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SUPPLEMENTARY INFORMATION

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

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Supplementary Information

Structural characteristics of kaolinite

The kaolin-group minerals are naturally occurring hydrous clay minerals, which form in various environments, such as terrestrial hot springs, hydrothermal systems, and sedimentary basins[1]. They are layered aluminosilicate minerals with an ideal chemical composition of $Al_2Si_2O_5(OH)_4$. The first description of the kaolinite structure was reported by Pauling[2] and subsequently expanded on by Giese and Datta[3], Bish and Vondreele[4], and Bish[5]. The repeat unit in the 1:1 phyllosilicate-type minerals of the kaolin-group consists of alternating SiO_4 tetrahedral and AlO_6 octahedral layers (Supplementary Fig. 1c). The kaolin-group minerals include three main polymorphs, namely kaolinite, dickite, nacrite and related phases such as halloysites [7Å phase: $Al_2Si_2O_5(OH)_4$, 10Å phase: $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$]. In kaolinite, each SiO_4 tetrahedron connects via three of its apices to neighboring tetrahedrons creating a hexagonal surface of oxygen atoms, while the AlO_6 octahedral sheet forms two planes that contain oxygen atoms and hydroxyl groups. In one of the octahedral planes, 2/3 of the oxygen atoms coordinate to SiO_4 tetrahedrons and the other 1/3 exist as 'inner' hydroxyls, whereas in the other octahedral plane, all the oxygen atoms exist as hydroxyls. In the octahedral site, the presence of Al^{3+} cations dictate that 1/3 of the octahedral sites are vacant resulting in three types of nonequivalent octahedral sites which characterizes the 1:1 layers that stack along the *c*-axis so that the 'outer' hydroxyls and basal oxygens pair up in the space between the layers and form hydrogen bonds. In kaolinite, the layers are stacked and shifted by $-\boldsymbol{a}/3$ thereby creating a one-layer monoclinic unit cell. In dickite, the layers are rotated by $\pm 120^{o}$ so that the vacancies alternate between two different sites creating a two-layer unit cell. In the nacrite, a two-layer unit cell results from shifting layers by $-\boldsymbol{a}/3$ and then the adjacent layers rotate by $\pm 60^{o}$. The appearance of stacking faults in kaolinite is well established, and a model was proposed by Bookin[6]. The X-ray diffraction patterns of kaolinite clearly reveal anisotropic stacking faults: reflections with $k \neq 3n$ shift and broaden

more than those with $k = 3n$[7].

