A role for subducted super-hydrated kaolinite in the Earth's deep water cycle.

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Water is the most abundant volatile component in the Earth and influences both physical and chemical properties of the Earth materials. It continuously enters the Earth through subduction zones where it reduces the melting temperature of rocks to generate magmas while the rest travels further deep into the Earth. Our understanding of the water cycle in the Earth has emphasized dehydration processes along the subduction zones. Here we show that the formation and subsequent breakdown of super-hydrated kaolinite have important implications for water transport, volcanism, and possibly seismicity along the subduction zones. We measured *in-situ* and time-resolved high-pressure/high-temperature synchrotron X-ray diffraction and infrared spectra to characterize

structural and chemical changes of kaolinite at conditions corresponding to those found in subduction zones. Synchrotron X-ray powder diffraction patterns of kaolinite at 2.7(1) GPa after heating to 200 °C in the presence of water, a condition corresponding to a depth of about 75km in cold slabs, show the appearance of a reflection with a d-spacing near 10Å which arises from pressure-induced insertion of water. This new super-hydrated phase of kaolinite has a ~31 % larger unit cell volume and a ~ 8.4% lower density than the original kaolinite and has, with 29 weight-% H₂O, the highest water content of any known aluminosilicate mineral in the Earth. As pressure and temperature approach 19 GPa and ca. 800 °C, we observe the sequential breakdown of super-hydrated kaolinite to phase-Pi, diaspore, and topaz-OH along with the formations of coesite and stishovite. Breakdown of super-hydrated kaolinite in cold slabs subducted below 200 km then leads to the release of water that may further affect seismicity and help fuel arc volcanism at the surface.

Current predictions of the global H₂O flux into the deep mantle amounts to about one ocean mass over the age of the Earth¹. Present-day estimates for the subduction efficiency reveal that ca. 68% of subducted water outgasses through arc volcanism¹⁻⁵. Trapped in the oceanic sediments or oceanic crust in hydrous minerals⁶ containing H₂O molecules or OH⁻ groups such as serpentine⁷, lawsonite^{8,9}, phlogopite¹⁰, and amphibole¹¹, 68% of the subducted water is released at different depths along the subduction zone: amphiboles at 75 km, phlogopite at 200 km and lawsonite at 300 km¹². Hyndman et al. (1997) demonstrated that clay sediments at the slab surface control the updip limit of a seismogenic zone in subduction thrust faults¹³. Interestingly, the temperature ranges of phase transformation from smectite to illite/chlorite coincide with this updip seismogenic limit. At depths between 410 and 660 km in the Earth's mantle transition zone, the presence of water-containing minerals such as wadsleyite and ringwoodite induce further dehydration melting¹⁴⁻¹⁶. Dehydration embrittlement where released aqueous fluids induce brittle shear failure at elevated pressures after creating a positive volume change has recently been reconsidered as a viable mechanism for nucleating earthquakes independent of depth provided hydrous minerals breakdown under differential stress^{17,18}.

Kaolinite [Al₂Si₂O₅(OH)₄] is the most abundant mineral of the kaolin-group making up between 5% and 60% of the oceanic sediments^{19,20}. There are few high-pressure and high-temperature studies of clay

minerals, although their behavior at moderate pressures and temperatures, especially under cold subduction zone conditions²¹, is extremely important to understand and model water transport and recycling in the Earth. Using X-ray diffraction and infrared (IR) spectroscopy, Laiglesia²² observed that kaolinite partially loses its crystallinity between ambient pressure and 2 GPa indicative of stacking faults perpendicular to the *c*-axis during compression. In a Raman study of dickite, Johnston, et al.²³ reported the observation of pressure-induced changes in the local environment of OH groups above 1.9 GPa. They also detected a reversible phase transformation to a high-pressure dickite phase above ~ 2.6 GPa, where both the stacking sequence and hydrogen bonding topology are altered. Recently, the existence of two high-pressure kaolinite polytypes were established by Welch and Crichton²⁴: kaolinite-I (the ambient polytype) which transforms to kaolinite-II near 3.7 GPa, which is stable up to 7 GPa, above which it transforms to Kaolinite-III. These polytypic transformations change the stacking vector sequence of the aluminosilicate sheets (Supplementary Figures 1-3).

