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## RELATIONSHIPS BETWEEN CLAY MINERALS AND WATER: INFLUENCE OF EXTERNAL AND STRUCTURAL FACTORS

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The combination of diffractometric (X-rays and neutrons) and thermal (TGA and DTA) analyses has revealed the existence of seven hydration states in 2:1 clay minerals (synthetic saponites), as a function of the partial water vapour pressure (P/P<sub>0</sub>). For low water vapour pressures, only layer edges and surfaces are concerned. With increasing P/P<sub>0</sub>, a progressive hydration of the compensating cation is observed, with an increase, by steps, of the basal distance  $d_{001}$ , from about 10 Å to about 15 Å. However, the classical model "onelayer" and "two-layers" is much more complicated.

For high  $P/P_0$  values (> 85%), pore water appears, indicating a saturation (edges, surface and interlayer space).

Compositional variations which strongly modify the clay mineral structures mainly influence the hydration properties. Structural factors like the ditrigonal distortion of the tetrahedral sheet and the layer stacking strongly affect the relationships between clay minerals and water. This has been demonstrated on the saponite group, with layer charge 0.33-1.0 [i.e., aspidolite, NaMg<sub>3</sub>(Si<sub>3</sub>Al)O<sub>10</sub>(OH)<sub>2</sub>] and on the aspidolite-preiswerkite join [Na(Mg<sub>2</sub>Al)(Si<sub>2</sub>Al<sub>2</sub>)O<sub>10</sub>(OH)<sub>2</sub>].

On the whole, the influence of the layer charge is negligible, as well as the origin of the charge (tetrahedral and/or octahedral). The main factors are the local structure and the layer stacking which determine the coordination of the compensating cation. When the coordination number of the interlayer cation drops from [12] to [6], the hydration properties progressively decrease, and when the six-fold coordination is reached, no water molecule can enter the interlayer space. The minor hydration is only due to the adsorption of water molecules on edges and surface.