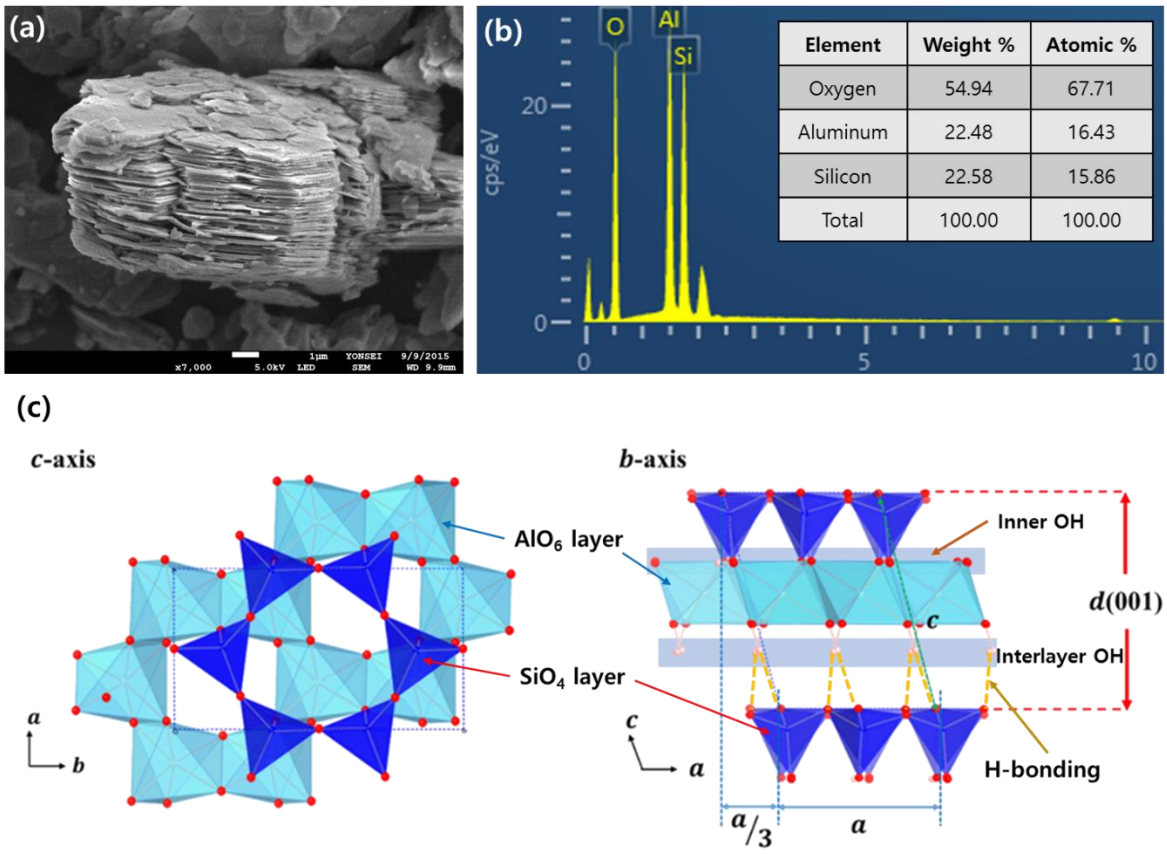
Phases of kaolinite having additional interlayer water molecules, however, have not been reported yet as water intercalation between kaolinite layers is difficult due to strong hydrogen bonding between the layers perpendicular to the *c*-axis[8,9]. Costanzo, et al.[10] reported that intercalation of water into kaolinite can be achieved by a stepwise treatment with dimethylsulfoxide (DMSO) and ammonium fluoride (NH_4F). Costanzo, et al.[11] showed that after exposure of kaolinite to DMSO disordering of the interlayer stacking along the *c*-axis occurs and the interlayer distance expands to about 10 Å. Subsequently, fluorine anions replace hydroxyl groups during the treatment with NH_4F and result in an additional weakening of interlayer forces, which subsequently allows water molecules to penetrate between the kaolinite layers. Up until now, kaolinite unlike smectite, is classified as a non-swelling clay mineral since water insertion requires the presence of an organic solvent like DMSO and fluorides.

