Structural Transformation of 2:1 Dioctahedral Layer Silicates during Dehydroxylation-Rehydroxylation Reactions

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Abstract: The structural transformation of dioctahedral 2:1 layer silicates (illite, montmorillonite, glauconite, and celadonite) during a dehydoxylation-rehydroxylation process has been studied by X-ray diffraction, thermal analysis, and infrared spectroscopy. The layers of the samples differ in the distribution of the octahedral cations over the *cis*- and *trans*-sites as determined by the analysis of the positions and intensities of the 11*l*, 02*l* reflections, and that of the relative displacements of adjacent layers along the *a* axis ($c \cos \beta/a$), as well as by dehydroxylation-temperature values. One illite, glauconite, and celadonite consist of *trans*-vacant (*tv*) layers; Wyoming montmorillonite is composed of *cis*-vacant (*cv*) layers, whereas in the other illite sample *tv* and *cv* layers are interstratified. The results obtained show that the rehydroxylated Al-rich minerals (montmorillonite, illites) consist of *tv* layers whatever the distribution of octahedral cations over *cis*- and *trans*-sites in the original structure. The reason for this is that in the dehydroxylated state, both *tv* and *cv* layers are transformed into the same layer structure where the former *trans*-sites are vacant.

The dehydroxylation of glauconite and celadonite is accompanied by a migration of the octahedral cations from former *cis*-octahedra to empty *trans*-sites. The structural transformation of these minerals during rehydroxylation depends probably on their cation composition. The rehydroxylation of celadonite preserves the octahedral-cation distribution formed after dehydroxylation. Therefore, most 2:1 layers of celadonite that rehydroxylate (~75%) have *cis*-vacant octahedra and, only in a minor part of the layers, a reverse cation migration from former *trans*-sites to empty octahedra occurred. In contrast, for a glauconite sample with a high content in ^{IV}Al and ^{VI}Al the rehydroxylation is accompanied by the reverse cation migration and most of the 2:1 layers are transformed into *tv* layers.

Key Words: Cation Migration • Celadonite • *Cis*-Vacant Octahedra • Dehydroxylation • Glauconite • Illite • Rehydroxylation • Smectites • Structure • *Trans*-Vacant Octahedra

Clays and Clay Minerals; October 2000 v. 48; no. 5; p. 572-585; DOI: 10.1346/CCMN.2000.0480510