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Thermodynamic properties of saponite, nontronite, and vermiculite derived from calorimetric measurements

Hélène Gailhanou[1,*], Philippe Blanc[1], Jacques Rogez[2], Georges Mikaelian[2], Katsuya Horiuchi[3], Yasuhisa Yamamura[3], Kazuya Saito[3], Hitoshi Kawaji[4], Fabienne Warmont[5], Jean-Marc Grenèche[6], Philippe Vieillard[7], Claire I. Fialips[8], Eric Giffaut[8] and Eric C. Gaucher[1]

[1]BRGM, 3 Av. C. Guillemin, BP6009, F-45060 Orleans, France
[2]IM2NP-CNRS Aix Marseille Université, FST Saint-Jérôme, F-13397 Marseille Cedex 20, France
[3]Department of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki, 305-8571, Japan
[4]Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, 226-8503, Japan
[5]CRMD-CNRS, 1b Rue de la Ferollerie, F-45071 Orleans, France
[6]LUNAM, Université du Maine, Institut des Molécules et Matériaux du Mans, UMR CNRS 6283, F-72085 Le Mans Cedex 9, France
[7]CNRS-IC2MP-UMR-7285 Hydrasa, 5 Av. Albert Turpain, 86022 POITIERS-Cedex, France
[8]Andra, F-92298 Châtenay-Malabry Cedex, France

Abstract

The stability of clay minerals is an important factor in assessing the durability of containment barriers for deep waste storage. In that context, the complete thermodynamic data set of three 2:1 ferro-magnesian clay minerals have been determined at 1 bar and from 2 to 520 K, using calorimetric methods. The studied clay samples were, respectively, the Na-saturated saponite Sap-Ca-1, $Na_{0.394}K_{0.021}Ca_{0.038}(Si_{3.569}Al_{0.397}Fe^{3+}_{0.034})(Mg_{2.948}Fe^{2+}_{0.021}Mn_{0.001})O_{10}(OH)_2$, the Ca-saturated nontronite NAu-1, $Ca_{0.247}K_{0.020}(Si_{3.458}Al_{0.542})(Mg_{0.066}Fe^{3+}_{1.688}Al_{0.268}Ti_{0.007})O_{10}(OH)_2$, and the Ca-saturated Santa Olalla vermiculite, $Ca_{0.445}(Si_{2.778}Al_{1.222})(Al_{0.192}Mg_{2.468}Fe^{3+}_{0.226}Fe^{2+}_{0.028}Ti_{0.018}Mn_{0.007})O_{10}(OH)_2$. The standard enthalpies of formation were obtained by solution-reaction calorimetry at 298.15 K. The heat capacities were measured between 2 and 520 K, using low-temperature adiabatic calorimetry, heat-pulse calorimetry, and differential scanning calorimetry. The standard entropies and the Gibbs free energies of formation at 298.15 K have been calculated from these values. Finally, the equilibrium constants at 298.15 K have been determined.

A comparison between these experimental data and estimated values obtained from prediction models available in the literature enabled the most usual calculation methods available to date to be assessed for each thermodynamic property.

Keywords: Clay mineral, saponite, nontronite, vermiculite, thermodynamic data, enthalpy, Gibbs free energy, entropy, calorimetry, dissolution