Structural changes of Kaolinite at high-pressure and room temperature

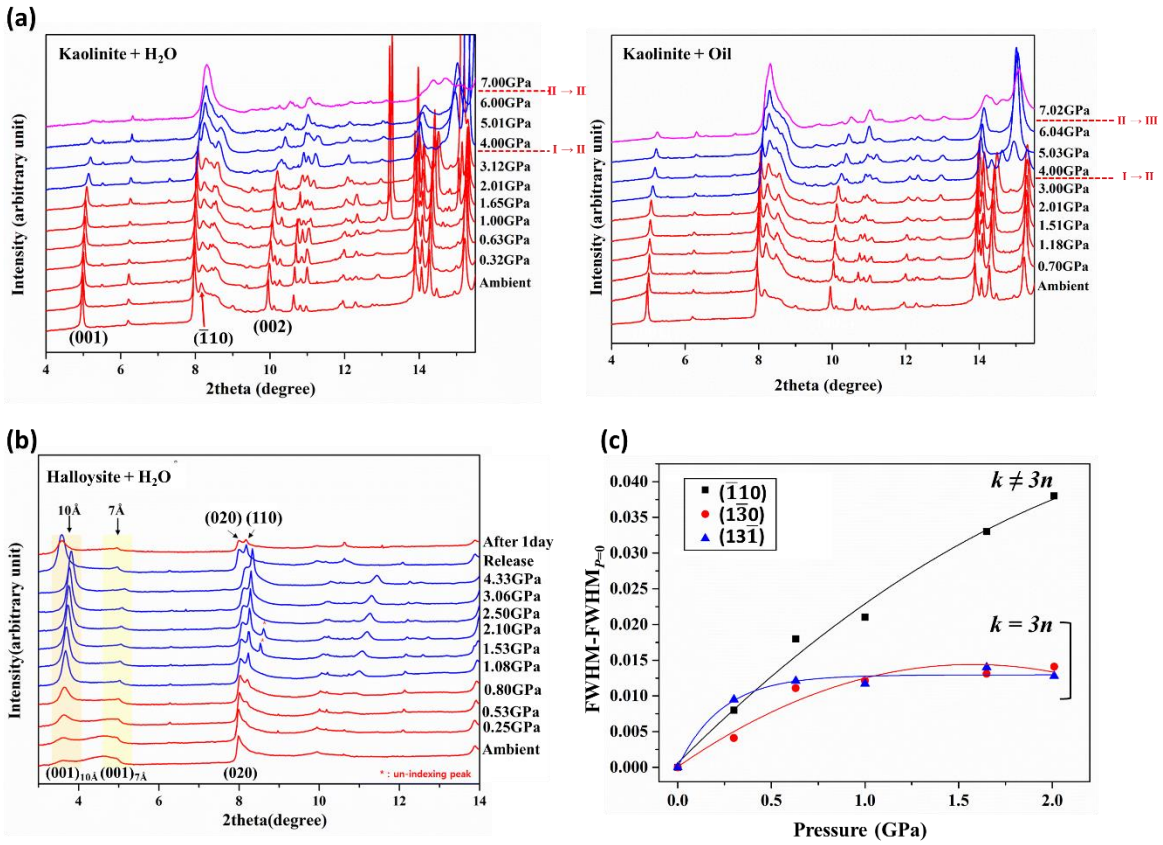
In the presence of water and silicone oil, pressure-dependent changes in the synchrotron X-ray powder diffraction patterns of kaolinite show the previously established transitions, i.e., kaolinite I → kaolinite II → kaolinite III[12]. (Supplementary Fig. 2a) Changes in the unit-cell volume from our data in the presence of water and silicone oil are compared to those reported by Welch and Crichton[12] using a methanol/ethanol mixture as a pressure-transmitting medium, and show similar transition pressures and derived bulk moduli (Supplementary Fig. 3 and Supplementary Table 2). In all data the first phase transition from kaolinite I to kaolinite II occurs between 3.0 and 4.0 GPa and the second one between 6.0 and 7.0 GPa. After an initial pressure increase, the width of the first (001) reflection broadens and its intensity decreases. Other peaks found between 7.9˚ and 9˚ in 2θ also broaden but to a lesser extent. After transition to kaolinite II near 4.0 GPa, a significant change of the diffraction pattern is observed near 15˚ in 2θ, where a strong and broad

reflection arises. After transition to kaolinite III above 7 GPa, this peak disappears again. These pressure-dependent phase transitions of kaolinite at room temperature are independent of the fluid present and seem to be insensitive to non-hydrostratic conditions. Using our data collected in the presence of water we monitored the anisotropic peak broadening of the reflections with $k \neq 3n$ and $k = 3n$ (Supplementary Fig. 2c). We observe the reflections with $k \neq 3n$ broaden more than those with $k = 3n$ as pressure increases. This agrees with previously proposed staking fault effect between layers[13,14] and points unequivocally to the emergence of disorder along the c-axis under compression.

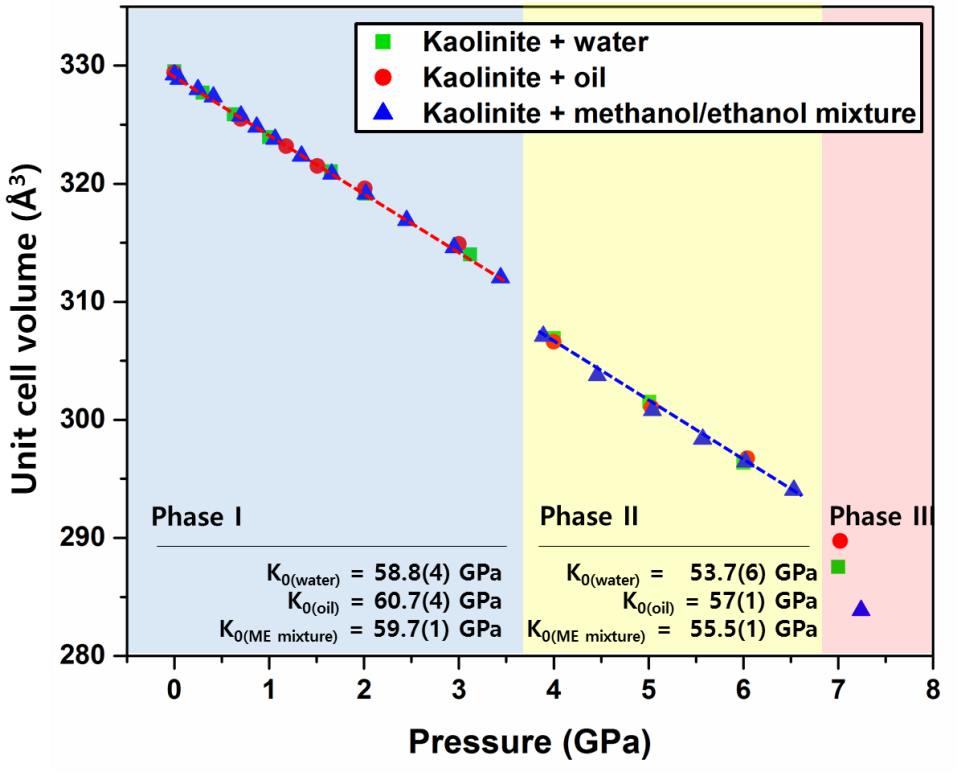
Supplementary Figure 1. (a) Scanning electron microscopy image of the original kaolinite specimen (KGa-1b), and (b) its chemical composition measured using energy dispersive X-ray spectroscopy. (c) Crystal structure of kaolinite based on the model of Bish and Von Dreele[36] viewed along the *c*-axis (left) and *b*-axis (right).



