

Supporting Information

Structural interpretation of the energetic performances of Pure Silica LTA-type Zeolite

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S2. Experimental

S2.3. NMR Spectroscopy and Thermogravimetric Analysis

Table S1. Recording conditions of the ²⁹Si MAS and ¹H-²⁹Si CPMAS NMR Spectra.

	²⁹ Si	
	MAS	CP MAS
Chemical shift standard	TMS ^a	TMS ^a
Frequency (MHz)	59.6	59.6
Pulse width (μs)	1.87	4
Flip angle	π/6	π/2
Contact time (ms)	/	8
Recycle time (s)	80	10 ^b
Spinning rate (kHz)	4	4
Scans number	1000	16000

^a TMS : TetraMethylSilane

^b The relaxation time t_1 was optimized

S2.5. Si-LTA at ambient pressure

Table S2. Cell parameters, atomic coordinates, occupancy factors and isotropic thermal parameters for Si-LTA at P_{amb} .

$a = 11.8539 \text{ \AA}$, $V = 1665.65 \text{ \AA}^3$						
	Site	x/a	y/b	z/c	Occupancy factor	UIISO
P_{amb}	Si	0	0.18292(4)	0.37007(5)	1	0.005(1)
	O1	0	0.2195(2)	0.5	1	0.010(5)
	O2	0.1105(1)	0.1105(1)	0.34247(11)	1	0.010(5)
	O3	0	0.2952(5)	0.29524(15)	1	0.010(5)
	W1	0.5	0.5	0.231(7)	0.070(6)	0.11(4)

Table S3. Bond distances (\AA) for the structural refinement of Si-LTA at P_{amb} . The H_2O distances with framework oxygen atoms and other H_2O molecules are larger than 3.2 \AA .

P_{amb}	Si_O1	1.600(1)	Si_O2 x2	1.600(1)	Si_O3	1.600(1)
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S3. Results

S3.2.a ^{29}Si MAS NMR.

The ^{29}Si MAS NMR spectra of Si-LTA before and after intrusion–extrusion porosimetric experiments with water and NaCl and CaCl_2 aqueous solutions are reported in Figure S1. The spectrum of the non-intruded sample exhibits one main resonance at -113 ppm ascribed to the one crystallographic silicon Q_4 site in LTA structure. No signals assigned to Q_3 groups, corresponding to defects as Si-OH groups, and expected at about -100 ppm are observed. After the intrusion-extrusion experiments the spectra change considerably. Two new broad resonances at -98 and -109 ppm appear and the resonance of Q_4 sites becomes broader and is shifted to -112 ppm . The resonance at -98 ppm is typical for Q_3 sites and reveals the formation of silanol ($\text{Si}(\text{OSi})_3\text{OH}$) groups. Thus, the intrusion of water, NaCl and CaCl_2 solutions leads to the formation of hydrophilic silanol groups that explains the bumper behavior with an irreversible intrusion of water. The resonance at -109 ppm is attributed to new Q_4 sites and might be explained as follows: the initial LTA structure is highly symmetric and there is only one crystallographic silicon Q_4 site (-113 ppm). At the short-range order, the formation of silanol groups, under water intrusion, leads to a distortion of the LTA framework and to the appearance of new Q_4 sites. The framework distortion explains also the shift and the broadening of the main Q_4 resonance. The Q_3 sites represent about 12 % of the total silicon sites in the case of CaCl_2 solutions and 15 % in the case of water and NaCl ones. These values correspond approximately to 2.5 and 3.2 silanol groups per unit cell, in quite agreement with the TG analysis. Thus, the lower content of silanol groups in the samples intruded with CaCl_2 is confirmed.

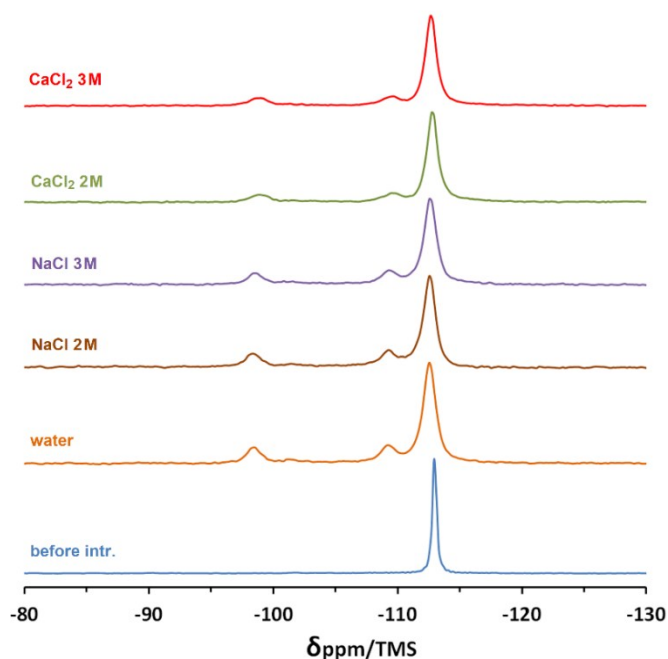


Figure S1. ^{29}Si -MAS NMR spectra of Si-LTAs before and after three intrusion-extrusion cycles in water, NaCl and CaCl_2 aqueous solutions (2M and 3M).

S3.2.b ^1H - ^{29}Si CPMAS NMR Spectroscopy

The ^1H - ^{29}Si CPMAS NMR spectra of the non-intruded sample and of the samples intruded with water, NaCl and CaCl_2 solutions are shown in Figure S2. These spectra were collected in order to enhance the signal of silicon atoms that bear protons and consequently to get evidence of the presence of silanol groups. Under these experimental conditions (short contact time – 8 ms), the spectrum of the non-intruded sample displays a low signal to noise ratio with a main signal at -113 ppm and three additional resonances at -98, -102 and -104 ppm. After porosimetric intrusion-extrusion experiments, two strong resonances are observed at -113 and -98 ppm corresponding to Q_4 and Q_3 sites, respectively. Two other smaller resonances at -102 and -109 ppm are also visible. As discussed above (Section ^{29}Si MAS NMR Spectroscopy), the resonance at -109 ppm might correspond to new Q_4 sites formed as a consequence of the LTA framework distortion after the formation of silanol groups (breaking of Si-O-Si bridges). The resonance at -102 ppm can be attributed to Q_3 sites. The relative intensity of the resonance corresponding to Q_3 sites is higher for the samples intruded with water and NaCl solutions in comparison with ones intruded with CaCl_2 solutions, result that is in quite good agreement with TG results.

