

## Nature of rehydroxylation in dioctahedral 2:1 layer clay minerals

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### ABSTRACT

Rehydroxylation of the previously dehydroxylated dioctahedral 2:1 layer clay mineral occurs preferentially in specific sites within the former octahedral sheet. The rehydroxylation of dehydroxylated Al-rich and Al,Mg-rich 2:1 layers occurs as *trans*-vacant (*tv*) structural arrangements, regardless of whether the initial structure was *tv* or *cis*-vacant (*cv*). In nontronite (Fe-rich 2:1 layer clay), the dehydroxylate *pseudo-cv* structure is probably directly reconstructed into the rehydroxylated *cv* structure without migration of octahedral cations. Rehydroxylation occurs preferentially in the  $R^{3+}\text{-O}_r\text{-R}^{3+}$  former octahedral structural arrangements ( $O_r$  = residual oxygen) over  $R^{2+}\text{-O}_r\text{-R}$  ( $R = R^{3+}$  or  $R^{2+} = \text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  or  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ). In the case of the  $R^{2+}$  octahedral substitution, the interlayer cation is attracted to the electrostatically undersaturated residual oxygen of the  $R^{2+}\text{-O}_r\text{-R}$  arrangement, which blocks the ability of water molecules to pass through the ditrigonal cavity and rehydroxylate the previously dehydroxylated local arrangement. The pyrophyllite-like type of octahedral  $R^{3+}\text{-O}_r\text{-R}^{3+}$  arrangements, formed due to the lack of tetrahedral substitution and resulting in the absence of interlayer cations, is thus favored for rehydroxylation over the mica-like  $R^{3+}\text{-O}_r\text{-R}^{3+}$  arrangements where Al occurs in the tetrahedral sheet. The valence of the interlayer cation and the charge density of the 2:1 layer clay mineral, which controls the interlayer cation content, also affect the degree of rehydroxylation.

Dehydroxylated 2:1 layer minerals with a high-rehydroxylation potential, including beidellite and illite, use all the adsorbed water molecules that persist above 200 °C for rehydroxylation; the water vapor from the ambient environment also becomes a source of H<sub>2</sub>O molecules for rehydroxylation. The high demand for water molecules to use for rehydroxylation results in a noticeable gain of mass in the temperature interval between 200 and 350 °C even during heating.

**Keywords:** Rehydroxylation, dehydroxylation, beidellite, montmorillonite, illite, aluminoceladonite, pyrophyllite