

## KAOLINITE-SMECTITE: NATURE OF THE LAYERS AND MECHANISM OF SMECTITE KAOLINISATION

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The present study is aimed to contribute to a better understanding of the nature, formation and evolution mechanisms of mixed layer clay minerals by studying kaolinite-smectite (K-S).

We examined K-S from three different localities. Twenty specimens are from the Los Trancos clay deposit of Tortonian age in Almeria, Spain (three samples are from palaeosols, the rest formed by hydrothermal activity). One sample is from a clay deposit formed by weathering of Eocene volcanic ash (Yucatan Peninsula, Mexico), and one from a Jurassic weathering crust developed on a bentonitic bed (Rushden, Northamptonshire, England). We used the < 2 µm particle size fraction containing K-S as a single phase.

The methods used in this study are the following: X-ray diffraction analysis of both random and oriented preparations, thermogravimetry (TG) and chemical analysis (X-ray fluorescence, wet analysis and ICP-AES). The proportion of kaolinite and smectite layers in K-S (%K) was calculated by fitting the experimental and theoretical XRD patterns calculated with the NEWMOD<sup>®</sup> computer program (Reynolds, 1985).

We find that the total dehydroxylation weight loss calculated from the TG curves is not linearly related to the evolution of K-S composition recorded by XRD. Thus, the collapse of layers to 7 Å is not linked directly to the increase of OH content of the octahedral sheet in K-S during the transformation. We interpret this trend as an effect of the development of patches within smectite layers in which part of the tetrahedral sheet is stripped off and OH groups are attached. The patches (henceforth called kaolinite-like patches) have the 1:1 layer structure, however they do not necessarily yield a 7 Å kaolinite spacing. At the beginning of the process, the patches are small and there is no change in the basal spacing. As the transformation proceeds, the point is reached when the patches become large enough to allow formation of 7 Å domains or layers, producing mixed layering. The TG curves of our samples show three dehydroxylation events: at cca. 450°C for kaolinite, cca. 620°C for smectite, and cca. 550°C for a component intermediate between them. We interpret the "intermediate" component as the parts of the smectite layers located in direct proximity of the kaolinite-like patches. Dehydroxylation of the octahedral sheet in these areas needs less energy than in smectite but more than

in kaolinite, because the diffusion of the evolving H<sub>2</sub>O is easier than in the former but more difficult than in the latter.

The chemical analyses show continuous release of Mg from K-S structure during smectite kaolinisation. In contrast, Fe remains in K-S or is removed much more slowly than the transformation happens. These data are supported by the non-linear evolution of the (060) peak position on the XRD patterns with increasing %K, indicating that the rate of change of the octahedral cation composition is lower than that of 7 Å layer formation. We associate this trend with the retention of Fe. The CEC examination indicates that some layer charge produced by the residual Al in the tetrahedral sheet is retained within kaolinite-like patches.

The evidence in this study indicates that the smectite-to-kaolinite reaction mechanism through mixed layer K-S is a solid-state transformation. We believe that the presented results apply to different environments of K-S formation. Our samples were formed in both hydrothermal and hypergenic conditions causing bentonite alteration. Also, K-S from palaeosols developed on chalk- and silica-rich rocks (Paris Basin, Brindley et al., 1983) and from present-day montmorillonitic soils (Alabama coastal plains, Karathanasis and Hajek, 1983) show the same relation between the dehydroxylation weight loss and K-S composition as in this study. Thus, smectite kaolinisation in non-bentonite systems proceeds also through the development of kaolinite-like patches, and our proposed mechanism operates in a variety of environments and conditions.

Our study also shows the complex nature of K-S layers. They can be partly smectitic and partly kaolinitic in terms of OH content, chemistry and basal spacing, and the smectite or kaolinite character of one layer can vary depending on the variable investigated.

### References

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