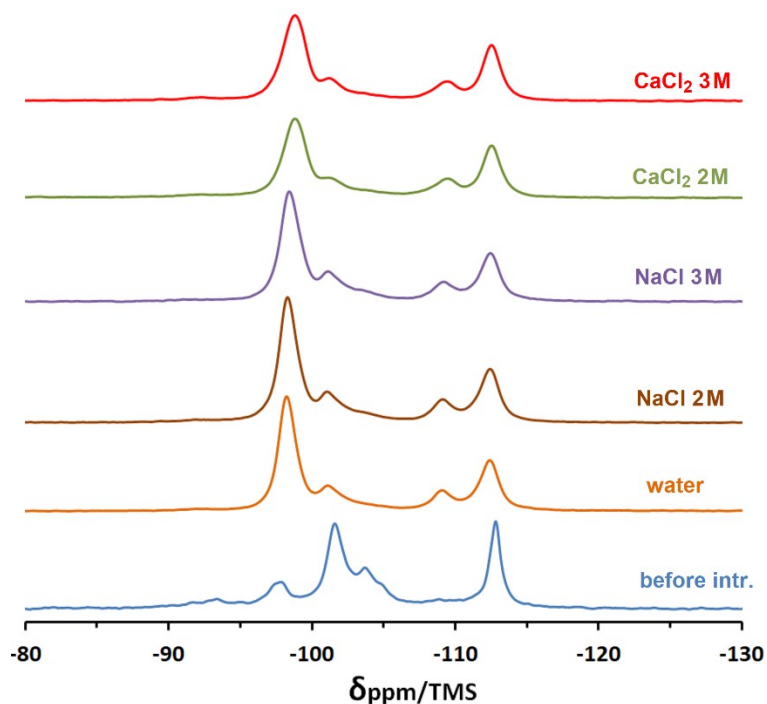


Figure S2. $^1\text{H}-^{29}\text{Si}$ CPMAS NMR spectra of Si-LTA samples before and after three porosimetric intrusion-extrusion cycles in water, NaCl and CaCl_2 aqueous solutions (2M and 3M).

S3.2.c Thermogravimetric analysis.

The results of thermogravimetric (TG) analysis of the Si-LTA samples before and after porosimetric intrusion-extrusion tests are shown in Figure S3. The total weight loss for the non-intruded sample is low (1.1 wt. %), confirming the hydrophobic character of the zeolite. A slight and continuous weight loss (about 0.25 wt %) between 300-800°C could be related to the removal of water molecules arising from condensation of silanol groups, corresponding to 0.4 OH-groups per unit cell ($\text{Si}_{24}\text{O}_{47.6}(\text{OH})_{0.4}$) (as also observed by $^1\text{H}-^{29}\text{Si}$ CPMAS NMR spectroscopy). After intrusion of water, NaCl and CaCl_2 solutions, the thermogravimetric curve of samples-LTA becomes completely different. The total weight loss varies from 9 to 12 wt. % and occurs in two main steps: the first one (6-9 wt. %), between 30 and 300 °C - but mainly below 100°C- is ascribed to the desorption of physisorbed water molecules; the second one, between 300-800 °C, can be ascribed to the removal of water molecules arising from condensation of silanol groups. In the case of the samples intruded with water and NaCl solutions, the weight loss is in the range of 2-2.7 wt. %, corresponding to 3.3-4 OH groups p.u.c., in the case of CaCl_2 solutions, particularly 3 M one, the weight loss is slightly lower 1.7 wt. %, equivalent to 2.8 silanol groups p.u.c.. Such result confirms the more reversible intrusion of CaCl_2 solutions found by the porosimetric analysis.

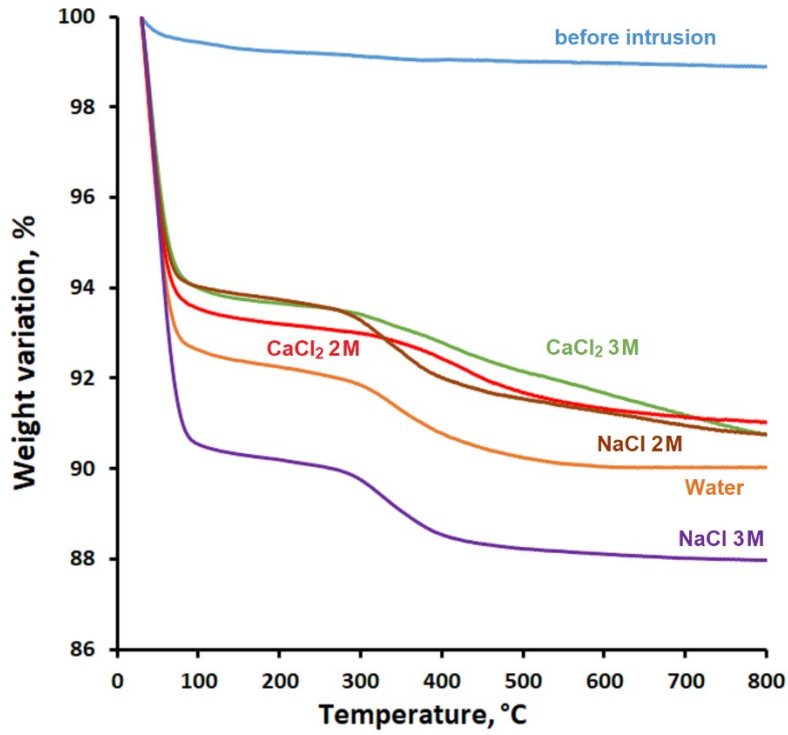


Figure S3. Thermogravimetric curves of Si-LTA samples before and after three porosimetric intrusion-extrusion cycles in water, NaCl and CaCl₂ aqueous solutions (2M and 3M).

S3.3. In situ HP XRPD

3.3.1 Unit Cell Parameter Evolution

Table S4. Cell parameter and volume of Si-LTA intruded by 2M and 3M NaCl and CaCl₂ electrolyte aqueous solutions at different pressure conditions.

