Crystal properties and energetics of synthetic kaolinite

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ABSTRACT

Six kaolinite $[Al_2Si_2O_3(OH)_4]$ samples were synthesized under different conditions of temperature, pressure, and pH from two different starting materials. Chemical composition and properties of the samples were characterized using classical methods (electron microprobe, atomic absorption spectrometry, X-ray diffraction, differential and thermal analyses, and Fourier transform infrared spectrometry). All synthetic kaolinite samples contained various amounts of a boehmite impurity. The defect density was different for each kaolinite, ranging from high to low. The enthalpy of formation of these kaolinites at 25 °C was investigated by drop solution calorimetry into molten lead borate at 700 °C. All data were corrected for impurities. Whatever the synthesis conditions and the kaolinite properties, the enthalpy of kaolinite dissolution into molten lead borate at 700 °C and the standard enthalpy of kaolinite formation from the oxides and from the elements at 25 °C are constant: 372.3 ± 1.0 kJ/mol, -46.6 ± 2.6 kJ/mol, and -4115.3 ± 4.1 kJ/mol respectively. Using entropy data from the literature, the standard Gibbs free energy of kaolinite formation from the elements at 25 °C is -3793.9 ±4.1 kJ/mol. This value is in excellent agreement with most of the literature data obtained for natural kaolinites. Furthermore, the standard Gibbs free energy of kaolinite formation at 25 °C and 1 atm is very close to that obtained using the same method for the San Juanito dickite, which is commonly used as a standard mineral, the value for kaolinite being slightly more negative than the value for dickite. This trend is also true for all the temperature and pressure range of kaolin minerals occurrences. Thus, dickite is a metastable phase relative to kaolinite, and kaolinite seems to be thermodynamically more stable than dickite, as already proposed by DeLigny and Navrotsky (1999) and Anovitz et al. (1991). The natural occurrence of dickite must result from specific reaction paths and be controlled by kinetic factors.