

# Hydrothermal experiments on clay minerals

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When we developed a new kind of diamond anvil cell [1], we had no idea that it would prove to be so useful in the study of clay minerals and how they influence the release and mobility of fluids in the Earth's crust and upper mantle. The new diamond anvil cell (DAC) allows us to observe changes in samples immersed in water at temperatures up to 1000°C and pressures up to 25 kbar (Figure 1). Although we have made many fascinating observations in this new DAC using a microscope, extending it to the study of clays by combining it with synchrotron radiation at CHESS has opened up some very promising avenues that can provide important new understandings of fluid-solid interaction in the Earth.

Understanding the behavior of the interlayer water in clay minerals is important because that water is released under the heating and compression that takes place during burial of sediments. The interlayer dehydration can cause overpressure in the pore space of rocks, affect the rock strength, and contribute to subsurface fluid flow. The flow of fluids in the pore spaces of rocks is important for mineral transport, and especially for the migration of hydrocarbons to trapping reservoirs in sedimentary basins. Water bound in clays may also be subducted along with the subducting lithospheric plates into the upper mantle. Thus, understanding the effect of temperature, pressure, and other variables on dehydration of clay minerals is of considerable importance in understanding a variety of geological processes.

We have turned our attention to montmorillonite, a clay mineral that is important because it carries a large amount of water and is also one of the most abundant hydrous minerals in buried sediments. Montmorillonite is a sheet silicate with very low negative charges on its sheets, charges that are balanced by cations filling the spaces between the sheets (Figure 2). Because of

the low charges, only a small number of cations fill the spaces and when they do, they carry with them envelopes or solvation shells of H<sub>2</sub>O molecules. These H<sub>2</sub>O molecules reside between the sheets forming discrete hydration states. These cations and their accompanying water molecules are readily exchanged when other cations are made available in the surrounding aqueous solution.

In order to carry out experiments on the retention and loss of water of hydration in montmorillonites, we place our sample in water along with an air bubble in a gasket consisting of a 500 μm diameter hole drilled in a 125 μm thick rhenium foil. We then trap the contents in the gasket hole between diamond anvil faces. The diamonds are heated by resistance heaters and the temperatures are measured by thermocouples attached to the outsides of the diamond anvils. Pressure is allowed to build up in the sample chamber as temperature is raised. If the gasket is prop-

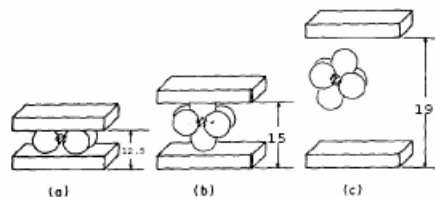


Figure 2. Schematic diagram of the structure of montmorillonite (inter-layer spacings in Å).

erly prepared, the volume of the sample chamber remains constant to within one or two percent. Pressure can then be determined with a precision of ± 300 bars from the equation of state of water.

The thickness of the water of hydration directly affects the (001) d-spacing of the montmorillonite and is therefore easily determined using energy dispersive x-ray diffraction. Experimentally, we pass a white beam of x-rays through our sample while it is heated and com-

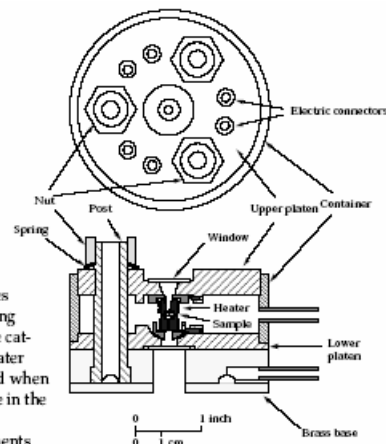


Figure 1. Diagram of the hydrothermal diamond anvil cell.

pressed in the DAC. An intrinsic germanium solid-state detector placed at a 2θ angle of 3° is used to collect the energy dispersive diffraction pattern (Figure 3). Less than a minute is required to collect enough information to measure the interlayer distances. This allows us to observe not only the changes in the layers of water but also the response rates when temperature and pressure are changed. The (001) basal d-spacings

measured by x-ray diffraction are about 19, 15 and 12.5 Å for third, second, and first hydration states. These hydration states are often referred to as the three, two, and one layer hydrates even though they do not correspond exactly to those number of layers.