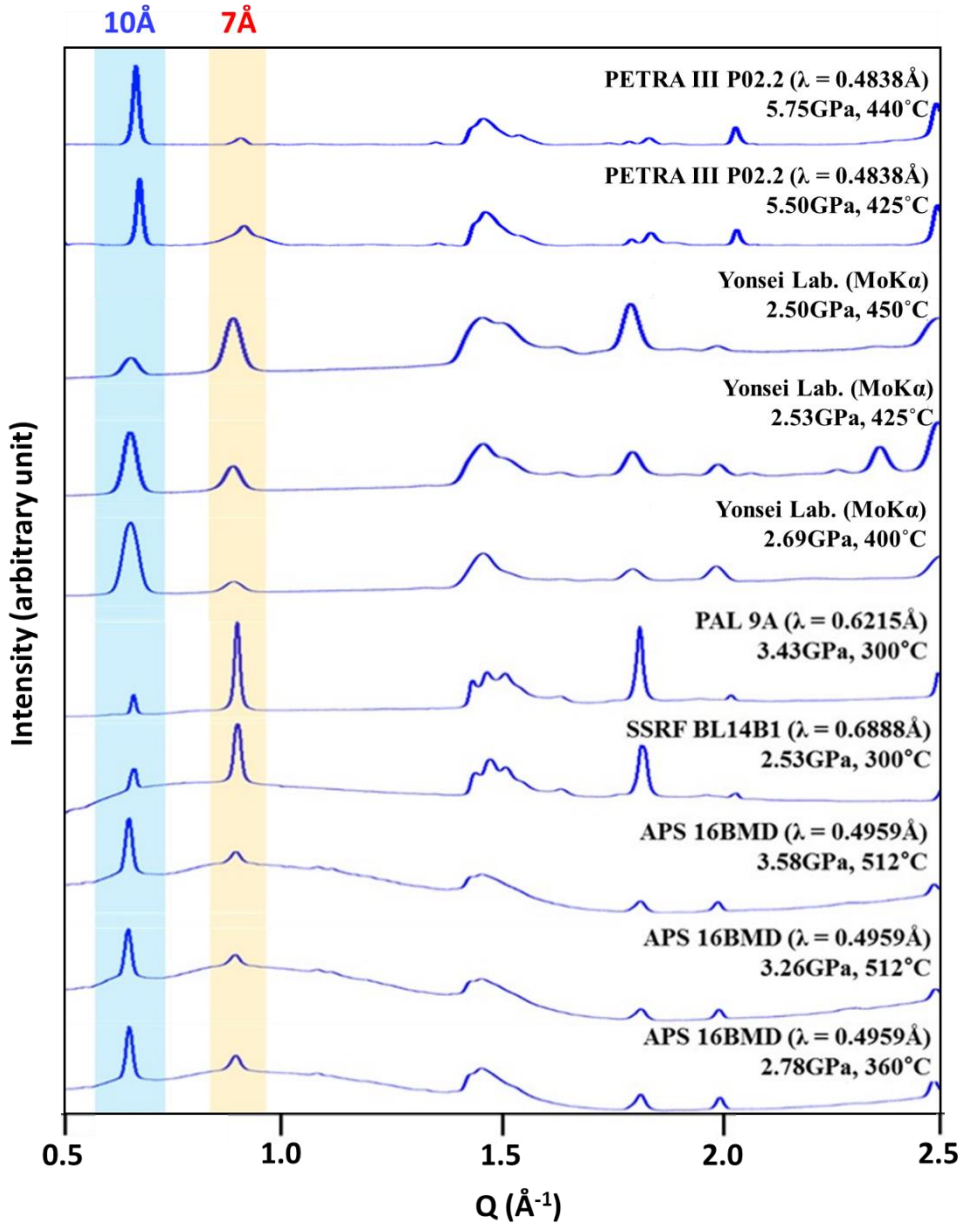
Supplementary Figure 2. (a) Synchrotron X-ray powder diffraction patterns of kaolinite at ambient conditions and high-pressures in the presence of water and silicone oil. (b) Synchrotron X-ray powder diffraction patterns of halloysite at ambient and high-pressures and after pressure release in the presence of water. (c) Pressure-induced changes of the full-width-at-half-maximum (FWHM) for $(\bar{1}10), (1\bar{3}0), \text{and } (13\bar{1})$ reflections of kaolinite.



