Ordering of the Al Cation Distribution in the Octahedral Sheets Related to the Ordering of Al in the Tetrahedral Sheets of Phlogopite Investigated by 2D CPMAS NMR and Monte Carlo Simulations

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This work is part of the ORION-project (Ordering of Ions in Minerals) within the EuroMinScI programme of the ESF which aims at the elucidation of ionic ordering by combining experimental investigations and theoretical calculations. Previous NMR solid state experiments in phlogopite, a trioctahedral 2:1 layer silicate, indicated a non-statistical distribution of cations and anions in the octahedral sheets: F prefers sites coordinated by three Mg, whereas OH prefers sites with Al as next-nearest-neighbours (Fechtelkord et al. 2003). Further investigations were carried out on phlogopites with various Al-contents and synthesized at different temperatures. Cross-polarization (CP) $\{^{1}H\}$ ^{29}Si CPMAS NMR experiments were performed to clarify whether the degree of ordering in the octahedral sheets is related to that in the tetrahedral layers. With this method, direct neighbourhoods of protons in the octahedral sheets to Si environments in the tetrahedral sheets can be correlated in one- and two-dimensional CPMAS NMR experiments. Moreover, information on the position of Al in both sheets can be achieved indirectly. These experiments clearly indicate a direct neighbourhood of aluminium in the tetrahedral sheets to aluminium in the octahedral sheets and, thus, a relationship between the ordering of ions in both sheets.

Support for these conclusions comes also from atomistic simulations of ordering using the so-called "J formalism" in which total-energy calculations with interatomic potentials are used to generate a set of pair interaction parameters which are then employed in Monte Carlo (MC) simulations (Bosenick et al. 2001, Warren et al. 2001). The method has proven its usefulness in previous investigations of cation ordering behavior, for example on dioctahedral phyllosilicates such as muscovite (Palin et al. 2001) and also minerals with the spinel structure (Palin & Harrison 2007). In phlogopite we have considered the OH-rich extreme, and performed MC simulations for several overall concentrations of Al in the range $0 < x < 1$, finding significant segregation of the Al atoms with a strong spatial correlation between the Al-rich domains in the two layers.

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