

Kinetics of partial dehydroxylation in dioctahedral 2:1 layer clay minerals

VICTOR A. DRITS,^{1,*} ARKADIUSZ DERKOWSKI,² AND DOUGLAS K. MCCARTY³

¹Geological Institute of the Russian Academy of Science, Pyzhevsky per. 7, 119017 Moscow, Russia

²Institute of Geological Sciences, Polish Academy of Sciences, Research Centre in Kraków, Senacka 1, PL-31002 Kraków, Poland

³Chevron ETC, 3901 Briarpark, Houston, Texas 77042, U.S.A.

ABSTRACT

A multi-cycle heating and cooling thermogravimetric (TG) method was used to study the kinetic behavior of partially dehydroxylated illite, aluminoceladonite, and dioctahedral smectite samples. The method consists of consecutive heating cycles separated by intervals of cooling to room temperature, with the maximum cycle temperatures (MCTs) set incrementally higher in each consecutive cycle.

In the studied samples, dehydroxylation of each portion of the initial OH groups follows the kinetics of a homogeneous zero-order reaction in each heating cycle. The activation energies (E_a) were calculated in terms of this model for separate heating cycles of each sample with regression coefficients $R^2 \geq 0.999$. A zero-order reaction determined at each heating cycle indicates that at each stage of partial dehydroxylation, there is no formation of an intermediate phase and the reaction is probably the direct transformation of the original layers into completely dehydroxylated layers.

The Wyoming montmorillonite and illite consisting of *cis*-vacant (*cv*) layers had the highest E_a values (53–55 kcal/mol). In the samples consisting of *trans*-vacant (*tv*) layers and having almost the same octahedral cation composition the maximum E_a values varied from 45 to 30 kcal/mol and the E_a of each sample in this group are similar over a wide range of the D_T . For the samples consisting of a mixture of *cv* and *tv* illite structures, a bimodal distribution of the E_a values exists with increasing MCT and D_T . The maximum E_a values for dehydroxylation of the *tv* and *cv* illite structures are different.

The activation energies from the *tv* aluminoceladonite and Otay *tv* montmorillonite samples have similar maximum E_a values (39.4 to 41.8 kcal/mol), but the variation in E_a with D_T has a skewed bell-like distribution that is probably related to a heterogeneous octahedral cation composition of the 2:1 layers.

The E_a values calculated for the mineral structures in this study are compared with those published and the main factors controlling the E_a variation at different stages of the partial dehydroxylation are discussed.

Keywords: Dehydroxylation, 2:1 layer clay minerals, kinetics, activation energy, thermogravimetry