NaCl 2M			NaCl 3M		
Pressure (GPa)	Cell Parameter (Å)	Cell Volume (Å ³)	Pressure (GPa)	Cell Parameter (Å)	Cell Volume (Å ³)
0.11	11.8398(1)	1659.69(3)	0.12	11.8444(1)	1661.66(3)
0.14	11.8368(8)	1658.49(3)	0.16	11.8445(1)	1661.70(4)
0.24	11.8237(1)	1652.94(3)	0.28	11.8096(1)	1647.03(5)
0.40	11.8091(1)	1646.84(4)			
0.59	11.8090(1)	1646.78(4)			
0.83	11.7720(3)	1631.4(1)			
CaCl ₂ 2M			CaCl ₂ 3M		
0.17	11.84765(7)	1663.02(3)	0.17	11.83958(6)	1659.62(2)
0.37	11.83021(9)	1655.69(4)	0.37	11.82110(8)	1651.86(3)
0.63	11.81294(8)	1648.44(3)	0.53	11.8139(1)	1648.87(5)
1.03	11.8161(2)	1649.78(9)	0.71	11.7682(2)	1629.77(7)
P _{amb} rev.	11.7728(3)	1631.7(1)			

S3.3.2 . Extraframework contents of Si-LTA/NaCl 2M and 3M

Table S5. Atomic coordinates, occupancy factors and isotropic thermal parameters for Si-LTA/NaCl 2M at different pressures.

	Site	x/a	y/b	z/c	Occupancy factor	UIISO
0.11 GPa	Si	0	0.18253(7)	0.3694(1)	1	0.024(1)
	O1	0	0.2169(4)	0.5	1	0.022(1)
	O2	0.1110(2)	0.1110(2)	0.3410(1)	1	0.022(1)
	O3	0	0.2958(3)	0.2958(3)	1	0.022(1)
	W2	0.372(4)	0.372(4)	0.372(4)	0.047(2)	0.09(8)
0.14 GPa	Si	0	0.1837(2)	0.3708(2)	1	0.019(1)
	O1	0	0.2230(5)	0.5	1	0.024(1)
	O2	0.1118(3)	0.1118(3)	0.3462(3)	1	0.024(1)
	O3	0	0.2966(3)	0.2966(3)	1	0.024(1)
	W1	0.5	0.5	0.176(3)	0.276(1)	0.18(2)
	W2	0.364(1)	0.364(1)	0.364(1)	0.258(4)	0.18(2)
	W3	0.5	0.5	0.5	0.13(1)	0.18(2)
0.24 GPa	Si	0	0.1836(2)	0.3719(3)	1	0.017(1)
	O1	0	0.2237(7)	0.5	1	0.025(2)
	O2	0.1164(3)	0.1164(3)	0.3459(4)	1	0.025(2)
	O3	0	0.2984(4)	0.2984(4)	1	0.025(2)
	W2b	0.319(1)	0.319(1)	0.392(1)	0.333	0.14(1)
	W3	0.5	0.5	0.5	0.87(1)	0.14(1)
	Cl	0.5	0.5	0.1345(6)	0.527(2)	0.28(1)
	Na	0.5	0.387(3)	0.241(1)	0.132(1)	0.12(1)
0.40 GPa	Si	0	0.1902(3)	0.3717(3)	1	0.026(1)
	O1	0	0.2197(7)	0.5	1	0.027(2)
	O2	0.1138(4)	0.1138(4)	0.3465(5)	1	0.027(2)
	O3	0	0.2975(5)	0.2975(5)	1	0.027(2)
	W2b	0.3286(7)	0.3286(7)	0.376(1)	0.303(2)	0.14(1)
	W3	0.5	0.5	0.5	0.80(1)	0.14(1)
	W4	0.097(9)	0	0	0.09(1)	0.14(1)
	Cl	0.5	0.5	0.1340(8)	0.602(3)	0.27(1)
	Na	0.5	0.6787(18)	0.240(1)	0.150(1)	0.06(1)

Table S6. Bond distances (Å) for Si-LTA/NaCl 2M at different pressures.

0.11 GPa	Si_O1	1.6000(5)	Si_O2 x2	1.600(3)	Si_O3	1.600(5)
0.14 GPa	Si_O1	1.6000(2)	Si_O2 x2	1.600(1)	Si_O3	1.600(2)
	W1_W2	3.18(2)	W2_W2	3.22(3)	W2_W3	2.788(2)
0.24 GPa	Si_O1	1.587(4)	Si_O2 x2	1.619(2)	Si_O3	1.612(3)
	Cl_O1 x4	3.633(7)	Cl_O3 x4	3.727(8)		
	Cl_W2b x8	3.314(7)	W2b_W3	3.29(1)	W2b_Na	2.330(5)

0.40 GPa	Si_O1	1.554(5)	Si_O2 x2	1.646(3)	Si_O3	1.541(3)
	Cl_O1 x4	3.669(8)	Cl_O3 x4	3.733(8)		
	Cl_W2b x8	3.39(1)	W2b_W3	3.214(9)	W2b_Na	2.369(9)

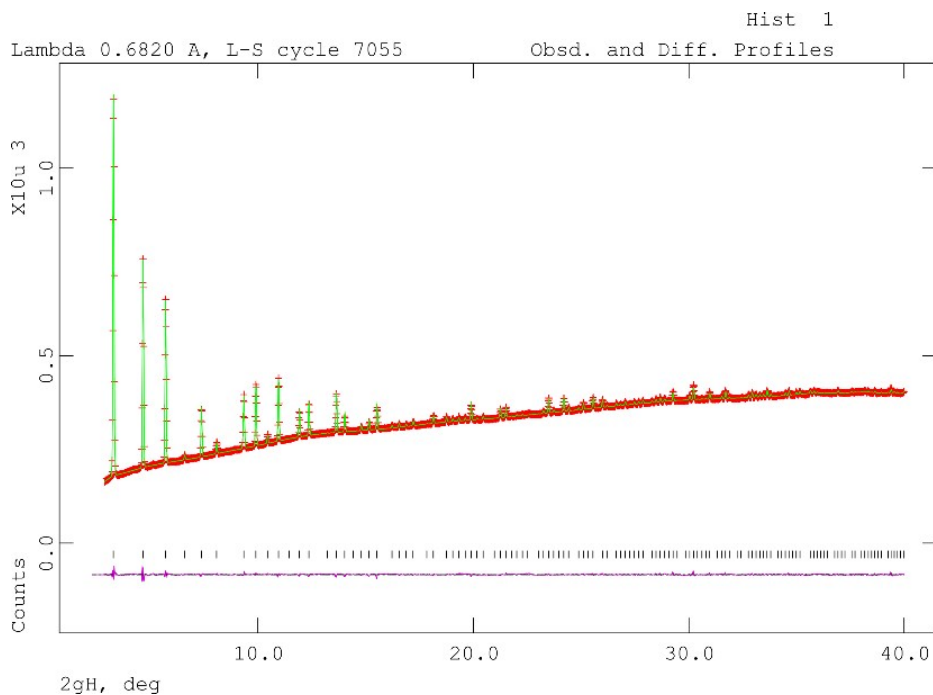


Figure S4. Observed (red dash marks) and calculated (green line) diffraction patterns and final difference curve (purple line) from Rietveld refinements of Si-LTA under intrusion of 2M NaCl aqueous solution at 0.11 GPa.

