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Pressure-Induced Water Insertion in Synthetic Clays[**]

Shujie You, Daniel Kunz, Matthias Stöter, Hussein Kalo, Bernd Putz, Josef Breu,* and Alexandr V. Talyzin*

Clays of the 2:1 structure family (e.g. montmorillonite, saponite, hectorite, or vermiculite; for nomenclature of clay minerals see Martin et al.[1]) are among the most important industrial materials and among the most abundant minerals on earth. One of the most intriguing properties of clays is their ability to swell (hydration of the interlayer) which affects all possible applications of these materials. Clay rocks are formed in nature by sedimentation and it is commonly supposed that water is released from hydrated clays under the influence of pressure increase, gravitational compaction, and formation of rock deposits. Here we demonstrate, however, the counterintuitive effect of pressure-induced water insertion into the interlayer space of a synthetic smectite (Na-hectorite) which occurs as reversible phase transition at about 1.7 GPa. Pressure-induced swelling of clay materials reported here is very similar to earlier discovered pressure-induced swelling of graphite oxide, thus suggesting that it is a general phenomenon typical for hydrophilic layered compounds.

Swelling as a general phenomenon was historically first discovered for graphite oxide (GO), a synthetic hydrophilic layered material obtained by strong oxidation of graphite, and only later re-discovered for clay minerals.[2] We have earlier observed that graphite oxide demonstrates a counter-intuitive pressure-induced water insertion and marks the first example of a layered material showing stronger hydration (swelling) at elevated gigapascal pressures.[3] From a geochemical point of view, it would be rather interesting, if pressure-induced water insertion similar to what was previously observed for GO, could also be found for clay minerals. If pressure-induced swelling of clays could indeed be established, it would have important implications in industry and for diverse phenomena occurring in nature. For instance, water-rich clay layers could be formed underground at certain depths, or in case of organoclays similar effects could possibly be relevant for oil accumulation (e.g. in clay-containing shales[4]) or as "sealing" material for oil deposits. It can also be expected that materials which exhibit the ability to structural breathing related to hydration/dehydration under variation of external conditions, could be highly suitable as environment for the accumulation of organic matter and thus could be an interesting facet in clay-related theories for the origin of life.[5,6]

Graphite oxide and clay minerals demonstrate a lot of similarities with respect to their swelling behavior in water since both are hydrophilic layered materials. Clay materials consist of negatively charged layers and charge neutrality is warranted by interlayer cations. It is the subtle balance between the solvation enthalpy of these cations and the electrostatic attraction between the two-dimensional polyelectrolyte and positive interlayer species that controls swelling. In a first approximation swelling of individual interlayers is decoupled but within a given interlayer discrete degrees of swelling must be realized. Only if the charge density and thus the concentration of interlayer cations is homogeneous, intracrystalline reactivity is uniform within a stack of layers (tactoid) and the degree of swelling is uniform throughout the tactoid. In this case, "crystalline" swelling is observed and water is, for instance, inserted in a well-defined stepwise fashion of discrete numbers of monolayers (1–3 water layers, 1 WL, 2 WL, and 3 WL).[7,8] The incremental increase of the basal spacing corresponds to the size of densely packed layers of water molecules (about 3 Å at ambient pressure). Hydration/dehydration cycles involve an activation energy and are expected to show hysteresis.[8] Graphite oxide also exhibited the ability of crystalline swelling (in alcohols) and pressure-induced insertion of an additional solvent layer under high-pressure conditions.[9]

The detailed mechanism of pressure-induced solvent insertion is not yet known. However, it is likely connected to a higher density of water confined between graphene oxide layers compared to the density of bulk water, the surrounding liquid medium. High pressure favors stronger dissociation of functional groups attached to graphene oxide which get hydrated thus forming the phase with higher density.[10] The swelling was also found to be significantly stronger for electrolyte solutions.[11]

Because of the similarities, the phenomenon of pressure-induced water/solvent insertion could be anticipated to be found as well in clay minerals which exhibit a strong ability to swelling. However, natural clay minerals are well-known to suffer from charge heterogeneities.[12] As a consequence, individual interlayers within a tactoid tend to adopt different discrete swelling states at any given activity of water, a phenomenon called random interstratification. X-ray diffraction then averages over the different basal spacings encountered in the tactoid and precise characterization of hydration/dehydration of clays is hampered by interstratifi-

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[*] Dr. S. You, Dr. A. V. Talyzin
Department of Physics, Umeå University
90187 Umeå (Sweden)
E-mail: alexandr.talyzin@physics.umu.se

D. Kunz, M. Stöter, H. Kalo, B. Putz, Prof. J. Breu
Lehrstuhl für Anorganische Chemie I, Universität Bayreuth
Universitätsstrasse 30, 95447 Bayreuth (Germany)
E-mail: josef.breu@uni-bayreuth.de

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cation because the underlying discrete stepwise swelling behavior is masked by this averaging effect.