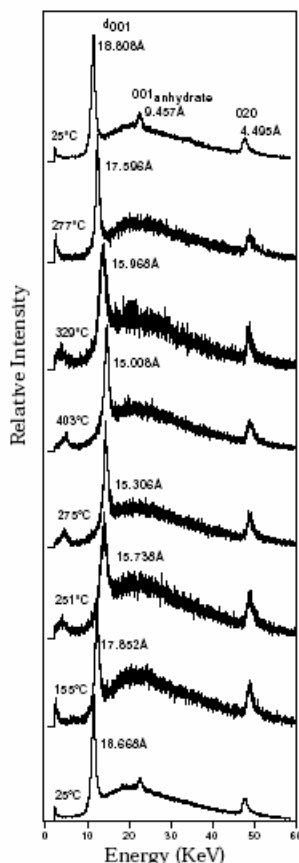
Dehydration and rehydration experiments have been performed on montmorillonites with Ca, Mg, and Na cations in the exchange positions. At pressures greater than 1 to 200 bars along the liquid-vapor coexistence curve (L-V), dehydration temperatures are rather insensitive to changes in pressure. Table 1 shows the temperature of the third-to-second hydration state conversion in each of our samples and the second-to-first hydration state conversion in Na-montmorillonite and Mg-montmorillonite. Our results show that these montmorillonites retain three layers of water

Cation	3 → 2	2 → 1
Na <sup>+</sup>	350-390 °C	485-500 °C
Ca <sup>2+</sup>	280-330 °C	-
Mg <sup>2+</sup>	200-250 °C	590-600 °C

(left, Table 1) The three-to-two and two-to-one layer dehydration temperatures for Mg, Ca, and Na montmorillonites at pressures greater than along the liquid-vapor curve of H<sub>2</sub>O.

up to 200-385 °C when water pressure is greater than along the L-V curve. The second layer of water is not released until 485-600 °C.

Although the dehydration temperatures above the L-V curve are not very sensitive to pressure, they are sensitive to the interlayer cation species. Mg-montmorillonite is found to have the



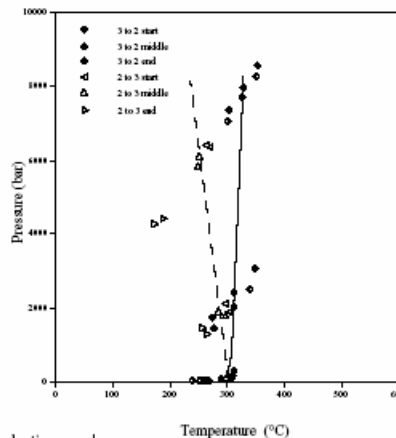
(Figure 3) Energy dispersive diffraction patterns of Ca-montmorillonite at increasing pressure and temperature in the diamond anvil cell on B-line at CHESS.

lowest dehydration temperature for three-to-two layer dehydration, even though it has the highest hydration energy in aqueous solution.

We interpret this as due to the screening effect of the water molecules in the primary solvation shell making the water molecules in the secondary or outer solvation shell rather loosely attached. The temperature of the two-to-one layer dehydration is in agreement with the trend of hydration energy of the various cations. This observation is consistent with our explanation since the conversion from two layers to one layer of water must break apart the first solvation shell.

Although our results show that pressure has little effect on the three-to-two layer dehydration with increasing temperature, they show that pressure has a strong effect on the two-to-three layer rehydration with decreasing temperature. This is especially well illustrated by the observations on Ca-montmorillonite (Figure 4). At the pressure of the L-V curve (1 to 200 bars), two-to-three layer rehydration takes place at the same temperature as the three-to-two layer dehydration. At 7000 bars rehydration takes place 80 °C lower than dehydration. The mechanism responsible for this hysteresis is not clearly understood at this time but almost certainly has to do with the effect of the structure of the water and location of the interlayer cations on the activation energy for the reaction.

Our observations that montmorillonite with three-layer hydrate is stable at high pressure up to 200-380 °C is important for sedimentary basin and petroleum generation modeling. So far, most people have assumed that when clays release water, there are only two layers of water being released. Our results indicate that for any water-releasing reaction shallower than 5 km, the three-layer hydrate probably dominates and may be responsible for the release of 33% more water and at considerably higher temperatures than previously thought. Another



(Figure 4) Experimental data of three-to-two layer dehydration and two-to-three layer rehydration of Ca-montmorillonite. The solid line connects midpoints of dehydration and the dotted line connects midpoints of rehydration.

consequence of our observations concerns the mechanical properties of montmorillonite clays. Our results show that those clays are expected to remain ductile down to considerable depths where they may be the best candidate to form good seals for deep oil reservoirs.

Our results also show that clays with two layers of water are stable up to 450-600 °C and with one layer of water up to even higher temperatures when the pressure is higher than the H<sub>2</sub>O L-V curve. The release of this remaining water may play an important role in transporting water to great depths in the subduction of ocean floor sediments into the Earth's mantle. Dehydration in subducting slabs is considered to be an important cause of earthquakes as well as the source of volatile materials that create volcanic activity along some of the boundaries of tectonic plates.

[1] Bassett, W.A., Shen, A.H., Bucknum, M., and Chou, I.-M. (1983) A new diamond anvil cell for hydrothermal studies to 2.5 GPa and from -190 to 1200 °C. *Rev. Sci. Instrum.* 64, 2340-2345.