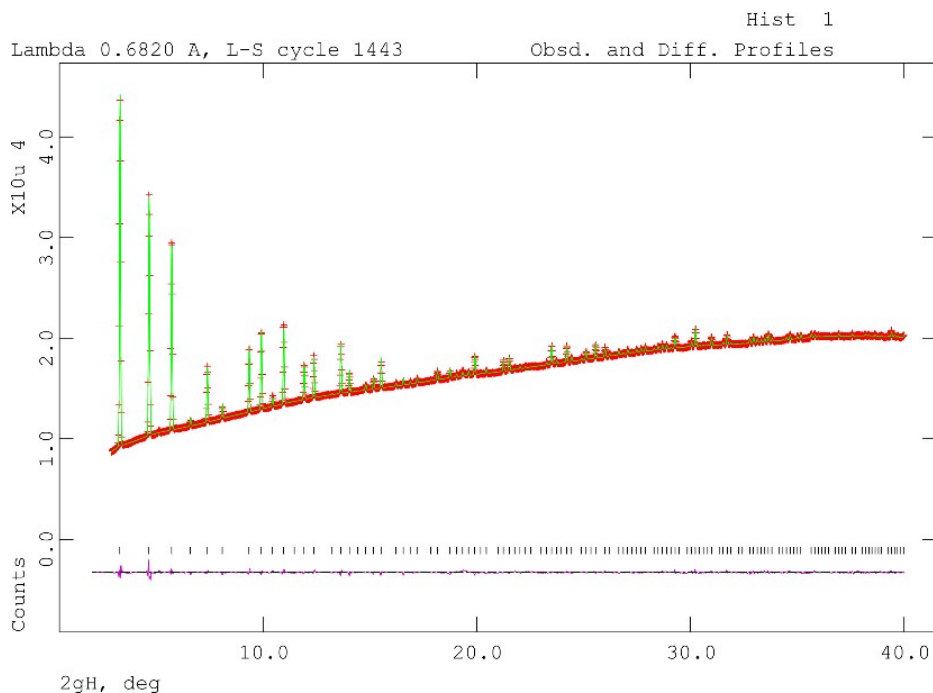


Figure S5. Observed (red dash marks) and calculated (green line) diffraction patterns and final difference curve (purple line) from Rietveld refinements of Si-LTA under intrusion of 2M NaCl aqueous solution at 0.14 GPa.

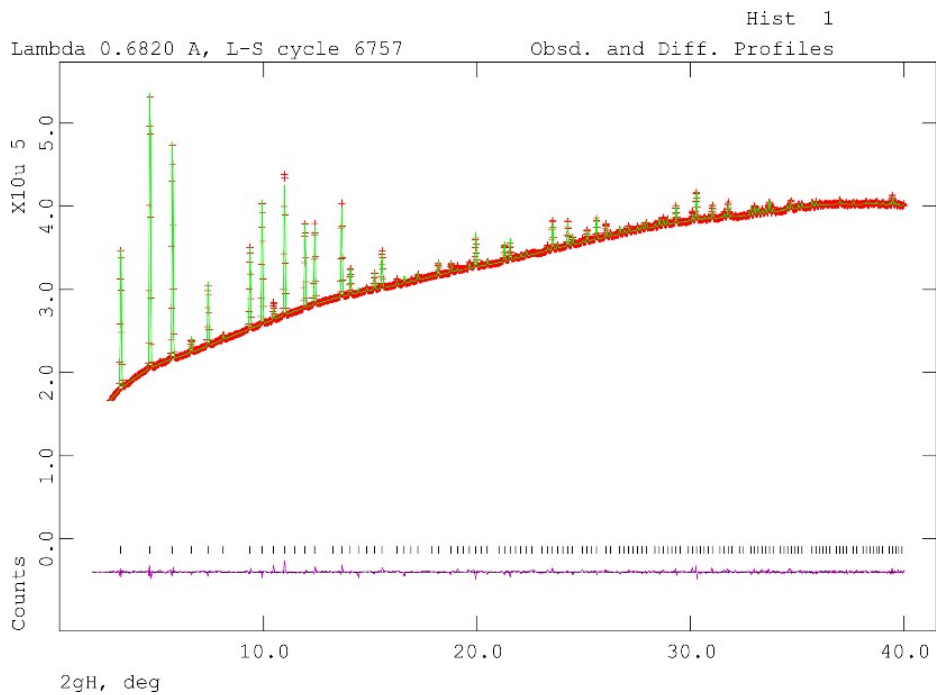


Figure S6. Observed (red dash marks) and calculated (green line) diffraction patterns and final difference curve (purple line) from Rietveld refinements of Si-LTA under intrusion of 2M NaCl aqueous solution at 0.24 GPa.

