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Water molecules in clay minerals: Thermodynamic functions and hydration

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Thermodynamic functions and adsorption of water molecules are very important properties for clay minerals. Smectite MX-80 and mixed-layer illite-smectite ISCz-1 were selected. They were first carefully characterized (HRTEM with EDX analysis), revealing original results. Then, the thermodynamic properties of water in clay were obtained by (i) comparison of the thermodynamic properties of anhydrous and hydrated minerals, between 0 and 350 K (adiabatic calorimetry, solution isothermal calorimetry), and (ii) water vapor adsorption isotherms, between 300 and 380 K (magnetic suspension thermobalance).

Solution isothermal calorimetry is used to determine the enthalpies of formation of the minerals (1 bar and 298 K). Comparison of the results, for the anhydrous and the hydrated minerals, leads to the enthalpies of hydration at 298 K.

Adiabatic calorimetry measurements give the heat capacities of the minerals from 5 to 350 K. Entropies, enthalpies of formation and Gibbs free energies of formation, for the anhydrous and the hydrated minerals, and then, entropies of hydration, enthalpies of hydration and Gibbs free energies of hydration, between 0 and 350 K, are finally obtained. Comparison of two close hydration states leads to the entropy, the enthalpy and the Gibbs free energy of the adsorption reaction: H_2O free $\rightarrow$ H_2O adsorbed.

The $C_p(T)$ curve, for the heat capacity of water in clay – $i.e.$, the difference between the heat capacities of the hydrated and the anhydrous minerals –, shows that water in clay is a glass at low temperature, undergoes one or two continuous glass transitions between 150 and 270 K, and behaves as free liquid water above 273 K. The two glass transitions might correspond to two types of water molecules: (i) first adsorbed water molecules, bound to the interlayer cations of the clay mineral; (ii) last adsorbed water molecules, not bound to the interlayer cations.

In addition, water vapor adsorption isotherms are obtained from 298 to 378 K (magnetic suspension thermobalance) and well fitted with a BET type model (with three layers of adsorbed water molecules). The Gibbs free energy of the adsorption reaction and the Gibbs free energy of hydration, for any hydration state, can be determined. They are in agreement with the above calorimetric values.

Gailhanou H., van Miltenburg J.C., Rogez J., Olives J., Amouric M., Gaucher E.C., Blanc P. (2007).Thermodynamic properties of anhydrous smectite, illite and illite-smectite. (Part 1) Geochim Cosmochim. Acta **71**, 5463-5473.