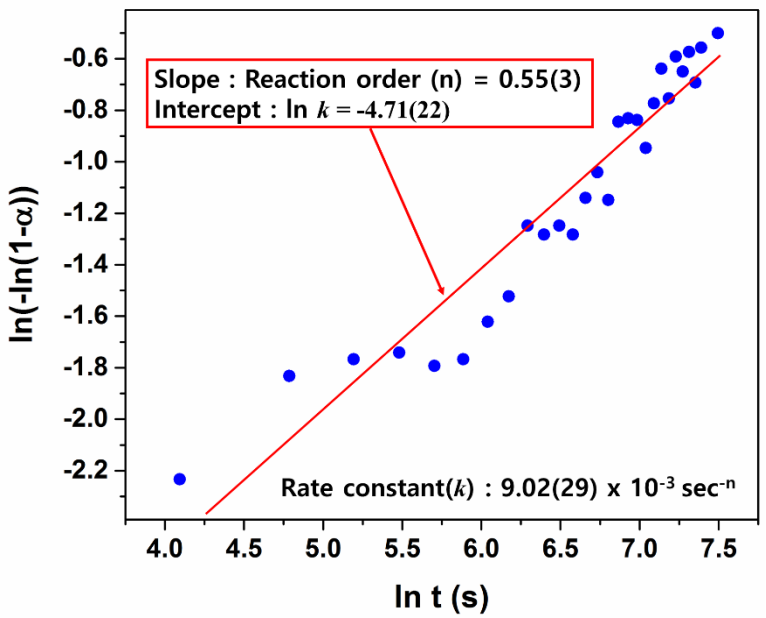
Supplementary Figure 3. Pressure-induced changes in the unit-cell volume of kaolinite in the presence of different fluids. Data using methanol+ethanol mixture are from Welch and Crichton[22].



Supplementary Figure 4. Synchrotron and laboratory X-ray powder diffraction patterns of kaolinite at various P-T conditions in the presence of water.



Supplementary Figure 5. A plot of ln(t) versus ln(-ln(1-α)) for the intensity of the basal (001) reflection of the original kaolinite at 2.7(1) GPa and 200˚C. Red line represents the linear fit using the Avrami equation[32].



Supplementary Table 1. Crystal data and details pertaining to the structure refinements of the kaolinite(7Å phase) at ambient condition and super-hydrated kaolinite (10Å phase) compared to the kaolinite (7Å phase) by Bish and Von Dreele[36].

	Kaolinite (reference)	**Kaolinite (ambient)**	**Kaolinite-10Å (4.1 GPa after heating at 200°C)**
Unit cell formula	$Al_2Si_2O_5(OH)_4$	$Al_2Si_2O_5(OH)_4$	$Al_2Si_2O_5(OH)_4 \cdot 3H_2O$
Space group	C*1*	C*1*	C*1*
Unit cell dimension (Å) for one layer	*a* = 5.1554 *b* = 8.9448 *c* = 7.4048 *α* = 91.700 *β* = 104.862 *γ* = 89.822	*a* = 5.1555(5) *b* = 8.9383(10) *c* = 7.3949(5) *α* = 91.682(8) *β* = 104.651(9) *γ* = 89.804(9)	*a* = 4.9996(7) *b* = 8.7309(13) *c* = 9.5257(14) *α* = 88.787(32) *β* = 101.98(4) *γ* = 90.038(32)
Unit cell volume ($Å^3$) for one layer	329.893	329.543(33)	406.65(8)
R_{wp}(%)		8.36	3.86
Reference	Bish and Von Dreele[1]	This study	This study

Supplementary Table 2. Pressure-induced changes in the unit-cell volume of kaolinite under H_2O, silicone oil, and methanol+ethanol mixture PTM. Data using methanol+ethanol mixture PTM is from Welch and Crichton[22].

