Comparison between the quasi-continuous quadrupole splitting distributions (QSD) for Mössbauer spectra of glauconites and the QSD-profiles simulated on the basis of crystal-chemical model

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Abstract. Structural peculiarities of Fe³⁺-rich dioctahedral mica, glauconite, such as a wide variety of isomorphous octahedral cation substitutions (Al, Fe³⁺, Fe²⁺, Mg) and the occurrence of these cations in cis-sites only, make it possible to consider glauconites as model locally inhomogeneous objects. To fit room and liquid-nitrogen Mössbauer spectra of two glauconite samples of close compositions with unusually low Fe³⁺/Fe²⁺ ratios, reconstruction of quadrupole splitting distributions (QSD) in terms of quasi-continuous model-independent approach was applied. Interpretation of the obtained QSD's became possible owing to application of a crystal-chemical model (CCM) taking account of the effects of the local structural and chemical heterogeneity of layer silicates. The main parameters of the CCM are individual quadrupole splittings, Δᵢ, for Fe³⁺ and Fe²⁺ in different local cationic arrangements (LCAs) having the occurrence probabilities, wᵢ, provided by two-dimensional simulation of the cation distribution (CD). The agreement between CD reconstructions, the QSD's profiles simulated on the basis of the CCM parameters and the QSD's provided, first, the corroborations of the Δᵢ values for Fe³⁺; second, the refinement of the Δᵢ values for Fe²⁺; and third, revealing the difference in the octahedral cation distributions for the studied glauconites.

1. Introduction
Glauconite belongs to Fe³⁺-rich dioctahedral micas. Distribution of isomorphous octahedral cations (Fe³⁺, Fe²⁺, Al, Mg) is of great importance in studying diagenetical transformation and in geochronological dating. According to X-ray and oblique-texture electron diffractions, and EXAFS spectroscopy [1 and references therein], of the available structurally independent octahedral sites (two cis- and one trans-) only the cis-sites are occupied by cations. Taking account of Fe cis-occurrence in the local cationic arrangement (LCA) consisting of three nearest cations, also in cis-positions, broadened Mössbauer spectra of glauconites display an immediate effect of the LCAs around Fe on the electric field gradient.
The crystal-chemical model (CCM) for interpreting the traditional Lorentzian fittings of Mössbauer spectra of 2:1 dioctahedral trans-vacant micas has been developed in [2 and references therein]. The main parameters of the CCM are individual quadrupole splittings, \( \Delta_i \), for Fe\(^{3+}\) and Fe\(^{2+}\) in the different LCAs with their occurrence probabilities, \( w_i \), provided by two-dimensional simulation of the octahedral cation distribution [3]. The \( \Delta_i^{\text{pred}} \) values for Fe\(^{3+}\) in the range of 0.0 – 1.40 mm/s are obtained from the empirical equation [4]. The assignment of the tentative \( \Delta_i^{\text{tent}} \) values for Fe\(^{2+}\) in the range of 1.20 – 2.96 mm/s to specific LCAs results from the correlation between the octahedral cation composition and the maximum quadrupole splitting Fe\(^{2+}\) extracted from Mössbauer spectra for a representative mineral collection [5].

The aim of the work is to apply quasi-continuous model-independent quadrupole splitting distribution analysis [6] for Mössbauer spectra of two glauconites, BSH and KUL, and to interpret the obtained QSD\(^{\text{exp}}\)s using the crystal-chemical model.

2. Samples and experimental results

Two samples of glauconites, BSH and KUL (mineralogical description is in [7]) with the crystal-chemical formulae K\(_{0.74}\)Ca\(_{0.02}\)Mg\(_{0.04}\)[Si\(_{3.71}\)Al\(_{0.29}\)](Al\(_{1.06}\)Fe\(^{3+}\)\(_{0.36}\)Fe\(^{2+}\)\(_{0.25}\)Mg\(_{0.35}\))O\(_{10}\)(OH)\(_2\) and K\(_{0.78}\)Ca\(_{0.01}\)Mg\(_{0.04}\)[Si\(_{3.71}\)Al\(_{0.29}\)](Al\(_{0.99}\)Fe\(^{3+}\)\(_{0.41}\)Fe\(^{2+}\)\(_{0.27}\)Mg\(_{0.33}\))O\(_{10}\)(OH)\(_2\), respectively, were investigated.

2.1. IR spectroscopy

The OH-stretching regions of the IR spectra recorded on a Nicolet ESP-260 FTIR spectrometer were decomposed using the Galactic PeakSolve\(^{\text{TM}}\) program. The assignment of the individual OH-stretching bands corresponding to specific types of OH-bonded cation pairs follows the band attributions suggested in [8]. The octahedral cation compositions of the samples calculated using relative integrated intensities of individual OH bands are in good agreement with crystal-chemical formulae.