Therefore, we performed our study of pressure effects on hydration/dehydration of clays using a certain type of synthetic smectite, namely Na-fluorohectorite (Na-Hect). The advantage of these melt-synthesized hectorites is their homogenous charge density which transforms into a uniform intracrystalline reactivity.[13] The structures of 1 WL and 2 WL hydrates of Na-Hect were recently solved using single-crystal methods (Figure 1).[14,15] Hectorites with interlayer cations of higher hydration enthalpy than Na$^+$, for example, Mg hectorite, are known to adopt the 3 WL hydration state.[13]

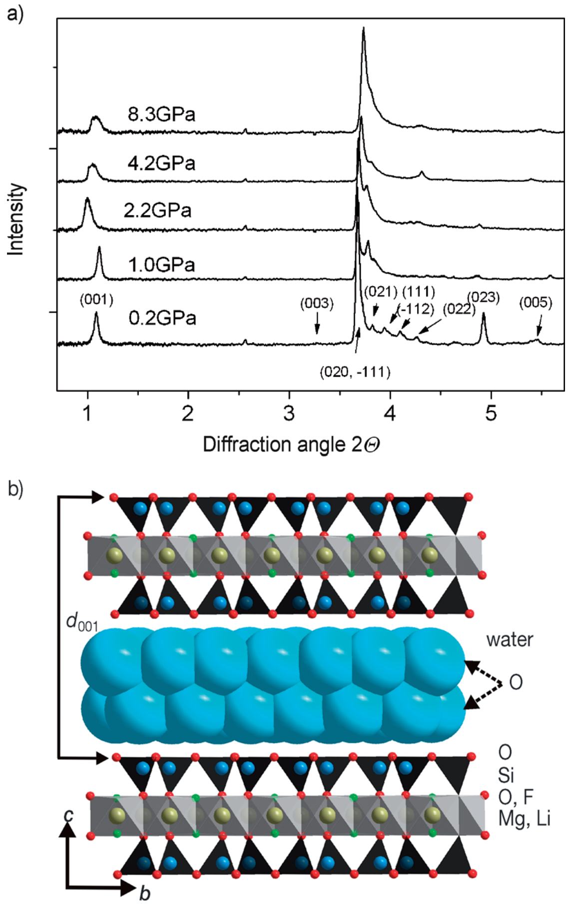

Figure 1. a) XRD patterns recorded from Na-Hect upon pressure increase ($\lambda = 0.29036$). Indexing of a 0.2 GPa pattern is according to the 2 WL structure (C2m, $a = 5.22$, $b = 9.07$, $c = 15.34$ Å, $\beta = 96.38°$). b) Structure of 2 WL Na-Hect under ambient conditions.

The results of our experiments with Na-Hect pressurized in the presence of an excess of liquid water show that the phenomenon of pressure-induced hydration is not limited to graphite oxide. The ability of synthetic smectites to swell stronger under gigapascal pressure conditions provides strong evidence that similar effects will be found in natural clay minerals in future.

Na-Hect was synthesized according to procedures published earlier[14–17] and loaded with an excess of liquid water into a diamond anvil cell (DAC) together with a piece of gold wire for pressure calibration. X-ray diffraction (XRD) patterns were recorded with 0.1–0.3 GPa steps up to 8.5 GPa.

