

Aluminum ordering and clustering in Al-rich synthetic phlogopite: $\{^1\text{H}\} \rightarrow ^{29}\text{Si}$ CPMAS HETCOR spectroscopy and atomistic calculations

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Cationic ordering in octahedral and tetrahedral sheets of Al-rich synthetic phlogopites with nominal composition $\text{K}(\text{Mg}_{3-x}\text{Al}_x)[\text{Al}_{1+x}\text{Si}_{3-x}\text{O}_{10}](\text{OH})_2$ ($0.0 \leq x \leq 1.2$) has been investigated using a combined approach of Monte Carlo simulations based on the 'J formalism' (Bosenick et al. 2001, Warren et al. 2001) and ^1H , ^{29}Si MAS and $\{^1\text{H}\} \rightarrow ^{29}\text{Si}$ CPMAS/HETCOR solid-state NMR spectroscopic experiments. $\text{Si}^{\text{IV}}\text{Al}$ and $\text{Mg}^{\text{VI}}\text{Al}$ ordering has been found to be controlled mainly by three mechanisms: $^{\text{IV}}\text{Al}-\text{O}-^{\text{IV}}\text{Al}$ linkages in tetrahedral sheets are avoided according to Loewenstein's rule (Loewenstein 1954). This leads to long-range ordering in the tetrahedral sheets at very high Al-contents with Al and Si occupying sites alternately. Secondly, $^{\text{VI}}\text{Al}$ neighbor pairs in the octahedral sheets are prevented in a similar manner, with Al atoms in the octahedral sheets always surrounded by six Mg atoms on adjacent sites. Finally, we observe a preference for $^{\text{VI}}\text{Al}$ and $^{\text{IV}}\text{Al}$ to occupy directly neighbored octahedral and tetrahedral sites. As a result the structure is separated into clusters of original phlogopite composition ($\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$) and clusters of 'eastonite' composition ($\text{K}(\text{Mg}_2\text{Al})[\text{Al}_2\text{Si}_2\text{O}_{10}](\text{OH})_2$) that encompass a whole T-O-T layer package, although Al is solved in the phlogopite structure homogeneously on a macroscopic level.

Reference:

Bosenick, A., Dove, M.T., Myers, E.R., Palin, E.J., Sainz-Diaz, C.I., Guiton, B., Warren, M.C., Craig, M.S., Redfern, S.A.T. (2001), *Mineralogical Magazine*, 65, 193–219.

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