H_2O		**Oil**		**Methanol+ethanol mixture**	
Pressure(GPa)	Unit cell volume ($Å^3$)	Pressure(GPa)	Unit cell volume ($Å^3$)	Pressure(GPa)	Unit cell volume ($Å^3$)
0.0001	329.51(3)	0.0001	329.40(3)	0	329.24
0.3(1)	327.71(3)	0.7(1)	325.47(3)	0.05	328.86
0.6(1)	325.88(3)	1.2(1)	323.17(3)	0.25	327.98
1.0(1)	323.95(2)	1.5(1)	321.48(3)	0.41	327.36
1.7(1)	321.04(3)	2.0(1)	319.58(3)	0.7	325.73
2.0(1)	319.15(3)	3.0(1)	314.89(3)	0.87	324.8
3.1(1)	314.02(2)	4.0(1)	306.62(3)	1.06	323.77
4.0(1)	306.91(2)	5.0(1)	301.03(3)	1.34	322.34
5.0(1)	301.53(3)	6.0(1)	296.76(3)	1.66	320.82
6.0(1)	296.35(3)	7.0(1)	289.73(3)	2.02	319.16
7.0(1)	287.56(3)			2.45	316.9
				2.95	314.61
				3.44	312.04
				3.89	307.09
				4.46	303.76
				5.04	300.82
				5.57	298.38
				6.02	296.45
				6.53	294.06
				7.24	283.88

Supplementary Table 3. Pressure- and temperature-induced changes in the lattice parameters, unit-cell volume, and calculated density of kaolinite.

Phase	Pressure (GPa)	Temperature treatment (°C)	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)	Unit cell volume (Å^3)	Calculated density (g/cm^3)
7Å	0.0001	Ambient	5.1580(2)	8.9307(4)	7.3998(1)	91.448(5)	104.947(4)	89.868(4)	329.23(2)	2.605
	1.1(1)		5.1302(3)	8.8834(5)	7.3361(3)	92.005(8)	105.070(5)	89.947(7)	322.62(3)	2.659
	1.2(1)	120°C, 1h	5.1312(1)	8.8788(4)	7.3378(2)	92.236(5)	105.026(3)	89.677(4)	322.62(2)	2.659
	1.6(1)		5.1241(3)	8.8671(5)	7.3054(4)	92.297(5)	105.099(4)	89.737(5)	320.21(2)	2.679
	1.6(1)	150°C, 1h	5.1272(5)	8.8814(7)	7.3051(4)	92.846(10)	104.901(7)	89.828(8)	321.05(2)	2.672
	2.2(1)		5.1073(4)	8.8513(9)	7.2880(5)	92.692(10)	105.415(9)	89.754(7)	317.25(3)	2.704
	2.1(1)	170°C, 1h	5.1141(2)	8.8638(3)	7.2881(2)	92.581(4)	105.331(3)	89.962(4)	318.27(1)	2.695
	2.5(1)		5.1062(2)	8.8534(9)	7.2840(4)	92.480(8)	105.545(6)	89.837(9)	316.94(3)	2.706
10Å	2.7(1)	200°C, 1h	5.0057(12)	8.8071(24)	9.6160(16)	88.674(39)	100.917(40)	90.757(36)	416.13(16)	2.48
	3.2(1)		4.9982(4)	8.7682(7)	9.5815(9)	89.617(7)	101.622(8)	90.448(8)	411.29(5)	2.509
	3.8(1)	220°C, 1h	4.9974(6)	8.7498(7)	9.5618(19)	89.603(13)	101.998(22)	90.613(9)	408.95(8)	2.524
	4.1(1)		4.9827(7)	8.7296(8)	9.4904(19)	89.647(13)	101.901(25)	90.471(9)	403.92(9)	2.555
	5.1(1)	250°C, 1h	4.9583(6)	8.7009(8)	9.4672(17)	89.580(12)	102.399(21)	90.667(9)	398.87 (7)	2.587

Supplementary Table 4. Refined atomic positional, occupancy, and displacement parameters of the kaolinite (7Å phase) at ambient condition and super-hydrated kaolinite (10Å phase) compared to the kaolinite (7Å phase) by Bish and Von Dreele[36]. Estimated standard deviations are in parenthesis.