The XRD pattern recorded from a sample loaded into the DAC at a first pressure point (0.2 GPa) could be indexed, as expected, using the 2 WL structure of Na-Hect and refined cell parameters were in good agreement with previously published data.[14]

Compression of this sample resulted in dramatic changes of the Na-Hect structure as shown in Figures 1 and 2. The 2 WL Na-Hect structure consists of rigid 2:1 layers intercalated by hydrated Na$^+$ cations. Relatively weak non-covalent bonding along the stacking direction (c^*) results in a strong compressibility along c^* whereas strong bonding in the 2:1 layer assures a small in-plane compressibility. Therefore, the volumetric compressibility is defined almost entirely by the change in the interlayer distance (basal spacing). The pressure dependence of interlayer distance (d) can be evaluated using the (001) reflection, the strongest in the (00ℓ) series. The pressure dependence of $d(001)$ shows a sharp anomaly around 1.7–2.2 GPa (Figure 2). The compressibility of Na-Hect along the c^* direction first follows a linear trend and $d(001)$ decreased approximately by 1 Å when reaching 1.7 GPa. It can also be noted that shear forces induced by compression introduced stacking faults: whereas the pristine material is three-dimensionally ordered as indicated by successful indexing, at 1 GPa only *hk* bands (e.g. 02 band) are preserved besides the basal reflections. This indicates that the well-defined phase relation between adjacent layers is lost and re-arranged into turbostratic stacking is realized (Figure 1). Note that the structural order along c^* is, however, fully preserved as indicated by symmetric, sharp, and rational basal reflections (00ℓ).

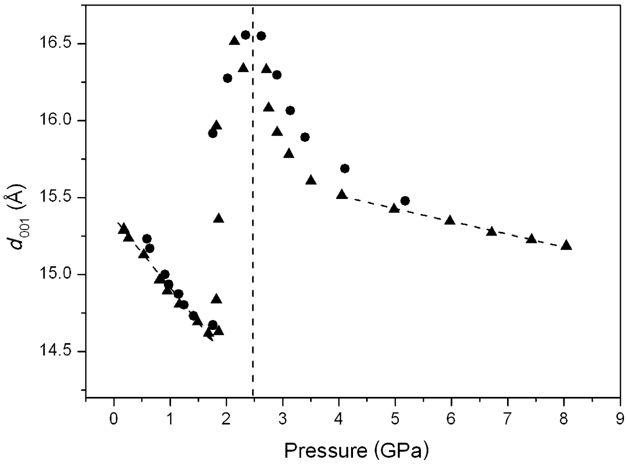

Figure 2. Pressure dependence of the (001) peak position in two consecutive cycles: -▲- first pressure increase, -●- second pressure increase. The vertical dashed line shows the pressure point of water solidification.

At 1.7 GPa a sharp and step-like increase of $d(001)$ is observed. At this pressure point we recorded several diffraction images since the d spacing was increasing with time, reflecting the kinetics of a phase transition into an expanded phase. The change in the *d* spacing is about 2 Å and corresponds well with what would be expected for a pressure-induced insertion of one additional layer of water at this pressure. It should be noted that the water medium surrounding the tactoids remained liquid at this pressure point and did not solidify until around 2.2 GPa with a consequent phase transition into the ICE VII phase. The pressure of water solidification observed in our experiments is higher compared to the well-known equilibrium phase diagram of water (1 GPa). However, it is known that water can be overcompressed and sometimes remains in liquid phase at significantly higher pressures.[18] Solidification pressures in the range of 1.4–2.2 GPa were also observed in our earlier experiments with graphite oxide[11] and it seems that the presence of a powder influences the nucleation of the solid phase.

The anomalous pressure region with respect to the *d*(001) dependence is completed at around 2.6 GPa and above this pressure the system returns to the expected standard compression trend with a similar slope as observed before the hydration phase transition. XRD patterns recorded at pressures above 2.6 GPa are entirely described by co-existing phases of ICE VII and the high-pressure 3 WL Na-Hect phase. However, an additional change of the slope is observed around 3.5 GPa. Beyond that pressure point the system is again compressed with linear *d*(001) dependence at least up to 8 GPa.

The sharp anomaly observed in Figures 1 and 2 is interpreted in our study as a phase transition from the 2 WL into the 3 WL structure. The phase transition is found to be completely reversible, the decompression of the Na-Hect/water sample resulted in a de-insertion of the additional third water layer and a return to the pristine 2 WL structure. The same sample was subjected also to a second cycle of compression–decompression which appeared to be almost identical to the first cycle.