Pressure-induced hydration (PIH) and the formation of super-hydrated phases has been established in numerous porous materials such as the small pore zeolites natrolite, scolecite and mesolite containing various mono- and divalent cations as extra-framework cations, as well as in synthetic clays such as Na-hectorite²⁵⁻²⁷. At elevated temperatures and pressures PIH occurs in laumontite^{28,29}, an important hydrous mineral found in low-grade metamorphic conditions along subduction zones. Using *in-situ* and *ex-situ* high-pressure X-ray powder diffraction and IR spectroscopy we report the observation of PIH in kaolinite above 2.5(1) GPa and 200°C and its sequential breakdown at higher pressures and temperatures. These are conditions, which exist along the subduction zones where water transport and release occurs, possibly inducing volcanism and seismicity.

Kaolinite in water under high pressures and temperatures

A kaolinite sample (from Washington County, Georgia, KGa-1b from the Source Clays of the Clay Mineral Society) is heated at 200°C for 1hr at 2.7(1) GPa in the presence of water to mimic conditions found along subduction zones (Fig. 1). Synchrotron X-ray powder diffraction pattern reveal the appearance of a new (001) reflection with d-spacing ~10Å concomitantly to the intensity of the original (001) reflection with

d-spacing $\sim 7\text{\AA}$ decreasing (Fig. 1a). This expansion of the basal (001) reflection is caused by water intercalation between the kaolinite layers. This new super-hydrated and expanded phase is stable over a temperature range between ca. 200 and 500 °C at pressures between ca. 2.5(1) and 5.0(1) GPa (Fig. 1b and Supplementary Figure 4). After pressure release, the (001) reflection with d-spacing $\sim 10\text{\AA}$ disappears indicating a reversible water intercalation process. Changes in the lattice parameters and unit cell volumes throughout this transition are depicted in Fig. 2 (Supplementary Table 3). The *c*-axis length contracts gradually by 0.12(1) Å while the *a*- and *b*-axis contract by 0.05(2) Å up to pressures near 2.5(1) GPa (Fig. 2a). Such an anisotropic contraction is also found in smectite²⁶. Above 2.7(1) GPa and heating at 200°C for 1 hour, the *c*-axis length increases by about 32 % while the *a*- and *b*-axis lengths decrease by 1.96 % and 0.52 %, respectively (Fig. 2a). This results in the expansion of the unit cell volume by ca. 31 % (Fig. 2b). This now super-hydrated kaolinite appears to be less resistant to pressure showing a smaller bulk modulus of $K_0 = 49.80(1)$ GPa compared to $K_0 = 57.38(1)$ GPa for kaolinite before the water intercalation. The calculated density of the super-hydrated kaolinite is also found to be lower than the original phase at ambient conditions, i.e., 2.48(6) g/cm³ vs. 2.61(1) g/cm³ (Fig. 2b). The lower density and bulk modulus of super-hydrated kaolinite compared to the original phase at ambient conditions indicates it might be further transformed or break down into dense phases at higher pressures and temperatures along the subduction zone.

Time-resolved study of kaolinite during super-hydration

We monitored changes during pressure- and temperature-induced expansion and super-hydration in kaolinite using time-resolved synchrotron X-ray powder diffraction in the presence of H₂O as a pressure transmission medium. Time-dependent XRD patterns measured after ramping the temperature to 200°C at 2.7(1) GPa are shown in Fig. 1c and show that the intensity of the original kaolinite (001) reflection with d-spacing of $\sim 7\text{\AA}$ decreases over time whereas that of the super-hydrated kaolinite (001) reflection at a d-spacing $\sim 10\text{\AA}$ grows concomitantly. At the same time, we observe a decrease in the intensity of the ice VII (110) reflection as the temperature reaches its melting point of 165°C at 2.7(1) GPa³⁰. It is interesting to note that the time-dependent changes in the intensities of the kaolinite basal reflections are continuous while the intensity of the ice VII (110) reflection decreases in steps and disappears.

