Reconstruction of octahedral cation distribution in 2:1 phyllosilicates and interpretation of their Mössbauer spectra

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Cation distribution (CD) in octahedral sheets of phyllosilicates, which are characterized by wide variety of isomorphous substitutions (Al, Fe^{3+}, Fe^{2+}, Mg), is an important crystal chemical feature of these minerals. Mössbauer spectroscopy supplemented with the data of other physical and spectroscopic methods as well as calculations of the electric field gradients (EFG) has always been considered to be promising for the CD reconstruction. However, despite the use of advanced MO calculations of the EFG, independent of the kind of approximation to fit Mössbauer spectra of trioctahedral micas was used (discrete Lorentzian-shaped doublets or quadrupole splitting distribution (QSD) analysis), this approach still fails to justify the traditional *cis-trans*-assignment or to provide a reliable crystal-chemical interpretation of the QSDs.

An empirical approach to obtain sets of individual quadupole splittings, Δ_i, for Fe^{3+} and Fe^{2+} assigned to certain local cation arrangements (LCA) turned out to be an alternative for sophisticated EFG calculations. Dioctahedral 2:1 *trans*-vacant micas (celadonites, illites, glauconites, aluminoceladonites, muscovite) with Fe in the LCA consisting of three nearest cations were used as model objects. The increase in Fe^{3+} Δ_i with increasing local distortion is assumed in the empirical equation that takes account of the charge and bond length heterogeneity. The Δ_i assignment for Fe^{2+} to specific LCAs results from the correlation between the octahedral cation composition and maximum quadrupole splitting Fe^{2+} extracted from Mössbauer spectra for a representative mineral collection.

The crystal-chemical model (CCM) for interpreting the spectra of 2:1 dioctahedral *trans*-vacant micas (Dainyak *et al.*, 2009 and references therein) incorporates Δ_i^{pred} and Δ_i^{ref} for Fe^{3+} and Fe^{3+}, respectively, and the occurrence probabilities for the corresponding LCAs provided by two-dimensional CD simulation. The CCM proved to be successful when applied to interpreting both discrete Lorentzian-lineshape fitting and QSD analysis results. With glauconite samples from different places taken as an example, combination of CCM and high resolution quasi-continuous QSD analysis (Rusakov, 1999) resulted in CD-reconstructions differing in the degree of Fe-clustering, in domain structure with domains of different compositions and in various trends to homogeneous charge dispersion (HCD) over octahedral sheet. To investigate the HDC realization over a whole layer and interlayer, the potential of the CCM should be increased by subsequent refinement of Fe^{2+} Δ_i^{ref}, improvement of the CD simulation, and estimation of the influence of tetrahedral Al.

References:
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