Analysis of the pressure dependence of the full-width at half-maximum (FWHM) of the (001) reflection further corroborates the interpretation of the anomaly as a change of the hydration state. The transition from the 2 WL to the 3 WL hydrate structure, as any first-order phase transition, is connected to an activation barrier[8] and the kinetics involved will impede an infinitely sharp transition. Nevertheless it is expected that co-operativity will assure that every individual interlayer space at the transition pressure is either 2 WL or 3 WL. Consequently, even synthetic clays with a uniform intracrystalline reactivity will represent a randomly interstratified material of 2 WL and 3 WL exactly at the transition pressure. According to Mering's principles,[19] interstratification will immediately show up as a major contribution to the FWHM. Figure 3 shows that the low-pressure 2 WL phase has a sharper (001) reflection compared to the high-pressure 3 WL phase, and moreover, that at the transition point the FWHM goes through a pronounced maximum. This significant broadening of the (001) peak can be explained by the simultaneous co-existence of individual interlayers with a different number of inserted water layers within the same tactoid (interstratification). The different magnitude and slop of the FWHM as a function of the pressure below the 2 WL/3 WL phase transition and above the pressure point of water solidification most likely is related to different stress/strain-broadening in liquid and ice media, respectively. A linear increase of the FWHM at higher pressures is a well-known effect, which is explained by stress increase upon compression at non-hydrostatic conditions.

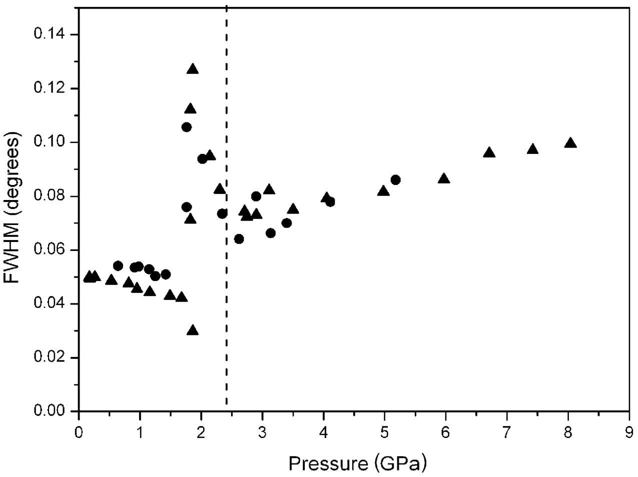

Figure 3. Pressure dependence of the FWHM of the (001) reflection in two compression cycles. -▲- first pressure increase, -●- second pressure increase. The vertical line shows the point of water solidification.

As noted above, the anomaly observed around 1.7 GPa is interpreted as pressure-induced insertion of an additional layer of water into the interlayer space. This interpretation is further supported by a control experiment in which we compressed the Na-Hect sample in methanol instead of aqueous media. It should be noted that a methanol/ethanol mixture is the standard medium for high-pressure experiments because it remains liquid over a broader pressure range and therefore is capable to provide conditions of compression close to hydrostatic. The interlayer distance calculated from the (001) peak position at 0.1 GPa in methanol media was found at 15.75 Å and decreases upon compression. It should be noted that although we used anhydrous methanol for these experiments, some trace amounts of water could have been present since the sample was loaded into the DAC in air and since the sample was stored in air. However, it is clear that compression of Na-Hect in methanol medium is profoundly different as compared to the Na-Hect/water system (Figure 4). No pressure-induced insertion of methanol is observed up to 8.5 GPa. The change of the slope in the pressure dependence of the (001) reflection at around 3.5–4 GPa is likely to correspond to methanol solidification. It is not possible to determine exactly the pressure point of methanol solidification using XRD since it is known to solidify into an amorphous phase under high-pressure conditions and strong variations of the solidification pressure point were reported in the literature.[20,21] Figure 4 provides clear evidence that the Na-Hect structure is stable upon compression in hydrostatic conditions and no pressure-induced insertion of methanol occurs in Na-Hect. In this respect the Na-Hect is different from graphite oxide which exhibits pressure-induced insertion for both water and methanol.