In order to further elucidate the kinetics of water intercalation and formation of the super-hydrated phase, we have modeled the reaction pathway using the classical Avrami equation $\alpha = 1 - \exp(-kt^n)$, where t is time, k is the rate constant, and n is the Avrami exponent³¹⁸. We followed the time-dependent isothermal decay of the basal (001) intensity of the original phase (I_t) while setting the zero-time intensity (I_0) as a reference so that $\alpha = 1 - (I_t/I_0)$. The reaction order, n , for the conversion of kaolinite to its super-hydrated phase is derived to be 0.55(3) with a k value of $9.0(3) \times 10^{-3}$ (see Supplementary Fig. 5). In previous work a n value in the range of 0.4 to 0.8 was seen as an indication for a heterogeneous nucleation and growth mechanism³². This supports the notion that the formation of the super-hydrated phase involves the migration of water molecules into the interlayers and proceeds in a topotactic manner from the original kaolinite structure. The dehydroxylation of kaolinite also revealed a diffusion-controlled process ($n \sim 0.5$)³³ as did the swelling behavior of the “10Å -phase” of talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$) in the presence of water and acetone ($n \sim 0.63$)³⁴. It is, however, important to note the structural and chemical differences between kaolinite and talc during super-hydration. In kaolinite, water intercalation proceeds by a weakening the hydrogen bonding between dioctahedral sheets under pressure and temperature whereas in talc, water-intercalation and formation of the “10Å -phase” is preceded by a hydrophobic to hydrophilic conversion of van der Waals bonded tri-octahedral sheets.³⁵⁻³⁷

Structural model of super-hydrated kaolinite

The structural model of the super-hydrated kaolinite has been derived using Rietveld refinements of synchrotron X-ray powder diffraction data taken at 4.1(1) GPa after heating at 200 °C. The measured diffraction peaks are indexed in space group CI , the same as the original kaolinite. Using the starting structural model of Bish and Von Dreele³⁸, difference-Fourier synthesis revealed maxima of electron densities between the layers (Fig. 3a). Subsequent modeling and refinement of the electron densities by the oxygen atoms of the H_2O molecules at three distinct interlayer sites results in a chemical composition of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2.97(2)\text{H}_2\text{O}$ (Supplementary Table 4). Details of the crystallographic models are summarized in the Supplementary Tables 4 and 5. The structural model of the super-hydrated kaolinite sheds new light on the origin of the hydrated analogue of kaolinite, halloysite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$]. Our experimental data show that when halloysite is compressed in the presence of water, the intensity of its basal

reflection at $d \sim 10\text{\AA}$ increases, indicating that additional water insertion forms a phase similar to the super-hydrated kaolinite with 3 H_2O molecule per unit cell (Supplementary Fig. 2b). It is also interesting to note the contrasting morphology of kaolinite and halloysite at ambient conditions. While kaolinite is platy (Supplementary Fig. 1a), halloysite is known to be a natural nanotube mineral. *In-situ* TXM studies are underway to elucidate the possible change in morphology from kaolinite to super-hydrated kaolinite.

Infrared spectroscopy on super-hydrated kaolinite

Hydroxyl vibrations of kaolinite are indicators of the changes in the interlayer hydrogen bonding and water intercalation under pressure and at elevated temperatures. IR reflectivity spectra were measured following decompression from the super-hydrated kaolinite at 3.5(1) GPa after heating to 200°C (Fig. 3b). Kaolinite at ambient conditions displays four characteristic OH^- stretching bands at 3620 cm^{-1} , 3655 cm^{-1} , 3669 cm^{-1} and 3695 cm^{-1} , respectively. The single OH^- band at 3620 cm^{-1} (red dotted line in Fig. 3b) corresponds to the inner OH group while the other bands (blue dotted line in Fig. 3b) indicate the coupled vibrations of the interlayer OH group³⁹. For halloysite, on the other hand, the IR spectra are characterized by two broad bands near 3695 cm^{-1} and 3620 cm^{-1} , while an additional weak band observed near 3550 cm^{-1} is only found in the hydrated form at ambient conditions^{40,41}.

In excellent agreement with the XRD results, the major changes in the OH^- stretching bands occur between 1.9(1) GPa and 2.7(1) GPa after releasing pressure from 3.5(1) GPa (Fig. 3b). Further decompression to ambient conditions results in the shifts of all OH^- stretching bands to lower wave numbers. Additionally, all the stretching bands attributed to the vibrations of the hydroxyls in kaolinite broaden prior to the formation of the super-hydrated kaolinite, which we interpret as being due to an increase in stacking disorder between the kaolinite layers, consistent with the anisotropic broadening effects observed in our and previous XRD studies^{22,42}. The IR reflectivity spectra of super-hydrated kaolinite above 2.7(1) GPa show a distinct OH^- stretching band near 3543 cm^{-1} (purple dotted line in Fig. 3b), which is assigned to the OH^- stretching mode of intercalated H_2O molecules and bears similarity to the band observed in the hydrated halloysite at ambient conditions^{41,43}.