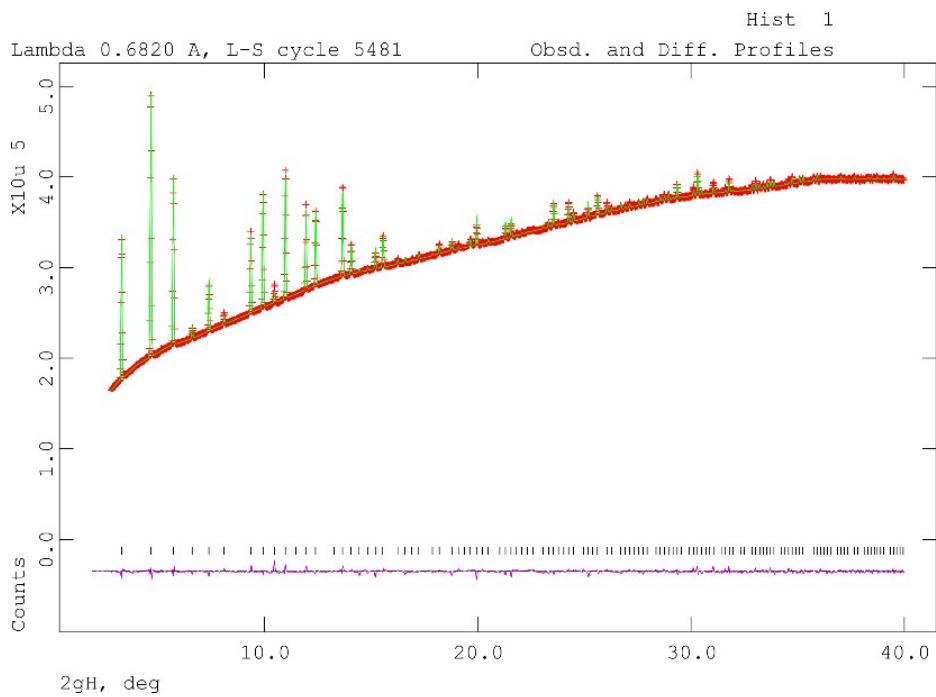


Figure S7. Observed (red dash marks) and calculated (green line) diffraction patterns and final difference curve (purple line) from Rietveld refinements of Si-LTA under intrusion of 2M NaCl aqueous solution at 0.40 GPa.

Table S7. Atomic coordinates, occupancy factors and isotropic thermal parameters for Si-LTA/NaCl 3M at different pressures.

	Site	x/a	y/b	z/c	Occupancy factor	UIISO
0.12 GPa	Si	0	0.18396(7)	0.3710(1)	1	0.024(7)
	O1	0	0.2243(4)	0.5	1	0.019(1)
	O2	0.1116(2)	0.1116(2)	0.3466(2)	1	0.019(1)
	O3	0	0.2964(3)	0.2964(3)	1	0.019(1)
	W1	0.5	0.5	0.194(2)	0.295(6)	0.10(2)
	W2	0.365(1)	0.365(1)	0.365(1)	0.198(3)	0.10(2)
0.14 GPa	Si	0	0.1872(2)	0.3713(2)	1	0.027(1)
	O1	0	0.2264(7)	0.5	1	0.022(2)
	O2	0.1131(4)	0.1131(4)	0.3452(4)	1	0.022(2)
	O3	0	0.2953(5)	0.2953(5)	1	0.022(2)
	W1	0.5	0.5	0.188(5)	0.35(1)	0.34(1)
	W2	0.352(1)	0.352(1)	0.352(1)	0.452(6)	0.34(1)

Table S8. Bond distances (Å) for Si-LTA/NaCl 3M at different pressures.

0.11 GPa	Si_O1	1.6000(6)	Si_O2 x2	1.601(4)	Si_O3	1.599(6)
	W1_W2 x4	3.05(1)	W2_W2	3.22(3)	W2_W3	2.788(2)
0.14 GPa	Si_O1	1.593(1)	Si_O2 x2	1.631(2)	Si_O3	1.564(3)
	W1_W2 x4	3.659(3)				

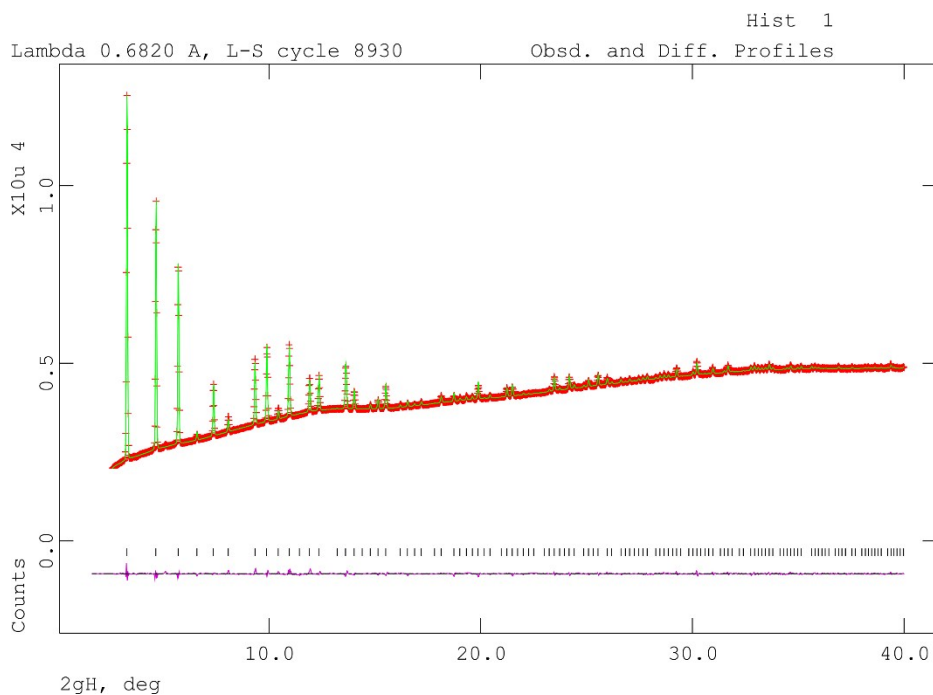


Figure S8. Observed (red dash marks) and calculated (green line) diffraction patterns and final difference curve (purple line) from Rietveld refinements of Si-LTA under intrusion of 3M NaCl aqueous solution at 0.12 GPa.