Kaolinite-7Å (Reference)						Kaolinite-7Å (Ambient)						Kaolinite-10Å (4.1 GPa after heating at 200°C)					
Al1	x	0.289	OH1	x	0.050	Al1	x	0.299(2)	OH1	x	0.066(2)	Al1	x	0.208(3)	OH1	x	0.005(3)
	y	0.4966		y	0.9710		y	0.498(1)		y	0.983(1)		y	0.535(1)		y	0.020(2)
	z	0.466		z	0.325		z	0.457(2)		z	0.307(2)		z	0.332 (2)		z	0.234(3)
	U_{iso}	0.040		U_{iso}	0.039		U_{iso}	0.006(2)		U_{iso}	0.002(2)		U_{iso}	0.026(1)		U_{iso}	0.026(1)
Al2	x	0.793	OH2	x	0.960	Al2	x	0.789(2)	OH2	x	0.996(3)	Al2	x	0.748 (3)	OH2	x	0.866(6)
	y	0.3288		y	0.1658		y	0.324(1)		y	0.165(1)		y	0.372(1)		y	0.199(2)
	z	0.465		z	0.607		z	0.459(2)		z	0.602(2)		z	0.340(2)		z	0.458(2)
	U_{iso}	0.040		U_{iso}	0.039		U_{iso}	0.006(2)		U_{iso}	0.002(2)		U_{iso}	0.026(1)		U_{iso}	0.026(1)
Si1	x	0.989	OH3	x	0.037	Si1	x	0.989(3)	OH3	x	0.027(2)	Si1	x	0.972(3)	OH3	x	-0.085(4)
	y	0.3395		y	0.4726		y	0.335(1)		y	0.477(2)		y	0.371(2)		y	0.549(2)
	z	0.0906		z	0.6046		z	0.092(2)		z	0.603(2)		z	0.040(2)		z	0.431(2)
	U_{iso}	0.042		U_{iso}	0.039		U_{iso}	0.006(2)		U_{iso}	0.002(2)		U_{iso}	0.026(1)		U_{iso}	0.026(1)
Si2	x	0.507	OH4	x	0.038	Si2	x	0.501(3)	OH4	x	0.025(3)	Si2	x	0.498(3)	OH4	x	-0.087(4)
	y	0.1655		y	0.8582		y	0.173(1)		y	0.840(2)		y	0.187(2)		y	0.860(2)
	z	0.0938		z	0.609		z	0.092(2)		z	0.606(2)		z	0.048(1)		z	0.414(3)
	U_{iso}	0.042		U_{iso}	0.039		U_{iso}	0.006(2)		U_{iso}	0.002(2)		U_{iso}	0.026(1)		U_{iso}	0.026(1)
O1	x	0.049				O1	x	0.066(2)				O1	x	0.010(3)			
	y	0.3482					y	0.338(1)					y	0.378(2)			
	z	0.3168					z	0.319(1)					z	0.217(2)			
	U_{iso}	0.044					U_{iso}	0.002(2)					U_{iso}	0.026(1)			
O2	x	0.113				O2	x	0.093(3)				O2	x	0.087(4)	OW1	x	0.102(4)
	y	0.6599					y	0.665(1)					y	0.706(1)		y	0.441(3)
	z	0.3188					z	0.319(1)					z	0.219(2)		z	0.697(3)
	U_{iso}	0.044					U_{iso}	0.002(2)					U_{iso}	0.026(1)		U_{iso}	0.027(1)
																occu.	1.000
O3	x	0				O3	x	0.009(3)				O3	x	-0.142(4)	OW2	x	0.586(4)
	y	0.5					y	0.501(1)					y	0.532(2)		y	0.330(3)
	z	0					z	0.020(2)					z	-0.029(2)		z	0.697(3)
	U_{iso}	0.044					U_{iso}	0.002(2)					U_{iso}	0.026(1)		U_{iso}	0.027(1)
																occu.	1.000
O4	x	0.204				O4	x	0.183(3)				O4	x	0.268(4)	OW3	x	0.554(4)
	y	0.2291					y	0.220(2)					y	0.318(3)		y	0.645(3)
	z	0.030					z	0.023(2)					z	0.000(3)		z	0.730(2)
	U_{iso}	0.044					U_{iso}	0.002(2)					U_{iso}	0.026(1)		U_{iso}	0.027(1)
																occu.	0.970(2)
O5	x	0.197				O5	x	0.180(3)				O5	x	0.242(4)			
	y	0.7641					y	0.780(2)					y	0.745(2)			
	z	0.001					z	0.001(2)					z	-0.030(2)			
	U_{iso}	0.044					U_{iso}	0.002(2)					U_{iso}	0.026(1)			