In addition, a new OH^- band at 3649 cm^{-1} (green dotted line in Fig. 3b) and the absence of OH^- bands at

3655 cm^{-1} and 3669 cm^{-1} are characteristic features observed in the super-hydrated kaolinite. After pressure release, all the stretching bands of the super-hydrated kaolinite revert to those found in well-crystallized kaolinite at ambient conditions.

Stability of super-hydrated kaolinite

In order to probe the stability of super-hydrated kaolinite at pressures and temperatures up to 19 GPa and 800 °C, synchrotron X-ray powder diffraction experiments were performed using a diamond-anvil cell equipped with a graphite resistive heater. As suggested by the decrease of density and bulk modulus with increasing pressure, super-hydrated kaolinite breaks down to phase Pi ($\text{Al}_3\text{Si}_2\text{O}_7(\text{OH})_3$)⁴⁴ and coesite (SiO_2) at 6.5(1) GPa and 510 °C. At 7.7 (1) GPa and 650 °C a mixture of diasporite ($\alpha\text{-AlOOH}$)⁴⁵, phase Pi and coesite coexist, which at 16.2 (1) GPa and 780 °C transform to a mixture of topaz-OH ($\text{Al}_2\text{SiO}_4(\text{OH})_2$)⁴⁶ and stishovite (SiO_2) (Fig. 1b, 1d, and 4). An inset diagram in Fig. 1b shows the relationship between super-hydrated kaolinite and other hydrous phases known in the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (ASH) system. Super-hydrated kaolinite is the most hydrated aluminosilicate mineral and its formation and sequential breakdowns are important new results to explain the origins of other mantle minerals in the ASH system. During the breakdown of super-hydrated kaolinite to phase Pi and coesite, water de-intercalates at pressures and temperatures corresponding to a depth near 200 km in a cold subducting slab (Fig. 4). The hydroxyl group remains present throughout the breakdowns to phase Pi, diasporite, and topaz-OH transitions, which occurs at depths between 200 and 480 km.

In this work, we reported for the first time the water intercalation into kaolinite above 2.7(1) GPa and 200 °C. Based on our structural model, the amount of water in super-hydrated kaolinite is ca. 17.3 wt.%, and taking into account the original OH^- species, the total amount of water is ca. 28.9 wt.%. This water content of super-hydrated kaolinite is the highest of any known aluminosilicate mantle minerals, e.g., near two- to three-fold the amount found in lawsonite (11.5 wt.% of H_2O), serpentine (14 wt.% of OH^-) and diasporite (15 wt.% of OH^-)⁴⁷. The water intercalation under increasing pressure and at elevated temperatures proceeds initially via the formation of a stacking disorder weakening the hydrogen bonding

between the layers. The super-hydration occurs with an *expansion* of the unit cell volume by ca. 31% and a *reduction* in density by ca. 8.4%. Sequential breakdowns of super-hydrated kaolinite to phase Pi ($\text{Al}_3\text{Si}_2\text{O}_7(\text{OH})_3$), diaspore ($\alpha\text{-AlOOH}$), and topaz-OH ($\text{Al}_2\text{SiO}_4(\text{OH})_2$) accompanied by the formations of coesite (SiO_2) and stishovite (SiO_2) are found up to 19 GPa and 800 °C. Our results bear important information for understanding deep water cycling and volcanism along the (cold) subduction zones as both super-hydration and dehydration occur at conditions corresponding to depths between ca. 75 km and 480 km (Fig. 4). Another possibility is that substantial removal of water (by up to 27 % assuming a 1:1 mixture of kaolinite and water) and changes in the grain morphology expected during the water intercalation in kaolinite below ~75 km depth might significantly alter the frictional properties at the interface between the subducting and overriding slabs. The flux of kaolinite alone, however, might be small compared to the total water flux in the subduction system, i.e., it is estimated that ca. 1/30, on average, of the total water in the subduction system can be accommodated into this single phase by super-hydration. We suggest that other (clay) minerals and/or multi-component systems in the oceanic sediment and crust could undergo similar super-hydration during subduction. It is also possible that the subduction interface might not be homogeneous but made up of patches of kaolinite, which will then serve as a clear rupture point due to super-hydration. Previous studies have assumed water release by dehydration of various hydrous minerals at depths below 100 km down to the transition zone^{16,48-51} (Fig. 4). The dehydration and breakdown sequence of super-hydrated kaolinite provides new insights into understanding geochemical and seismic processes occurring along subduction zones and need to be incorporated in future modeling studies.

