

AN INTERPRETATION OF OCTAHEDRAL ORDERING AND SITE OCCUPANCIES OF Fe^{2+} IN MUSCOVITE AND ILLITE.

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Recent experimental and theoretical, structural models have been used to infer the site occupancies of Fe^{2+} in muscovite and illite and to account for their Mössbauer spectra. Octahedral site preferences have been discussed for Al, Fe^{3+} and Mg by several authors (e.g., Drits et al., 1997; Cuadros et al., 1999; Sainz-Diaz et al., 2003; Palin et al., 2004) but, to date, Fe^{2+} has not been considered. The model proposed for the dioctahedral sheet in glauconite by Dainyak et al. (1992) that recognizes illite-like and celadonite-like domains appears to be valid for phengitic muscovites and illites as well. The trans-vacant dioctahedral sheets are separated into exclusively Al-bearing and mixed-cation domains. The mixed-cation domains have symmetrically non-equivalent cis sites with different R^{2+} and R^{3+} preferences. A high ordering energy is predicted when R^{2+} fully occupies one of the two cis sublattices in the mixed-cation domains.

Inasmuch as muscovites and illites are essentially trans-vacant, octahedral cations occupy the two cis (M2) sites in mixed-cation domains. Each cis site has three nearest neighbors on the other cis sublattice. In the lowest energy configuration, Fe^{3+} forms clusters on the R^{3+} sublattice. In accord with previous studies, it is assumed that Mg^{2+} and Fe^{2+} are randomly distributed on the R^{2+} sublattice. With this ordering, the proportions of the different local environments of Fe^{2+} cations will be determined by the Fe^{3+} -content of the dioctahedral sheet and the sizes of the mixed-cation domains and Fe^{3+} clusters. Thus, in muscovite and illite the Fe^{3+} -rich clusters within the mixed cation domains encompass much less Mg^{2+} (and Fe^{2+}) than do the Fe^{3+} -poor regions.

Mössbauer spectra of most muscovites and illites exhibit two Fe^{2+} doublets having quadrupole splittings of ~ 3.0 mm/s and ~ 2.1 mm/s. The former, which has the greater site fraction and narrower linewidth appears to represent a unique local configuration of Fe^{2+} surrounded by three Al nearest neighbors while the latter, whose splitting is smaller and more variable, appears to represent local environments of Fe^{2+} cations surrounded by from one to three Fe^{3+} nearest neighbors. Quadrupole splittings of Fe^{2+} cations will vary depending on the positions of Fe^{3+} cations relative to the crystal electric field gradient. Intermediate splittings observed in some muscovites and illites may result from cation disorder between the R^{3+} -rich and R^{2+} -rich sublattices.

Cuadros, J. et al. (1999) *Am. J. Sci.*, 299, 289-308. Dainyak, L.G., Drits, V.A., and Heifits, L.M. (1992) *Clays Clay Min.*, 40, 470-479. Drits, V.A. et al. (1997) *Clay Min.*, 32, 153-197. Palin, E.J., Dove, M.T., Hernandez-Laguna, A. (2004) *Amer. Min.* 89, 164-179. Sainz-Diaz, C.I. et al. (2003) *Amer. Min.*, 88, 1033-1045.

(Powerpoint presentation: <http://defects.physics.wsu.edu/papers/CMS-04-Illite-Symp.pdf>)