Mössbauer Spectroscopy of Minerals

II. Problem of Resolving cis and trans Octahedral Fe$^{2+}$ Sites

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Abstract. We demonstrate by trade-off and error analysis of representative spectra that paramagnetic state Mössbauer spectroscopy of 2:1 layer silicates cannot resolve the octahedral Fe$^{2+}$ cis (M2) and trans (M1) sites. We show that it is impossible to extract cis/trans population ratios from two Fe$^{2+}$ doublet analyses of the spectra and that, instead, one has a single continuous Fe$^{2+}$ quadrupole splitting distribution (QSD) that cannot reliably or uniquely be partitioned into its constituents. Whereas extracted cis/trans ratios do not contribute to evaluating site occupancies, the QSDs themselves in principle contain much local structural and chemical information that should be the focus of future work.

Key words: Mössbauer – spectral analysis – cis-site – trans-site – layer silicate – mica

Introduction

It has become widespread practice to fit the majority Fe$^{2+}$ contribution in the room temperature (RT) Mössbauer spectra of 2:1 layer silicates with two Lorentzian line doublets and to ascribe these doublets to the cis and trans octahedral sites (e.g., Dyar 1987). Many authors and one reviewer (Dyar 1987) go so far as to interpret the spectral areas of the doublets as evidence for cation ordering which, in the micas, is not seen by other methods (Bailey 1984a, b; Manceau et al. 1990).

We agree with the idea of trying to relate different parts of the Fe$^{2+}$ contribution to different local environments. For example, local environments corresponding to higher quadrupole splittings (QSs) are seen to oxidize (Fe$^{2+}$ + OH$^-$ → Fe$^{3+}$ + O$^{2-}$ + H$^+$) first on heating Fe-bearing micas in air (Ferrow 1987; Rancourt et al. 1993; Christie et al. 1993). Also, different parts of the Fe$^{2+}$ contribution are seen to have different electric field gradient orientations in oriented single crystal Mössbauer measurements (Hargraves et al. 1990). One must admit, however, that various local structural and local chemical features (e.g., displaced coordinating anions; substitution of OH$^-$ by O$^{2-}$ or F$^-$ or Cl$^-$; particular arrangement of Al and Si in neighboring tetrahedral sites; size, charge and identity of neighboring octahedral cations; etc.) may affect the Fe$^{2+}$ Mössbauer parameters more than the cis or trans arrangements of the OH groups in the ideal structure.

In any case, we show here that irrespective of the true cause(s) of the Fe$^{2+}$ quadrupole splitting distribution (QSD) it is impossible, for unavoidable mathematical reasons, to extract reliable cis/trans populations from two doublet analyses of RT (or liquid nitrogen temperature (LNT)) Mössbauer spectra. Instead, one has a single well defined Fe$^{2+}$ QSD that cannot be reliably or uniquely partitioned into its constituents.

We argue that the correct question concerning the Fe$^{2+}$ spectral contribution is not “What are the cis and trans populations?” but rather “What causes the observed QSD?” We start to answer the latter question in III (Rancourt et al. 1994a) whereas accompanying paper I (Rancourt 1994) sets the ground work by demonstrating the inadequacy of Lorentzian doublets in attempting to answer any such question.

Choice of Samples and Experimental Methods

The Fe$^{2+}$ cis/trans trade-off problem described in the present paper is present in the paramagnetic-state spectra (at both RT and LNT) of all the Fe$^{2+}$-bearing layer silicates we have studied, except in rare cases where only one Fe$^{2+}$ contribution or sub-spectrum is required. This trade-off is a general problem that one does not notice unless one specifically looks for it. We illustrate it by a detailed analysis of the spectra of two samples:

1) Sample M-Bi (MOC 2661, Rancourt et al. 1993), also used in 1, is a low Fe$^{3+}$/Fe ratio biotite containing no tetrahedral Fe. (Rancourt et al. 1992).

2) Sample S-Ann is a nickel-nickel oxide buffered synthetic annite that has been described elsewhere (Rancourt et al. 1994b).

Both samples have been extensively characterized (see above references).

Sample M-Bi was selected because its spectrum is relatively simple with regards to Fe$^{3+}$. Our focus is Fe$^{2+}$ trade-offs and
the low Fe\(^{3+}\) content of M—Bi minimizes complicating Fe\(^{2+}/Fe^{3+}\) trade-offs that are amplified by large Fe\(^{3+}\) contributions.