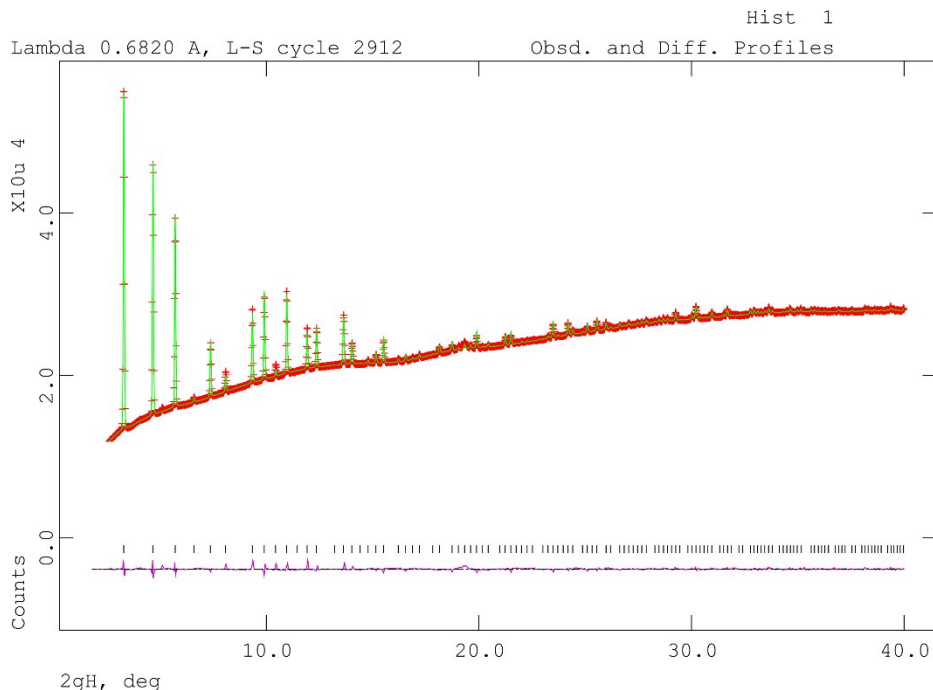


Figure S9. Observed (red dash marks) and calculated (green line) diffraction patterns and final difference curve (purple line) from Rietveld refinements of Si-LTA under intrusion of 3M NaCl aqueous solution at 0.14 GPa.

Table S9. Details of structural refinement parameters of Si-LTA/NaCl 2M and 3M at different pressures.

	P (GPa)	Rwp (%)	Rp (%)	RF ² (%)	Nobs	Nvar
Si-LTA/NaCl 2M	0.11	0.4	0.2	12.5	223	50
	0.14	0.4	0.3	15.0	222	52
	0.24	0.4	0.2	18.12	222	57
	0.40	0.4	0.2	25.9	222	61
Si-LTA/NaCl 3M	0.12	0.5	0.3	10.8	235	50
	0.14	0.5	0.3	17.3	236	50

According to the data on Si-LTA collected at P_{amb} in capillary, 0.4 H₂O molecules are located in W1 site. When Si-LTA/NaCl 2M system is compressed at 0.11 GPa, we observe the migration of H₂O from W1 to a new site, named W2, without any increase of the overall water content (Figure 3 in the paper). When pressure rises to 0.14 GPa, 3.6 H₂O molecules, bonded each other, occupy the Si-LTA large cage in three different sites: W1, W2 and W3. In the case of Si-LTA/NaCl 3M, W1 and W2 sites are already occupied at 0.12 GPa, for a total of 3.3 molecules (Figure 4 in the paper). Then, the number of water molecules increases up to 5.6 at 0.16 GPa, increasing the occupancy factors of W1

and W2. For Si-LTA/NaCl 3M system, no further structural considerations are possible, due to the low quality of the XRPD data above 0.16 GPa.

In Si-LTA/NaCl 2M, the ion intrusion occurs between 0.14 and 0.24 GPa (Figure 3 in the paper). At 0.24 GPa, H₂O molecules are distributed over W3 and the new site W2b (multiplicity changes from 8 in W2 to 24 in W2b since the site moves out from the threefold axis), both highly occupied, giving a total amount of 9 H₂O molecules. The molecules in W2b site interact with three chlorine (placed in the same site of W1) and three sodium ions. Two H₂O molecules coordinate each sodium cation, while the chlorine anion bonds a number of H₂O molecules ranging between two and four (Figure 3 in the paper). Moreover, chlorine anions are located at ~3.6 -3.7 Å from eight framework oxygen atoms. These distances are compatible with O-H---Cl⁻ hydrogen bonding interactions and hence suggest the presence of framework silanol groups (Si-OH) pointing towards the chlorine anions. The presence of silanol groups inside the intruded samples is confirmed by the results of ²⁹Si MAS NMR spectroscopy and thermogravimetric analysis. At 0.40 GPa the extraframework configuration is essentially maintained, with the only migration of 0.3 H₂O molecules from W3 site to the new position W4 inside the sodalite cage. A similar pressure-induced penetration of additional H₂O molecules in the sodalite cage was observed also by Likhacheva et al. compressing Na-LTA in pure water ¹.

S3.3.3. Extraframework content of Si-LTA/CaCl₂ 2M and 3M

Table S10. Atomic coordinates, occupancy factors and isotropic thermal parameters for Si-LTA/CaCl₂ 2M at different pressures.

	Site	x/a	y/b	z/c	Occupancy factor	UIISO
0.17 GPa	Si	0	0.1840(2)	0.3705(2)	1	0.0316(7)
	O1	0	0.2237(5)	0.5	1	0.03(1)
	O2	0.1124(3)	0.1124(3)	0.3455(3)	1	0.03(1)
	O3	0	0.2956(4)	0.2956(4)	1	0.03(1)
	W2	0.3086(3)	0.3086(3)	0.3086(3)	0.36(1)	0.31(1)
	W3	0.5	0.5	0.5	0.33(2)	0.31(1)
	Cl	0.5	0.5	0.1654(3)	0.293(3)	0.34(1)
	Ca	0.5	0.3439(3)	0.3439(3)	0.073(1)	0.18(2)
0.37 GPa	Si	0	0.1822(2)	0.3723(2)	1	0.0285(7)
	O1	0	0.2289(5)	0.5	1	0.032(1)
	O2	0.1146(3)	0.1143(3)	0.3458(3)	1	0.032(1)
	O3	0	0.2956(4)	0.2956(4)	1	0.032(1)
	W2	0.3054(2)	0.3054(2)	0.3054(2)	0.84(1)	0.343(5)
	W3	0.5	0.5	0.5	0.89(2)	0.343(5)
	Cl	0.5	0.5	0.1631(3)	0.733(3)	0.37(1)

	Ca	0.5	0.3289(3)	0.3289(3)	0.183(1)	0.34(1)
0.63 GPa	Si	0	0.1827(2)	0.3721(0)	1	0.0303(7)
	O1	0	0.2289(5)	0.5	1	0.035(1)
	O2	0.1153(3)	0.1153(3)	0.3450(3)	1	0.035(1)
	O3	0	0.2951(4)	0.2951(4)	1	0.035(1)
	W2	0.3031(2)	0.3031(2)	0.3031(2)	0.815(9)	0.198(7)
	W3	0.5	0.5	0.5	0.82(1)	0.198(7)
	W4b	0.055(4)	0.055(4)	0.055(4)	0.053(2)	0.198(7)
	Cl	0.5	0.5	0.1637(3)	0.804(3)	0.503(9)
	Ca	0.5	0.3187(2)	0.3187(2)	0.200(1)	0.29(1)

Table S11. Bond distances (Å) in Si-LTA/CaCl₂ 2M at different pressures.

