Energetics of kaolin polymorphs

DOMINIQUE DE LIGNY AND ALEXANDRA NAVROTSKY*

Thermochemistry Facility, Chemistry Building, Department of Chemical Engineering and Materials Science, University of California at Davis, Davis, California, 95616, U.S.A.

ABSTRACT

The enthalpy of formation of kaolin polymorphs at 298 K has been determined by drop-solution calorimetry into molten lead borate at 975 K. Corrections have been made for impurities in the samples. The standard enthalpy of formation from the elements is: kaolinite $-4120.2 \pm 6.6$ kJ/mol, dickite $-4107.6 \pm 5.7$ kJ/mol, nacrite $-4104.0 \pm 7.6$ kJ/mol, and halloysite $-4097.5 \pm 5.6$ kJ/mol. Using entropy data from the literature, the standard free energy of formation from the elements at 298 K is $-3799.4 \pm 6.4$ kJ/mol for kaolinite, $-3785.1 \pm 5.6$ kJ/mol for dickite, and $-3776.8 \pm 5.8$ kJ/mol for halloysite. The effect of crystallinity (Hinckley index ranging from 1.6 to 0.4) on the enthalpy of formation of kaolinite is smaller than 5 kJ/mol, the experimental error. The relative stability of the polymorphs probably does not change significantly with pressure and temperature over their range of occurrence. Thus the geological occurrence of halloysite, nacrite, and dickite, which are metastable phases, must be interpreted in terms of kinetics or as the result of a specific synthesis path, rather than as resulting from changes in the thermodynamically stable phase assemblage.

INTRODUCTION

Kaolin minerals are dioctahedral clays of 1:1 layer type with chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Kaolinite, dickite, and nacrite are polytypes. The kaolinite stacking sequence consists of identical layers with an interlayer shift of $-\frac{1}{3}$. Dickite and nacrite have a two-layer stacking sequence where the vacant site of the octahedral sheet alternates between two distinct sites (Brindley 1980); their interlayer shift is also $-\frac{1}{3}$, but for nacrite the $a$ and $b$ axes are interchanged from those of kaolinite and dickite. The poor crystallinity commonly observed in kaolinite minerals is understood as a series of stacking faults. Giese (1988) has shown that no difference occurs within the layers from one polymorph to another and that only the stacking differs. Accordingly, the thermodynamic difference among the polytypes are related mostly to the energy of the interlayer connection.

The strength with which the layers are held together has been related to the orientation of the hydroxyl groups, for which many different structural data are available (Prost et al. 1985; Frost 1997). This orientation is thought to be highly dependent on stacking. The present study of the enthalpy of formation of the polytypes and of several kaolinites with different degrees of stacking disorder provides insight into the magnitude of the interlayer bonding.

In contrast, halloysite is a hydrated polymorph of kaolinite with curved layers and a spacing of 10 Å when fully hydrated; the spacing decreases to 7 Å upon dehydration. We studied a 7 Å sample with strong stacking disorder.

Kaolinite, the most abundant polymorph, is found as a weathering product in sedimentary rocks and in hydrothermal systems. Halloysite is found in hydrothermal and surface-weathering deposits. Dickite and nacrite are less common and are restricted to hydrothermal settings. These occurrences have been described by Murray (1988) who presents a review of the genesis of kaolin minerals. The formation of these kaolin minerals may be the result of thermodynamic equilibrium or kinetically limited reaction paths. The enthalpy (and free energy) of formation of each polymorph, as well as the energetics of various kaolinites with different degrees of crystallinity, defines their relative stability. Starting from this thermodynamic base, one can better constrain the conditions of formation of the different polymorphs and, therefore, the history of the sediments and soils that contain them.

Drop-solution calorimetry in molten lead borate at 975 K has become an accepted method for measurement of heat of formation of hydrous phases (Navrotsky et al. 1994) and has been applied to a number of amphiboles (Smelik et al. 1994), micas (Circone and Navrotsky 1992), and zeolites (Kiseleva et al. 1996a, 1996b). Nevertheless, clays present a special challenge both because of their extremely high water content (up to 17 wt%) and because one must deal with natural samples in which water content, chemical purity, and crystallinity all vary. Thus, successful thermochemical study of the kaolin minerals, which are a relatively simple and well-characterized system, is a prelude to the study of more complex clays. Previous calorimetric studies exist for kaolinite, dickite, and halloysite (Barany and Kelley 1961; Hemingway et al. 1978) and provide a basis for comparison.