



Prediction of enthalpy of formation of minerals: application to solid solutions and low-temperature compounds

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Reliable thermodynamic data are necessary to assess mineral equilibrium during metamorphic processes and to predict mineral-fluids reactivity in waste storage sites.

The thermodynamic properties of most metamorphic minerals are well constrained by equilibrium bracketing and calorimetric measurements. However, the thermodynamic properties of low-grade minerals (such as clay minerals) remain poorly known: most data rely on dissolution experiments that provide information on G° of mineral only ($\text{Ln}K_{\text{dissol}}$), and equilibrium bracketing can hardly be done at low temperature because the reaction kinetics is too sluggish. The high compositional variability of low-grade minerals brings additional problems.

In order to improve on the situation, we have developed the approach of Vieillard (1982, 1988, 1994), based on the prediction of enthalpy of formation using the $\Delta H_{\text{O}^{2-}}$ cation parameter method on refined crystal structures of multisite components. We have calculated enthalpies of formation of a large number of silicates with different structures along several solid solutions joints. Results show good agreement with measured enthalpies for end-members in the $\text{Na}_2\text{O} - \text{K}_2\text{O} - \text{MgO} - \text{MnO} - \text{CaO} - \text{FeO} - \text{Fe}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ system at standard conditions, independently of crystal structure. Our approach allows computation of non-ideal behavior of cationic exchange, so that variations of H° of minerals with chemistry, but also with pressure and temperature can be modeled when refined crystal structures data are available.

When such refined structures are not available, we propose to constrain them with available thermodynamic data or with variations of structure observed in others minerals showing comparable solid solutions. Application to computation of excess enthalpy in solid solutions for low-temperature phyllosilicates, including clays minerals and solid solutions showing strong solvi, is in progress.