0.17 GPa	Si_O1	1.605(3)	Si_O2 x2	1.606(1)	Si_O3	1.593(2)
	Cl_O1 x4	3.815(6)				
	Cl_W2 x4	3.629(3)	Ca_W2 x2	2.344(4)	Ca_W3	2.616(6)
	Ca_Cl x2	2.810(2)				
0.37 GPa	Si_O1	1.608(3)	Si_O2 x2	1.605(2)	Si_O3	1.620(2)
	Cl_O1 x4	3.743(5)	W2_O2 x3	3.227(7)		
	Cl_W2 x4	3.666(2)	Ca_W2 x2	2.336(3)	Ca_W3	2.863(4)
	Ca_Cl x2	2.819(2)				
0.63 GPa	Si_O1	1.606(3)	Si_O2 x2	1.610(2)	Si_O3	1.610(2)
	Cl_O1 x4	3.741(5)	W2_O2 x3	3.177(6)		
	Cl_W2 x2	3.678(2)	Ca_W2 x2	2.340(3)	Cl_Ca x2	2.818(2)

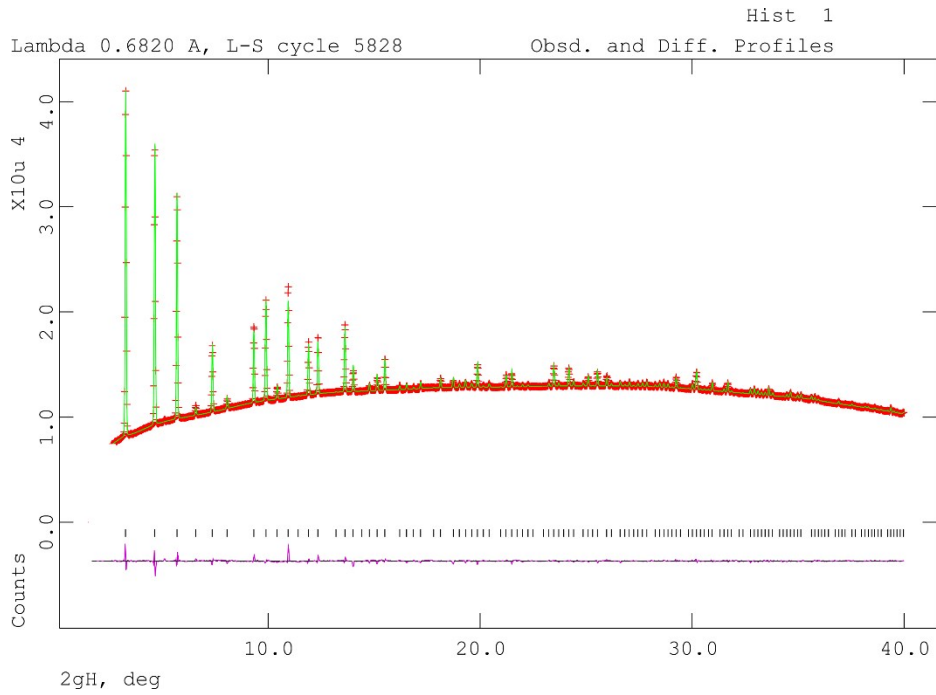


Figure S10. Observed (red dash marks) and calculated (green line) diffraction patterns and final difference curve (purple line) from Rietveld refinements of Si-LTA under intrusion of 2M CaCl₂ aqueous solution at 0.17 GPa.

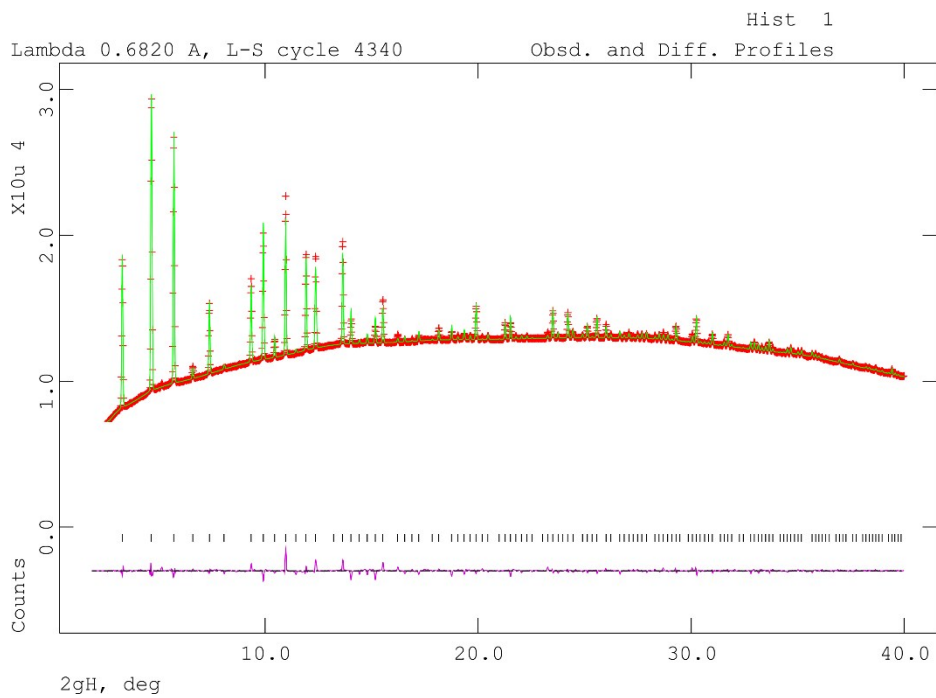


Figure S11. Observed (red dash marks) and calculated (green line) diffraction patterns and final difference curve (purple line) from Rietveld refinements of Si-LTA under intrusion of 2M CaCl₂ aqueous solution at 0.37 GPa.