Methods

Methods, including other structural details of kaolinite with associated figures, tables and references, are available in the online version of this paper.

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324

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Additional Information Supplementary Information is available in the online version of the paper. Correspondence and requests for materials should be addressed to Y. L. (yongjaelee@yonsei.ac.kr)

Figure Captions

Figure 1 Formation and breakdown of super-hydrated kaolinite. (a) Synchrotron X-ray powder diffraction patterns of kaolinite at ambient and high-pressures as well as annealed at different temperatures in the presence of water. X-ray powder diffraction Debye-Scherrer cones of kaolinite at ambient conditions and at 2.7(1) GPa after heated at 200°C for 1hr. (b) Results of high-pressure and heating experiments on kaolinite. Errors are smaller than the size of the symbols. The geotherms for subducting slabs are from Syracuse et al. 2010²¹. Colored lines are the P-T paths of the subducting slab surfaces for North Antilles (normal), New Zealand (normal), Kermadec (cold), Tonga (cold), and hot (Cascadia, Mexico, Nankai and South Chile) subducting slabs. Dotted lines in matching color indicate the P-T paths of the corresponding Moho. Blue solid lines are phase boundary of diaspore, topas-OH, phase egg from Wunder et al. (1993)⁵² and Sano et al. (2004)⁵³. An inset shows ternary diagram for selected phases in the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system (ASH). The arrows indicate the super-hydration and breakdown sequence of kaolinite. (c) A 3-dimensional plot of time-resolved synchrotron X-ray powder diffraction patterns of kaolinite. The scan started when the temperature reached 200°C at 2.7(1) GPa. (d) Synchrotron X-ray powder diffraction patterns showing the super-hydration and breakdown sequence from kaolinite.

Figure 2 Volume expansion of super-hydrated kaolinite. Pressure- and temperature- induced changes in (a) the lattice parameters and (b) unit-cell volume and calculated density of kaolinite.

Figure 3 Structural details of super-hydrated kaolinite. (a) Rietveld fit of the structural model of kaolinite measured at 4.1(1) GPa after heating at 200°C. Difference curve is shown below, and the positions of Bragg reflections of the super-hydrated and original kaolinite are shown as black and red vertical bars, respectively. Difference-Fourier synthesis map reveals residual electron densities indicating the oxygen location of interlayer water molecules. (b) *In-situ* high-pressure IR reflectivity spectra of kaolinite during decompression from 3.5(1) GPa. For comparison, IR absorption spectra measured at ambient conditions of the original kaolinite and halloysite are shown as references on the bottom and top, respectively. The vertical dotted lines indicate the positions of the OH^- stretching bands.

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Figure 4 A role of super-hydrated kaolinite in the subduction water cycle. A schematic illustration of a (cold) subduction zone showing the super-hydration and breakdown sequence of kaolinite. Dehydration of amphiboles, phlogopite $[K_2(Mg,Fe)_6Si_6Al_2O_{10} \cdot H_2O]$ and lawsonite $[CaAl_2Si_2O_8 \cdot 2H_2O]$ are overlain for reference⁸⁻¹¹. Dashed black lines are the isotherms by Tsujimori, et al.⁵⁴.

Experimental Method

Sample preparation and high-pressure experiments

We used a well-crystallized kaolinite powder (KGa-1b) sample from Washington County, Georgia. Crystal morphology and chemical composition were investigated using a scanning electron microscope (JEOL-7800F) equipped with an energy-dispersive X-ray spectroscopy system (Oxford Instruments, Abingdon, UK) operating at 15 kV accelerating voltage.

