If it's not in the QSD, it's not there. More precisely, it may or may not be there but you can't tell from the Mössbauer spectrum.

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