2.2. Mössbauer spectroscopy

Room (figure 1) and liquid-nitrogen (RT and NT, respectively) spectra were measured on a constant acceleration spectrometer using a Co\(^{57}\)(Rh) source (source half-width \( \Gamma_s = 0.105 \text{ mm/s} \)) and calibrated with reference to \( \alpha\)-Fe. Orientation effects were eliminated preparing the absorbers in a hollow cone form with 55º half-cone angle. The absorber thickness was less than 5 mg Fe/cm\(^2\).

2.2.1. Quasi-continuous model-independent QSD analysis

The QSD\(^{\text{exp}}\)s, which were obtained with the DISTRI code from the software MSTools [6], are shown for Fe\(^{2+}\) in figure 2 (solid circles). Because the source line width \( \Gamma_s = 0.105 \text{ mm/s} \) is close to the natural line width \( \Gamma_i = 0.097 \text{ mm/s} \), a Lorentzian line shape for the resonance line has been used in the QSD reconstruction. The linear correlation coefficients for the main Fe\(^{3+}\) and Fe\(^{2+}\) contributions to the QSD\(^{\text{exp}}\)s correspond to the narrow variation ranges for isomer shifts: \( \Delta \delta_{\text{main}}(\text{Fe}^{3+}) \leq 0.03 \text{ mm/s} \) and \( \Delta \delta_{\text{main}}(\text{Fe}^{2+}) \leq 0.05 \text{ mm/s} \).

A comparative analysis of the RT and NT data made it possible to choose the \( \Delta \) range for the simulation of the RT QSD\(^{\text{sim}}\) profiles, and to identify the minor unsimulable \( P(\Delta) \) values at \( \sim 1.6 \text{ mm/s} \).
for Fe$^{3+}$ QSD as the effect of the boundary octahedra sharing only two edges with the nearest two octahedra [9] and at ~1.0 – 1.2 mm/s for Fe$^{2+}$ QSD as the presence of some Fe-sulphate [10].

Figure 2. Comparison between experimental Fe$^{2+}$ QSD$^{\text{exp}}$s (solid circles) and Fe$^{3+}$ QSD$^{\text{sim}}$ profiles (solid envelope) simulated using the refined $\Delta_i^{\text{ref}}$ values and the occurrence probabilities, $w_i$, for the LCAs corresponding to the “pref”- and “nonpref”-models used in CD reconstruction.

3. Comparison between QSD$^{\text{exp}}$s and QSD$^{\text{sim}}$ profiles

3.1. Two-dimensional CD simulation

The CD simulation uses the integrated optical densities of individual bands, $w_{ik}$, where i and k are cations (Al, Fe$^{3+}$, Fe$^{2+}$, Mg) bound to the OH groups, as initial parameters. Such a technique yields a solution that satisfies the two spectroscopic methods. Because the $w_{ik}$ values are proportional to the sum of occurrence probabilities, $w_{ik}$ and $w_{ki}$, any cation may equally well occupy the M2 and M2′ cis-sites or with variable preference to one of these sites. This feature, combined with the set of optional limitations along the directions running at ±120° or ±60° with respect to the OH-bonded cationic pair (b-direction), allows analyzing a wide variety of CD reconstructions in terms of the obtained IR data for a given sample.

3.2. CD models satisfying QSD$^{\text{exp}}$ for glauconites BSH and KUL

Using successive approximations during CD simulation, both for glauconites BSH and KUL, the preset individual occurrence probabilities, $w_i$, for Fe$^{3+}$ and Fe$^{2+}$ in different LCAs, as well as the $\Delta_i^{\text{tent}}$ values, were gradually changed so as to co-ordinate the CD reconstructions, the simulated QSD$^{\text{sim}}$ profiles and the experimental QSD$^{\text{exp}}$. Table 1 shows $\Delta_i^{\text{pred}}$ for Fe$^{3+}$, the refined $\Delta_i^{\text{ref}}$ for Fe$^{2+}$ and the sets of $w_i$ values for Fe$^{3+}$ and Fe$^{2+}$ in specific LCAs corresponding to the preferable Fe$^{2+}$,Mg-occurrence (“pref”-model) in one of cis-sites (columns 1) and to equally probable occupancy (“nonpref”-model) of cis-sites by di- and tri-valent cations (columns 2). The differences between the refined, $\Delta_i^{\text{ref}}$, and tentative, $\Delta_i^{\text{tent}}$, values do not exceed 0.1 mm/s, and $\Delta_i^{\text{ref}}$ sequence for Fe$^{2+}$ corresponding to specific LCAs has not changed.

