

## SHORT RANGE ORDER IN PHYLLOSILICATES 2:1

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Ionic distributions are mainly controlled by local charge balance requirements, in all organised compounds. In phyllosilicates 2:1, the charge balance around the OH group, and on the apical oxygens of tetrahedra is a fundamental criterion which manages the cationic distribution in the octahedral layer. Around an OH position, cationic associations can carry 4 (i.e.  $2M^{2+}\square$ ) to 8 charges ( $2M^{2+}Ti^{4+}$ ), and possibly  $3M^{3+}$  in non-protonated compounds. In this respect, it is possible to explain why all Li-bearing phyllosilicates 2:1, hectorite, lepidolites, are trioctahedral (exclusion Li- $\square$ ) and why Li is always in a trioctahedral local environment in mixed tri-dioctahedral solid solutions (Monier and Robert, 1986). Vacant octahedral sites can be either in cis or trans configuration in clays, and systematically trans in micas. Small high-charge cations, generally favour the small octahedron M2 (cis), whereas large cations enter the larger M1 site (trans), but this scheme is rarely completed, and most of structures with differently charged cations, exhibit polycationic sites. The replacement of  $OH^-$  by  $F^-$  drastically changes the cationic distribution in the octahedral layer, since  $F^-$  acts as a point charge, whereas  $OH^-$  is a dipole and can share a part of the  $H^+$  charge with the oxygens of adjacent tetrahedra (Robert et al., 1993). This is sufficient to explain the local association between Li and F, as well as Al-F and Ti-F exclusions, for example. Other cases of ordering around an OH group are recognised, as the local association between a protonated apical oxygen of  $M^{2+}O_4$  tetrahedron, and an octahedral vacancy. A rare case of  $M^{2+}O_4-[6]\square-M^{2+}O_4$  ordering along  $c^*$ , is observed in these phyllosilicates. Also interesting is the case of local cationic ordering between tetrahedral and octahedral layer, required to balance charge on apical oxygens of tetrahedra. Local electrostatic considerations lead to conclude that high charge cations in octahedral coordination are associated with Al rather than Si in tetrahedra. So, the well known Al-Tschermak substitution, which involves both tetrahedral and octahedral layers, does not only concerns the whole structural formula, but also the local ordering pattern of Al atoms in adjacent sites.

The distribution of tetrahedrally coordinated cations,  $Si^{4+}$  and  $Al^{3+}$ , complies first with the Al-Al avoidance rule, i.e. the Loewenstein rule, but a further dispersion of cations is observed, so that the charge distribution is homogeneous

(HDC model of Herrero et al., 1989). In other words, the local Si,Al distribution closely follows the bulk tetrahedral layer composition. In high-Al compounds like clintonite, a monosilicic mica, where  $[^4]Al-[^4]Al$  pairs are dominant, the silicon distribution also shows some ordering, then, this mica does not follow a maximum charge dispersion pattern. On the whole, there is a temperature-dependent equilibrium between the electrostatic energy which favours the cationic dispersion, and the entropic term which favours a disordered distribution (Sanz et al., 2003). Disilicic compounds ( $Si_2Al_2$ ), like preiswerkite, ephesite, kinoshitalite and margarite should be serious candidates to a perfect Si,Al ordering. But, in these compounds, a minor deviation to stoichiometry is systematically observed, which generates Si-Si associations, for entropy reasons. On the other hand, the structure of these phyllosilicates, deduced from XRD data, are more symmetric than expected, which means the existence of antiphase domains.

In the interlayer space, local ordering of compensating cations are recognised in some cases. In mixed OH-F trioctahedral compounds, divalent cations, e.g.  $Ba^{2+}$ , favour those  $6TO_4$  rings adjacent to  $F^-$ , whereas monovalent cations, e.g.  $K^+$  are preferentially associated with  $OH^-$ . Small cations, like  $Li^+$ , in the anhydrous form, strongly order between two  $[^4]AlO_4$  tetrahedra of two consecutive layers, for local charge balance requirements.

Dimensional factors also control cationic ordering. This is particularly true with the large cation  $Mn^{2+}$  which needs to be associated with a smaller one. This requirement explains the common Al- $Mn^{2+}$  association in manganous phyllosilicates. Another example is offered by the  $[^6]Mn^{2+}-[^6]Zn^{2+}$  association in hendricksite, with an average resulting dimension of octahedra similar to that produced by  $Fe^{2+}-Fe^{2+}$  pairs.

## References

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