

New thermochemical evidence on the stability of dickite vs. kaolinite

**CLAIRE-ISABELLE FIALIPS,^{1,2,3,*} JURAJ MAJZLAN,² DANIEL BEAUFORT,³ AND
ALEXANDRA NAVROTSKY²**

¹Los Alamos National Laboratory, Department of Earth and Environmental Sciences, EES-6, Mail Stop D469, Los Alamos, New Mexico 87545, U.S.A.

²Thermochemistry Facility, Department of Chemical Engineering and Materials Science, University of California at Davis, Davis, California 95616, U.S.A.

³Laboratoire Hydr'ASA, UMR6532-CNRS, Université de Poitiers, 40 avenue du Recteur Pineau, F-86022 Poitiers Cedex, France

ABSTRACT

The energetics of the Saint Claire dickite sample, a highly pure and low defect material, have been studied by high-temperature oxide-melt solution calorimetry. Data were corrected for adsorbed water, the only significant impurity to the ideal formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Enthalpies of dickite dissolution into molten lead borate at 702 °C and of dickite formation from the oxides and from the elements at 25 °C and 1 bar are 356.3 ± 3.3 kJ/mol, -31.1 ± 4.2 kJ/mol, and -4099.8 ± 4.8 kJ/mol, respectively. Using entropy data from the literature, the standard Gibbs free energy of dickite formation from the elements at 25 °C is -3777.5 ± 4.8 kJ/mol. This value is 7 to 25 kJ/mol more endothermic than literature values obtained for other dickites by calculations, solubility measurements, or calorimetry. Since the Saint Claire dickite is almost pure, the applied corrections are very small and these results are likely to be the most reliable of the available data. The Gibbs free energy of formation of the Saint Claire dickite at 25 °C and 1 bar is 12 to 25 kJ/mol less negative than data obtained for kaolinite using the same and different techniques. This trend is unlikely to reverse at higher temperature and/or pressure in the range of kaolin mineral occurrences. Thus, the new data further corroborate our earlier findings that dickite is thermodynamically metastable relative to kaolinite. This is in agreement with results obtained by mineral synthesis and with most of the observations of kaolinite and dickite occurrences in natural environments. However, further investigations are required to fully explain the transformation of kaolinite to dickite, which appears to occur during diagenesis.