We performed *in-situ* high-pressure experiments of kaolinite using a diamond anvil cell (DAC) equipped with 700 μm diameter culets. We used two different pressure transmitting media (PTM): water a pore-penetrating medium and silicone oil a non-pore-penetrating medium. Kaolinite powder was loaded into a 350 μm width and 110 μm high sample chamber drilled by electro-spark erosion in a pre-indented stainless steel gasket. A few small ruby spheres (~ 20 μm) added into the sample chamber were used as pressure gauge. The pressure of the sample inside the DAC was measured by detecting the shift of the R1 emission line of ruby (precision: ± 0.1 GPa)⁵⁵.

In-situ high-pressure synchrotron X-ray powder diffraction

High-resolution *in-situ* high-pressure synchrotron X-ray powder diffraction data of kaolinite were collected at beamline BL10-2 at the Stanford Synchrotron Radiation Lightsource (SSRL) at the SLAC National Accelerator Laboratory. At beamline BL10-2, the primary white beam from the wiggler source impinged on Si (111) focusing crystals to produce monochromatic X-rays with a wavelength of 0.6199(1) Å. The wavelength of the incident beam was determined using a LaB₆ standard reference material (SRM 660c). A Pilatus 300K-w Si-diode CMOS detector was used to collect powder diffraction data at a 1126 mm sample-to-detector distance and with 2-theta coverage up to 30°. Pressure was increased up to 7.0(1) GPa in intervals of about 0.2-0.5 GPa. The sample equilibrated for about 10 minutes in the DAC at each measured pressure. The pressure treatment sequences are summarized in Supplementary Tables 2 and 3 along with the resulting changes of the unit-cell volume.

In order to mimic conditions in a subduction zone, occasional *ex-situ* heating was done by placing the sample containing water in a DAC inside an oven for one hour. The pressure and temperature sequences are listed in Supplementary Table 3 along with the resulting changes in the unit-cell volume. Pressure

dependent changes in the lattice parameters and unit cell volumes were derived by whole-pattern profile fitting using the Le Bail method implemented in the GSAS suite of programs⁵⁶. The background curve was fitted with a Chebyshev polynomial using 32 coefficients. The pseudo-Voigt profile function proposed by Thompson, et al.⁵⁷ was used to model the observed Bragg peaks. Bulk moduli from normalized volume (V/V_0) were calculated using the second-order Birch-Murnaghan equation of state⁵⁸.

Additional *in-situ* high-pressure synchrotron X-ray powder diffraction experiments for kaolinite under water medium were performed at beamline 9A at Pohang Accelerator Laboratory (PAL) and beamline BL14B1 at Shanghai Synchrotron Radiation Facility (SSRF). At beamline 9A at PAL, Rayonix SX165 CCD detector and monochromatic X-ray with a wavelength of 0.6215Å were used while at beamline BL14B1 at SSRF, Rayonix mx225 CCD detector was used with monochromatic X-ray of 0.6888Å wavelength. *In-situ* high-pressure laboratory X-ray diffraction was also performed at the department of Earth System Sciences at Yonsei university using a MicroMax-007HF (Rigaku) system equipped with a micro-focusing rotating anode Mo-K α radiation, multilayer optics (VariMax-Mo, Rigaku), and R-axis IV⁺⁺ imaging plate detector (Rigaku).

We have also performed *in-situ* high-pressure and high-temperature synchrotron X-ray powder diffraction on kaolinite under water medium at beamline 16BMD of HPCAT at the Advanced Photon Source (APS) at Argonne national laboratory and the “Extreme Conditions Beamline” P02.2 of PETRA III at Deutsches Elektronen-Synchrotron (DESY). At beamline 16BMD in APS, we used a cylinder-type diamond anvil cell that consists of one ring-shaped ceramic heater surrounding the gasket. A platinum wire of thickness 0.3 mm and resistance 0.6 Ohm was used as heating element. Monochromatic X-ray beam with a wavelength of 0.4959Å and a MAR345 detector were used for data XRD measurement. At beamline P02.2 of PETRA III, we used a DAC equipped with a graphite resistive heater to perform *in-situ* high-pressure and high-temperature experiments. Pressure and temperature of the sample in the DAC increased up to 19 GPa and 800 °C. The description of this DAC is found in Comboni et al. and Liermann et al.^{59,60}. Synchrotron X-ray powder diffraction was performed using a monochromatic X-ray beam of 0.4838(1)Å wavelength and a PerkinElmer XRD 1621 flat-panel detector.

