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Fabienne Trolard, Guilhem Bourrie

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

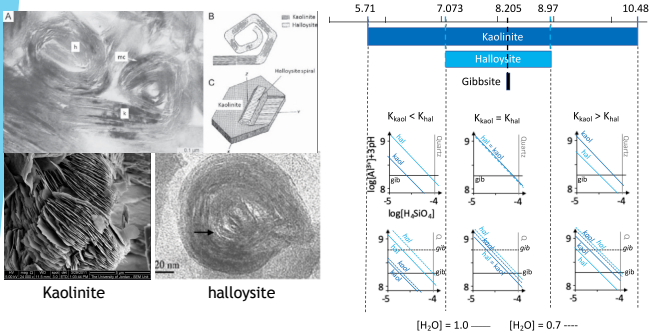
Fabienne TROLARD¹ & Guilhem BOURRIE²

INTRODUCTION 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.

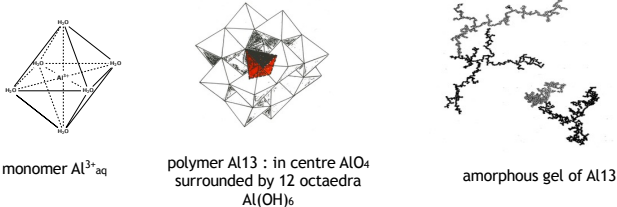
Two examples of such anomalies are developed here, concerning major elements of Earth crust: Al, Fe, Si and H₂O.

The Al₂O₃ - SiO₂ - H₂O system

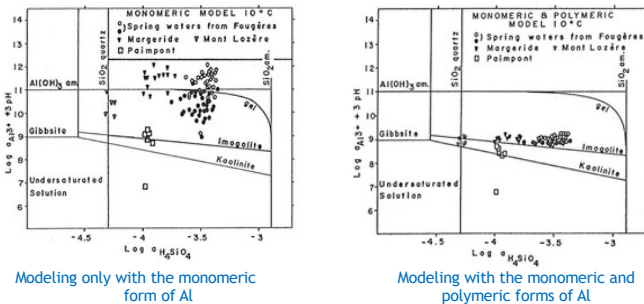
There is **only one experimental value** for the enthalpy of halloysite formation. However, by over-interpretation of the system and, in particular, in the definition of the degree of hydration of halloysite, other values have been proposed for this mineral.



When the solubility of kaolinite, at saturation, is larger than that of halloysite, there is a value of the activity of water from which the solubility of halloysite becomes larger than that of kaolinite. It is in this case that it is necessary to consider to represent simultaneous equilibria between halloysite and kaolinite (photo A).



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.



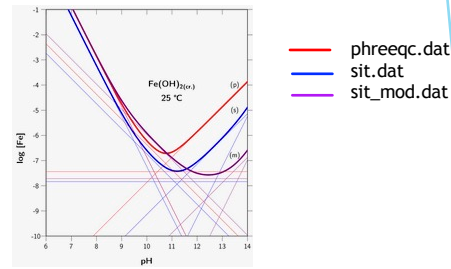
At 10 °C, spring water on granites with young soils from Fougères, Margeride, or from Mont Lozère, the Al₁₃ polymer must be considered in order not to obtain implausible supersaturations compared to amorphous aluminum hydroxide; at Paimpont, these are waters from podzols, acidic and undersaturated compared to gibbsite.

CONCLUSION 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.

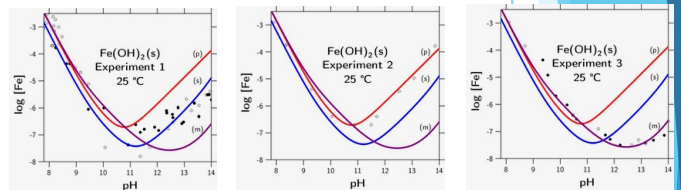
REFERENCES Ben Nacib et al., 2016, J. of Environ Sci & Engineering, A5, 383; Bottero et al., 1990, Chem Geol, 84, 308-310; Bourrié et al., 1981, Chem Geol, 76,403-417; Trolard et al. 1990, Chem Geol, 84, 294-297

The Fe - Fe(OH)₂ - H₂O system

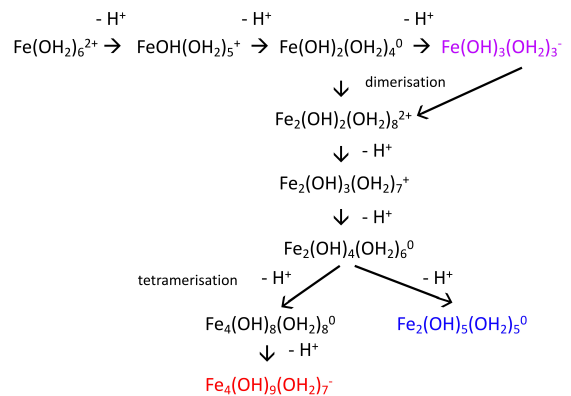
Under alkaline conditions, in the literature, **three solubility curves of Fe(OH)₂ compound** are proposed, depending on reference databases.



Experimental data



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 reducing and alkaline conditions, Fe(II) solubility is 100 times larger when polymerization occurs than predicted on the basis of the monomeric model.