Clay molar volume variations during dehydration as a function of chemical composition, water activity and humidity

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This study is conducted in the context of deep buried petroleum reservoirs set at high temperatures and pressures. In some reservoirs, overpressures are observed and can be corroborated with the presence of clay minerals (smectites). We have investigated the role played by the release of water during smectite dehydration and how it relates to the genesis of observed overpressures.

Smectites are clay minerals belonging to the phyllosilicates 2:1 family. They have an unique feature which is to insert in their structure water molecules in amount depending on the temperature, the relative humidity, the water activity and the chemical composition. Those different hydration states confer them huge variations of molar volumes, in the order of 40% between a water saturated state and a dry state. It commonly accepted that this water, named interlayer water, has a density which is greater than about 5% of the density of free water but without any precise value.

The aims of this study are to estimate the molar volume variation of smectites as a function of their chemical composition and to calculate the density of interlayer water. All measurements are done on synthetic smectites in order to better control their chemical composition. The synthetic smectites are produced by making a gel which has a known stoechiometric composition and by crystallising the gel in hydrothermal conditions. Analysis made by transmission electronic microscopy (TEM) with an energy dispersive spectroscopy probe (EDS) enable to obtain the real chemical compositions of the samples. The calculations of the volumes are done with two different methods: firstly by an inverse method that consists in the indexation and inversion of X-ray diffraction patterns and secondly by the Rietveld method, that consists in simulating X-ray diffraction patterns and varying structural parameters such as cell parameters, atomic positions until both the experimental and simulated patterns fit.

We successfully synthesised Na-smectites. The first results of molar volume calculations show volumes variations as a function of the chemical composition and as a function of the hydration state. The order of the variations were in the order of 5vol% and 40vol% respectively for the two parameters. These preliminary results can be related to the influence of both parameters on the molar volume. These data have been completed with thermogravimetric measurements (TGA) of the released water in order to estimate the interlayer water density.