



Thermodynamics of low-temperature phyllosilicates : from the macroscopic perspective towards atomistic simulation

B. Dubacq (1), O. Vidal (1), and V. de Andrade (2)

(1) Laboratoire de Géodynamique des Chaînes Alpines, Observatoire des Sciences de l'Université de Grenoble, Saint-Martin d'Hères, France, (2) European Synchrotron Radiation Facility, Grenoble, France

Phyllosilicates are ubiquitous minerals and play an important role in both metamorphic petrology and waste storage sites, where clays are extensively used. Despite this fact, there is no thermodynamic model which properly describes and predicts the behaviour of low-temperature clay minerals (for example, variation of volume with dehydration), and their phase relations with other minerals in metamorphic conditions. Inversely, the thermodynamic models of phengites are well constrained at high pressure and temperature but do not allow accurate thermobarometric estimations at temperatures less than about 350°C. Moreover, hydration of K-deficient low-temperature, high-pressure phengites, has been verified by FTIR means, and cannot be accounted for by current thermodynamic models.

We propose a new and unique thermodynamic formalism for smectites, illites, mixed-layers illites / smectites and phengites. Experimental results of i) clay dehydration, ii) nature of stable phases, iii) calorimetric measurements, as well as known pressure-temperature crystallization conditions of phyllosilicates analyses, provided useful constraints to calculate thermodynamic properties of these minerals. However, at low temperature, additional constraints from atomistic calculation are required because of the difficulty of reaching equilibrium and of the compositional complexity and small-scale heterogeneities of these phases, making them difficult to analyse.

We investigated several approaches in order to find an independent way of estimating thermodynamic properties of phyllosilicates. All these methods prove to be insufficiently accurate to estimate standard enthalpy of formation; calculated enthalpies of formation can then not be directly used for thermobarometric estimations with internally coherent thermodynamic datasets. However, new state-of-the-art atomistic simulations allowed the calculation of mixing enthalpy terms along solid solution binaries in phengites and carpholites - minerals of interest in low-temperature petrology. Results are in agreement with observations in natural systems: the calculated excess enthalpy between Mg-carpholite and Fe-carpholite was found to be near ideality, on the contrary of the calculated excess enthalpy between muscovite and pyrophyllite which was found to be positive and strongly asymmetric, leading to the apparition of a large solvus oriented towards pyrophyllite at low temperature. This last result confirms that some external agent, such as hydration, enhances clay stability.