Grand potential approach to water-swelling clay minerals

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Water-swelling of clay minerals is one of the most important phenomena that can be applied in many industrial fields related to agriculture, catalysis, petroleum, waste shielding, and so on. Many research efforts have been made for swelling properties of clay and clay minerals until now, and the knowledge of these properties has been accumulated, that is, for example, many micas and several some smectites does not seem to swell easily in a typical situation (and/or swelling is limited to some extent), or some of the others may exhibit unlimited swelling (i.e. nanosheets). For understanding of these phenomena more comprehensively using the numerical methods, we have investigated theoretical approaches to find equilibrium swelling-phases of such substance as a clay mineral.

In general, an environmental humidity should have an important influence to a swelling degree of clay minerals. For modelling this situation, we employ a grand ensemble picture where a clay mineral is connected to a particle reservoir of water molecules. In this picture, the environmental humidity, i.e. vapour pressure of water, is defined as the chemical potential parameter, μ, of a H_2O molecule, and each phase energy for finding a stable phase can be directly compared through the swelling energy, Ω, that has a grand potential scheme [1]:

$$\Omega(\mu,n) = E(n) - E(0) - n\mu$$

where $E(n)$ is the lattice energy of the swollen phase with n water molecules estimated by the first-principles density-functional theoretical (DFT) calculation. We present here an adaptation of this scheme to a model vermiculite swelling system with typical interlayer cations and discuss the swelling trend of them based on the DFT calculation results with related our previous works[2].

[1] Sholl and Steckel (2009) *Density Functional Theory, A Practical Introduction*. John Wiley & Sons Inc., New York (*Japanese translation text by Yoshioka Shoten is also available*). [2] Suehara and Yamada (2013) *GCA* **109**, 62-73; Suehara, Yamada and Sasaki (2012) *Phys. Rev. B* **85** 224203.