Time-resolved synchrotron X-ray powder diffraction

In order to probe the transformation pathway of kaolinite during the pressure- and temperature-treatment, time-resolved synchrotron X-ray powder diffraction experiments were performed at beamline BL10-2 at SSRL using a Pilatus 300K-w detector. The pressure was fixed at 2.7(1) GPa, and the temperature was gradually raised to 200°C. When the sample reached 200°C, synchrotron XRD data were measured in 1 minute intervals during 30 minutes at a fixed 2 theta angle containing the 10Å reflection. The pressure and temperature of the sample inside the DAC was determined by using the shift of the (002) reflection of an internal Cu standard and its EOS⁶¹.

Rietveld structure refinement

Structural characterization of the super-hydrated kaolinite measured at 4.1(1) GPa after heating at 200°C were performed using the Rietveld refinement program from the EXPGUI suite of programs^{56,62}. The background curve and peak shape were modeled using the Le Bail method⁵³. The starting structural model used was the one proposed by Bish and Vondreele³⁸. After initial refinements, an inspection of difference-Fourier maps suggested three interlayer sites showing residual electron densities, which were subsequently modeled as oxygen atoms of water molecules, i.e., OW1 at (0.102(4), 0.441(3), 0.697(3)), OW2 at (0.586(4), 0.330(3), 0.697(3)), and OW3 at (0.554(4), 0.645(3), 0.730(2)). The refined occupancies of the OW1 and OW2 sites converged to unity while that of the OW3 site was refined to be 0.970(2). Geometrical soft restraints were applied for the layer inter-atomic distances assuming ideal tetrahedral and octahedral geometries, i.e., Si-O = 1.610(1) Å and O-O = 2.630(5) Å for SiO₄ and Al-O = 1.885(1) and O-O = 2.668(5) for AlO₆. All the atom displacements were modeled using one isotropic displacement parameters (U_{iso}) in order to reduce the number of parameters. The basal (00 l) reflections indicated the presence of preferred orientation and therefore corrections by March-Dollase⁶³ were applied and March-Dollase preferential orientation parameter was refined, on average, to a value of 1.1814(2). The final convergence of the refinement was achieved by simultaneously varying all background and profile parameters, preferred orientation parameters, scale factor, lattice constants, 2 θ zero, and the atomic positional and displacement parameters. The parameters of the final refined models are listed in Supplementary Tables 4-5.

***In-situ* high-pressure Infrared spectroscopy**

High-pressure IR experiments were carried out at the Infrared Lab of NSLS-II at Brookhaven National Laboratory. To avoid absorption saturation from the water present, all IR spectra were collected in reflection mode using a Bruker Vertex 80v FTIR spectrometer and a Hyperion 2000 IR microscope equipped with a liquid nitrogen cooled mid-band MCT detector. Some experiments were done at beamline 1.4.3 at the Advanced Light Source (ALS). A diamond anvil cell (DAC) containing a pair of type-II diamond anvils with 400 μm culet size was used. The ruby fluorescence technique was utilized to estimate the pressures for all experiments at room temperature. Kaolinite was loaded into a 200 μm wide and 80 μm thick sample chamber drilled using electro-spark erosion in a pre-indented stainless steel gasket. Near the edge of the chamber, a few small ruby spheres ($\sim 20\mu\text{m}$) were added as pressure gauges. The reflectance from the sample-diamond interface ($R_{\text{sd}}(\omega)$) is calculated using:

$$R_{\text{sd}} = I_{\text{sd}} I_{\text{d}} / I_{\text{e}} I_0 \quad (1)$$

where R_{sd} is the reflectivity of the sample–diamond interface, I_{sd} the intensity reflected from the sample–diamond interface, I_{d} the intensity reflected from the air–diamond interface, I_{e} the intensity reflected from the empty cell, and I_0 the intensity reflected from the gold foil⁶⁴. Although it is impossible to obtain accurate reflectivities of the sample-diamond interface due to the both sample and water being present, our goal was to monitor the changes of the O-H stretching vibrational modes. The changes of the frequencies of the O-H stretching vibrational modes are related to the structural changes occurring during the insertion of the water molecules in-between the layers in the kaolinite structure.

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