Crystal properties and energetics of synthetic kaolinite

CLAIRE-ISABELLE FIALIPS,1 ALEXANDRA NAVROTSKY,1,* AND SABINE PETIT2

1Thermochemistry Facility, Department of Chemical Engineering and Materials Science, University of California at Davis, Davis, California 95616, U.S.A.
2Laboratoire Hydr’ASA, UMR6532-CNRS, Université de Poitiers, 40 avenue du Recteur Pineau, F-86022 Poitiers Cedex, France

ABSTRACT

Six kaolinite [Al₂Si₂O₅(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.

INTRODUCTION

Kaolinite is the most widespread mineral of the kaolin group, which also contains dickite, nacrite, and halloysite. Kaolinite can be formed as a residual weathering product or as an authigenic sedimentary mineral (Murray 1988). In soils, kaolinite is formed at P-T conditions of the Earth’s surface (i.e., 25–30 °C and atmospheric pressure; Singer and Munns 1996; Šrodni 1999). However, kaolinite and dickite also persist until late diagenesis (e.g., Beaufort et al. 1998) at temperature lower than 200 °C, and lithostatic pressure lower than 1 kbar or hydrostatic pressure of 300–400 bars. Kaolinite can also result from hydrothermal alteration, at 100–200 °C and 1–100 bars (Murray et al. 1993).

Numerous attempts to synthesize dickite have been performed (e.g., Eberl and Hower 1975; Fialips et al. 2000a, 2000b). But, whatever the starting material (crystalline or amorphous) and the synthesis conditions (200 to 450 °C, 150 to 3000 bars, 0.3 to 182 d), no P-T-X domain of dickite formation was found. In contrast, kaolinite was formed in a wide range of synthesis conditions (Fialips et al. 2000a), suggesting that kaolinite is thermodynamically more stable than dickite.

The relative stability of kaolinites and dickites was widely investigated using different thermodynamic approaches (e.g., Anovitz et al. 1991; Ztov et al. 1998; Deligny and Navrotsky 1999), but the results are still not completely clear. Some authors concluded that kaolinite is the only stable kaolin mineral and that dickite is a metastable mineral whose natural genesis must be explained in terms of kinetics and/or special reaction paths (e.g., DeLigny and Navrotsky 1999). Others concluded that dickite is more stable than kaolinite (Ztov et al. 1998).