Sample S—Ann was selected because, as first pointed out by Häggström et al. (1969) in the context of resolving cis and trans sites, end-member annite has all possible Fe\(^{2+}\) sites fully occupied. In other words, in examining whether the large-QS Fe\(^{2+}\) contribution can be attributed to a larger spectral fraction, one should not use a sample in which it is possible that only the large-QS sites (or only the small-QS sites) are occupied. Using a synthetic annite ensures that both cis and trans sites are populated and enables one to test whether supposed cis and trans contributions will be in the ideal population ratio of 2:1.

Experimental conditions related to the spectrometer are given in I. The RT spectrum for sample M—Bi is the same as that used in accompanying paper I. The RT and LNT spectra for sample S—Ann are the same as those used elsewhere (Rancourt et al. 1994b). The thick viscous mount method (paper I) did not need to be used with the S—Ann material (Rancourt et al. 1994b). All absorbers were random orientation absorbers such that symmetric elemental doublets could be imposed in the spectral analysis.

Given the results of I (Rancourt 1994), Lorentzian-line doublets were avoided. The Voigt-based QSD method of Rancourt and Ping (1991) was used with each generalized site having its own QSD consisting of only one Gaussian component, except when the full Fe\(^{2+}\) QSD was required. In the latter case, two or three Gaussian components needed to be used to model the complete QSD of the generalized Fe\(^{2+}\) site.

Results and Discussion

Biotite Sample M—Bi

The first thing that is apparent in analysing the RT spectrum of M—Bi is that the Fe\(^{2+}\) contribution is not adequately modeled by a QSD consisting of a single Gaussian component or by any type of doublet composed of two symmetric lines such as Voights, Gaussians or Lorentzians. This is because the measured Fe\(^{2+}\) absorption lines are themselves asymmetric as is particularly apparent in the high energy (or high velocity) Fe\(^{2+}\) line at ~2.3 mm/s (Fig. 1).

The failure of single component Fe\(^{2+}\) QSD models is illustrated in Fig. 1. The two fits denoted 1—1a and 1—1b in Table 1 are shown. Both models have single Gaussian component QSDs for Fe\(^{2+}\) and Fe\(^{3+}\). Model 1—1a imposes zero \(\delta - \Delta\) coupling (\(\delta_1 = 0\) for both species) and has 10 adjustable parameters whereas model 1—1b allows linear \(\delta - \Delta\) coupling and has 12 adjustable parameters. The corresponding values of reduced chi squared are 9.0 and 6.2, respectively.

By contrast, models that acknowledge the asymmetries of the low and high velocity Fe\(^{2+}\) absorption lines by using two Fe\(^{2+}\) components (or subspectra or doublets) achieve \(\chi^2_{red} \sim 2\) with 12-14 free parameters (see below). This situation holds for all Fe\(^{2+}\)-bearing micas: One Fe\(^{2+}\) doublet does not work but two often does. Most authors then attempt to ascribe meaning to the Fe\(^{2+}\) doublets obtained in their particular analyses. We now show that such doublets merely produce the required line asymmetries and cannot be ascribed to particular sites (or families or groups of sites) because they are not resolved as unique contributions. That is, many significantly different possible pairs of Fe\(^{2+}\) doublets produce the same lineshape asymmetries and give statistically equivalent fits.

Consider 1—1—1 fits having three assumed generalized sites (one Fe\(^{3+}\) and two Fe\(^{2+}\)) each with a single assumed Gaussian component. We impose zero \(\delta - \Delta\) couplings for simplicity and to avoid excessive Fe\(^{2+}/Fe^{3+}\) trade-offs. Precisely such a fit of the RT spectrum of M—Bi was described in paper I where it was denoted 1—1—1 V. It used a fixed value of \(\Gamma = 0.2\) mm/s, had 13 free parameters and gave \(\chi^2_{red} = 1.50\). Allowing \(\Gamma\) to be adjustable results in 14 free parameters. The corresponding fit is referred to as 1—1—1 h in Table 1 and has \(\chi^2_{red} = 1.47\). This fit (and all fits given in Table 1) converged onto a true minimum of the \(\chi^2\) surface and is shown in Fig. 2a. What now does this fit mean?

Since the work of Häggström et al. (1969), the great majority of authors have ascribed high-QS Fe\(^{2+}\) doublets to cis octahedral sites and low-QS Fe\(^{2+}\) doublets to trans octahedral sites. We stress that the latter assignment incorrectly assumes that the main structural/chemical feature affecting the QS of octahedral Fe\(^{2+}\) is the cis or trans arrangement of the unit cell site. Nonetheless, for the sake of comparison and clarity we denote our