For Fe$^{3+}$, the contributions of cluster-forming LCAs (2Fe$^{3+}$Al and 2Fe$^{2+}$Fe$^{3+}$), which include three or four nearest neighboring Fe cations, are approximately the same for both models for the two samples providing good agreement between QSD$^{\text{exp}}$s and QSD$^{\text{sim}}$ profiles (not shown). For Fe$^{2+}$, such agreement is only achieved with “nonpref”-model (figure 2, solid envelope). Table 1 shows that the main $w_i$ values satisfying the QSD$^{\text{exp}}$ for sample BSH, in contrast to sample KUL, belong to the LCAs which are homogeneous with respect to charge distribution (3Fe$^{3+}$, 2Fe$^{2+}$Al, 2AlFe$^{3+}$ and 3Al).
Table 1. Individual occurrence probabilities, \( w_i \), for Fe\(^{3+}\) and Fe\(^{2+}\) in specific LCAs with preferable Fe\(^{2+}\)-Mg-occupancy in one of two cis-sites (1) and with equally probable occupancy of cis-sites by di- and tri-valent cations (2).

| LCAs          | \( \Delta_{\text{pred}} \) mm/s | For Fe\(^{3+}\) QSD\(^{\text{mm}}\) profile | \( \Delta_{\text{ref}} \) mm/s | For Fe\(^{2+}\) QSD\(^{\text{mm}}\) profile |
|---------------|----------------------------------|---------------------------------------------|---------------------------------|---------------------------------------------|
|               | KUL 1 2 BSH 1 2 | KUL 1 2 | BSH 1 2 | KUL 1 2 | BSH 1 2 |
| 3Fe\(^{2+}\)  | 0.0 0.025 0.003 | 1.20 | - | - | - |
| 2Fe\(^{2+}\)Mg | 0.13 | - 0.002 | 1.40 | - | - | - |
| 3Fe\(^{3+}\)  | 0.17 0.003 0.006 | 1.56 | 0.019 0.037 0.117 | 0.127 |
| 2MgFe\(^{2+}\) | 0.26 0.009 0.012 | 1.76 | 0.083 0.135 | - |
| 2Fe\(^{3+}\)Al | 0.33 0.338 0.314 | 0.323 0.301 | 1.95 | 0.096 0.015 0.126 | 0.131 |
| 2Fe\(^{2+}\)Fe\(^{3+}\) | 0.34 0.141 0.160 | 0.112 0.12 | 2.00 | - | 0.085 | - |
| 3Mg           | 0.39 | - | 0.041 0.041 | 2.00 | - | - | - |
| MgFe\(^{2+}\)Fe\(^{3+}\) | 0.48 0.066 0.121 | 0.131 0.213 | 2.20 | 0.126 0.127 | 0.085 |
| 2Fe\(^{2+}\)Al | 0.49 0.023 0.041 | 0.076 0.045 | 2.37 | 0.066 0.066 | 0.082 |
| 2AlFe\(^{3+}\) | 0.51 0.017 0.128 | 0.123 0.060 | 2.55 | 0.141 0.127 0.147 | 0.140 |
| 2MgFe\(^{2+}\) | 0.61 0.004 0.002 | 0.017 0.025 | 2.60 | 0.012 0.051 | - | 0.010 |
| AlMgFe\(^{2+}\) | 0.63 0.015 0.018 | 0.028 0.030 | 2.70 | 0.026 0.081 | - | 0.017 |
| 2Fe\(^{2+}\)Fe\(^{3+}\) | 0.65 0.041 0.020 | 0.011 0.018 | 2.75 | 0.007 0.007 | 0.015 |
| 3Al           | 0.74 0.005 0.010 | 0.014 0.010 | 2.84 | 0.126 0.020 0.331 | 0.220 |
| 2MgAl         | 0.78 | - | - 0.004 0.010 | 2.85 | - | 0.002 0.068 | 0.039 |
| 2Fe\(^{2+}\)Mg | 0.79 0.022 0.013 | 0.008 0.010 | 2.87 | 0.035 0.025 0.025 | 0.004 |
| AlFe\(^{2+}\)Fe\(^{3+}\) | 0.86 0.059 0.047 | - | 0.015 0.015 | 2.87 | 0.078 0.114 | - 0.051 |
| AlMgFe\(^{2+}\) | 1.02 0.042 0.035 | 0.040 0.035 | 2.87 | 0.139 0.068 0.132 | 0.075 |
| 2AlFe\(^{3+}\) | 1.06 0.033 0.030 | 0.058 0.045 | 2.90 | - | 0.023 | - 0.005 |
| 2AlMg         | 1.40 0.009 0.004 | - | 0.029 0.029 | 2.96 | 0.039 0.013 | 0.054 |

4. Conclusion

- The CCM proved to be consistent with QSDs for Mössbauer spectra of two investigated glauconites, thus filling these QSDs with the crystal-chemical meaning.
- The high resolution of the quasi-continuous model-independent QSD analysis provided, first, corroboration of the \( \Delta_{\text{pred}} = 0.0 \) mm/s for Fe\(^{3+}\) in the arrangement 3Fe\(^{2+}\) previously assumed as the minimum value in the \( \Delta_{\text{pred}} \) sequence; and second, refinement of the \( \Delta_{\text{ref}} \) set for Fe\(^{2+}\) in specific LCAs.
- For the CD reconstruction corresponding to the absence of preference of di-valent cations to one of the two cis-sites, the studied glauconites obey Pauling’s principle of homogeneous dispersion of charge to different extents.

5. References

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