Supplementary Table 5. Selected interatomic distances (Å) and angle (°) of the kaolinite (7 Å phase) at ambient condition and super-hydrated kaolinite (10Å phase) compared to the kaolinite (7Å phase) by Bish and Von Dreele[36].

	Kaolinite-7Å Bish and Von Dreele[12]	Kaolinite-7Å (This study, ambient)	Kaolinite-10Å (This study, 4.1(1)GPa after heating at 200°C)
Al1-O1	1.930(6)	1.956(14)	1.916(8)
Al1-O2	1.965(5)	1.981(14)	1.855(8)
Al1-OH1	1.932(6)	1.978(13)	1.919(9)
Al1-OH2	1.880(6)	1.945(12)	1.949(10)
Al1-OH3	1.892(6)	1.982(13)	1.902(8)
Al1-OH4	1.868(6)	1.998(13)	1.896(9)
Mean	1.911	1.973	1.906
Al2-O1	1.969(5)	1.973(14)	1.929(8)
Al2-O2	1.936(5)	1.873(14)	1.936(8)
Al2-OH1	1.920(5)	2.005(13)	1.899(9)
Al2-OH2	1.884(5)	1.945(13)	1.882(8)
Al2-OH3	1.900(5)	1.938(13)	1.893(9)
Al2-OH4	1.898(5)	1.943(13)	1.948(9)
Mean	1.918	1.946	1.915
Si1-O1	1.626(5)	1.627(13)	1.661(8)
Si1-O3	1.609(5)	1.597(14)	1.596(8)
Si1-O4	1.628(5)	1.593(15)	1.670(8)
Si1-O5	1.617(5)	1.636(14)	1.638(8)
Mean	1.620	1.613	1.641
Si2-O2	1.630(5)	1.631(13)	1.612(8)
Si2-O3	1.614(5)	1.618(15)	1.630(8)
Si2-O4	1.597(5)	1.647(16)	1.616(8)
Si2-O5	1.611(5)	1.600(14)	1.631(8)
Mean	1.613	1.624	1.622
Al1-O1-Al2	100.333	102.3(7)	89.9(9)
Al1-O2-Al2	100.094	98.3(7)	102.4(8)
Al1-OH1-Al2	100.102	96.0(6)	105.4(12)
Al1-OH2-Al2	105.196	97.1(7)	100.9(9)
Al1-OH3-Al2	104.314	102.7(7)	91.4(9)
Al1-OH4-Al2	103.291	97.3(7)	104.4(12)
Al1-O1-Si1	124.087	119.1(8)	123.9(12)
Al1-O2-Si2	129.661	124.4(9)	118.2(11)
Al2-O1-Si1	128.141	121.5(9)	131.9(12)
Al2-O2-Si2	122.790	119.4(8)	133.9(13)
Si1-O3-Si2	130.558	140.0(12)	117.6(11)
Si1-O4-Si2	142.543	136.3(12)	138.4(15)
Si1-O5-Si2	132.628	127.9(11)	123.4(11)
OW1-O3			3.21(4)
OW1-O4			3.007(30)
OW1-O5			3.72(4)
OW1-OH2			3.19(4)
OW1-OH3			2.666(26)
OW1-OH4			3.47(4)
OW2-O3			3.25(4)
OW2-O4			3.58(4)
OW2-O5			2.649(30)
OW2-OH2			3.14(4)
OW2-OH3			3.54(4)
OW2-OH4			2.66(4)
OW3-O3			2.648(23)
OW3-O4			3.01(4)
OW3-O5			3.166(35)
OW3-OH2			2.601(9)
OW3-OH3			3.78(4)
OW3-OH4			3.89(4)
OW1-OW2			2.609(14)
OW1-OW3			2.620(8)
OW2-OW3			2.783(8)
***d*(001)**	7.157	7.154	9.316(1)

Reference

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