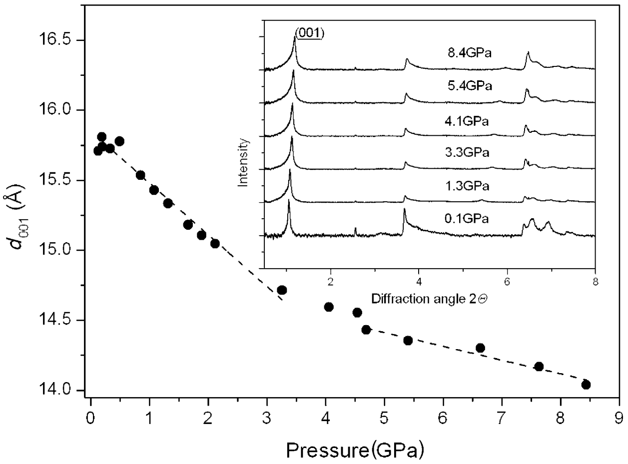

Figure 4. Pressure dependence of *d*(001) for the Na-Hect sample compressed in methanol medium. The inset shows XRD patterns recorded at different pressures.

It can be noted that graphite oxide in the "dry" state does not contain interlayer cations which appear only as a result of hydration and dissociation of certain functional groups attached to graphene oxide sheets. The dissociation is affected by a pressure change and the number of cations is one of the variables which affect pressure-induced phase transformations. Hectorites are obviously materials with a certain number of cations which does not change upon compression and observed structural changes are controlled entirely by hydration effects.

Otherwise, high-pressure behavior of Na-hectorite in water media shows surprisingly strong similarities to graphite oxide compression in liquid medium considering a rather different chemical composition and structure of these two types of materials. Crystalline swelling with pressure-induced insertion of an additional solvent layer (not correlated with the pressure point of liquid medium solidification) was observed previously for GO immersed in methanol, ethanol, DMF (dimethylformamide), and acetone.[9,22–23] Similarly, well-defined step-like insertion of an additional solvent monolayer is observed at a certain pressure for Na-Hect immersed in water and shows no correlation with medium solidification. It should be noted that GO compression in water results in gradual lattice expansion and in aqueous solutions it shows a behavior similar to osmotic swelling of clay minerals.[3,10]

Despite completely different compositions and structures of Na-Hect and graphite oxide, both of them can be considered as hydrophilic layered materials capable to insert different numbers of solvent layers. As it is found in two very different kinds of materials, it can be concluded that pressure-induced water insertion is a general phenomenon for hydrophilic layered structures. Many other kinds of layered materials which exhibit swelling at ambient pressures (e.g. layered titanates[24] or manganese oxides[25]) could possibly be tested for pressure-induced water insertion in the future. As noted in the introduction, pressure-induced swelling of synthetic and natural clay minerals could have enormously important implications for various applications and natural processes. Especially exciting appears the possibility of pressure-induced swelling of clays in nature. The range of pressures where the insertion of additional solvent was so far found for graphite oxide and Na-hectorite (0.1–1.7 GPa) is expected to broaden with further materials being tested, eventually providing a wide range of possible environments where this effect can be observed. It should be mentioned again that the phase transition into an expanded (stronger swollen) phase is completely reversible.

In summary, Na-Hect immersed in an excess of water is found to exhibit a pressure-induced structure expansion at around 1.7 GPa. This phase transition is reversible and attributed to the insertion/de-insertion of additional water layers driven by variations of pressure. The phenomenon of pressure-induced water insertion in synthetic smectite materials reported here is qualitatively similar to what has been discovered by us earlier with graphite oxide.[5,11] Since the structures and compositions of smectites and graphite oxide are very different, it appears that pressure-induced insertion of additional solvent from liquid media is a quite general phenomenon for hydrophilic layered materials. It can be expected that similar pressure-induced swelling will be found for other hydrophilic layered materials, including possibly some natural clay minerals.

Experimental Section

In situ high-pressure X-ray diffraction experiments of samples immersed in water were performed in DAC equipped with beryllium seats using synchrotron radiation at the PETRA III, beamline P02.2 ($\lambda = 0.29036$). Preliminary experiments were also performed at the ELETTRA X-ray diffraction beamline. The well-grinded powder sample was loaded into a 0.3 mm sized hole in a stainless steel gasket and then excess water or methanol was added. Distilled water and anhydrous 99.8% methanol were used for loading. A gold wire was added for pressure calibration. The pressure was increased in steps of 0.1–0.3 GPa up to 8–8.5 GPa. The Fit2D software was used to integrate the diffraction images into diffraction patterns.

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