Acquiring thermodynamic data on mineral and organic systems and linking them with mobilities of elements in natural environments: an ongoing challenge

Fabienne Trolard[1*] & Guilhem Bourrié[2]

[1] INRAe, UMR 1114 Emmah, Avignon, France
[2] Académie d'Agriculture de France, Paris, France
*Corresponding author

Throughout the 20th century, chemists and mineralogists acquired basic data experimentally to characterize the enthalpies of formation of many inorganic and organic constituents identified on Earth. These works gave birth to thermodynamic databases, which are an essential link between thermodynamic chemical modeling and mobilities of elements in solutions in different pH and redox conditions.

If, as a first approximation, we can be satisfied with the values accumulated in the literature, quickly, when we study a particular system, we notice inconsistencies, contradictory results or even the propagation of errors over time.

To illustrate our point of view, two examples of such anomalies concerning major elements of Earth crust: Al, Fe, Si and H_2O, will be developed.

The first example concerns the Al_2O_3 - SiO_2 - H_2O system with the Halloysite - Kaolinite - Gibbsite parageneses. By this example, we show that in the literature, there is only one experimental value for the enthalpy of halloysite formation. However, by over-interpretation of the system and in particular in the definition of the degree of hydration of halloysite, other values have been proposed for this mineral. Based on these values, there are inconsistencies, which do not explain certain parageneses observed in nature.

Aluminum condensation in solution and its polymerization explains its solubility is more than 100 times the classical value based upon the monomeric model. The Gibbsite – Kaolinite – Quartz system was thus reevaluated.

The second example concerns the $Fe(OH)_2$ - H_2O system under alkaline conditions. In the literature, three solubility curves of $Fe(OH)_2$ are proposed. By acquiring new data in the laboratory, it was possible to demonstrate that the three curves were valid. The explanation was obtained from the analysis of the speciation of Fe in solution, which leads to different condensation pathways of the solution to the hydroxide. In this case too, in reducing and alkaline conditions, Fe(II) solubility is 100 times larger when polymerization occurs than predicted on the basis of the monomeric model. A better knowledge of speciation in solution is thus required to link thermodynamic properties of minerals and mobilities of elements in natural environments differing by P, T, pH and redox conditions.