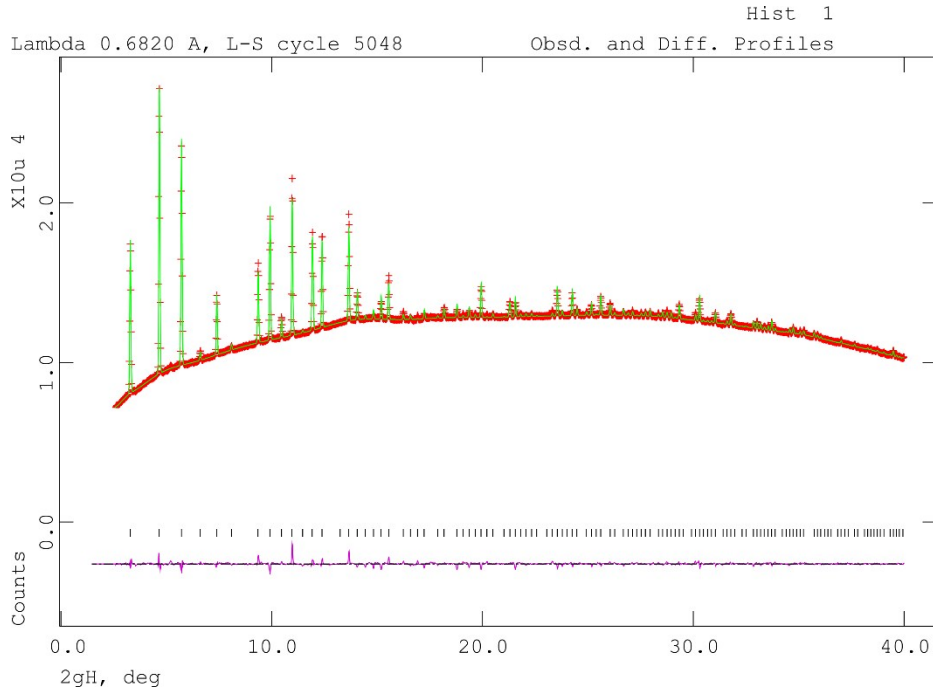


Figure S12. Observed (red dash marks) and calculated (green line) diffraction patterns and final difference curve (purple line) from Rietveld refinements of Si-LTA under intrusion of 2M CaCl_2 aqueous solution at 0.63 GPa.

Table S12. Atomic coordinates, occupancy factors and isotropic thermal parameters for Si-LTA/ CaCl_2 3M at different pressures.

	Site	x/a	y/b	z/c	Occupancy factor	UIISO
0.17 GPa	Si	0	0.18376(17)	0.3714(2)	1	0.0358(6)
	O1	0	0.2202(5)	0.5	1	0.030(1)
	O2	0.1115(2)	0.1115(2)	0.3430(3)	1	0.030(1)
	O3	0	0.2947(2)	0.2947(3)	1	0.030(1)
	W2	0.310(3)	0.3100(3)	0.3100(3)	0.301(8)	0.34(1)
	W3	0.5	0.5	0.5	0.12(1)	0.34(1)
	Cl	0.5	0.5	0.1664(3)	0.295(2)	0.37(1)
	Ca	0.5	0.3494(4)	0.3494(4)	0.079(1)	0.17(2)
0.37 GPa	Si	0	0.18181(22)	0.3722(3)	1	0.0302(9)
	O1	0	0.2278(6)	0.5	1	0.029(2)
	O2	0.1147(4)	0.1147(4)	0.3436(4)	1	0.029(2)
	O3	0	0.2953(4)	0.2953(4)	1	0.029(2)
	W2	0.30618(31)	0.30618(31)	0.3062(3)	0.84(1)	0.360(6)
	W3	0.5	0.5	0.5	0.68(2)	0.360(6)
	Cl	0.5	0.5	0.1623(4)	0.739(4)	0.391(7)
	Ca	0.5	0.3299(4)	0.3299(4)	0.184(1)	0.33(1)

Table S13. Bond distances (Å) in Si-LTA/CaCl₂ 3M at different pressures.

0.17 GPa	Si_O1	1.582(3)	Si_O2 x2	1.609(2)	Si_O3	1.597(2)
	Cl_O1 x4	3.854(5)				
	Cl_W2 x2	3.607(3)	Ca_W2 x2	2.344(4)	Ca_W3	2.522(6)
	Ca_Cl x2	2.806(3)				
0.37 GPa	Si_O1	1.605(4)	Si_O2 x2	1.607(2)	Si_O3	1.621(3)
	Cl_O1 x4	3.746(6)	W2_O2 x3	3.231(8)		
	Cl_W2 x4	3.659(3)	Cl_Ca x2	2.823(3)	Ca_W2 x2	2.325(4)
	Ca_W3	2.844(6)				

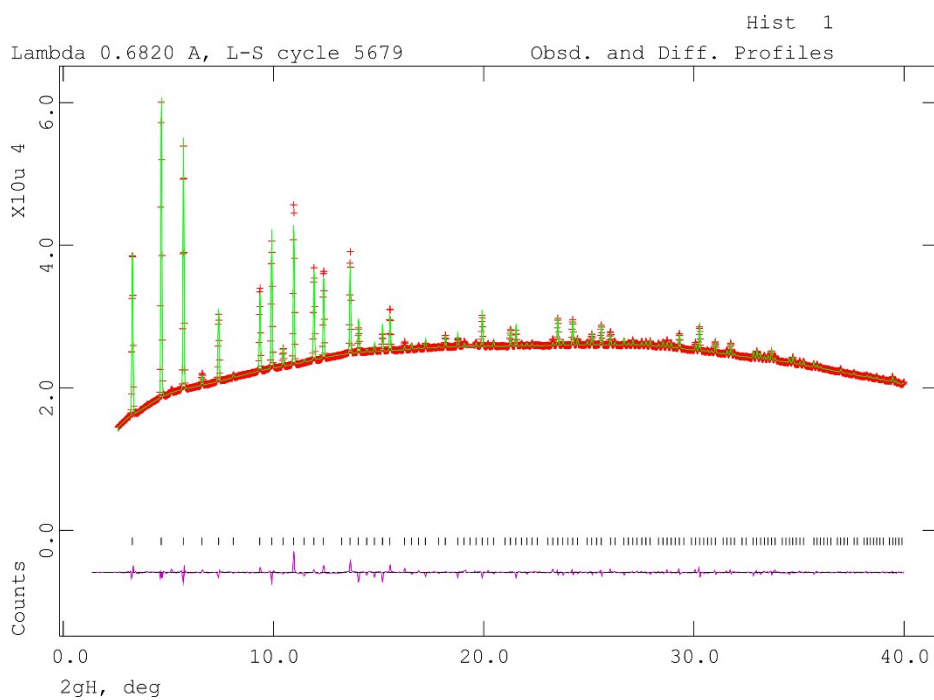


Figure S13. Observed (red dash marks) and calculated (green line) diffraction patterns and final difference curve (purple line) from Rietveld refinements of Si-LTA under intrusion of 3M CaCl₂ aqueous solution at 0.17 GPa.

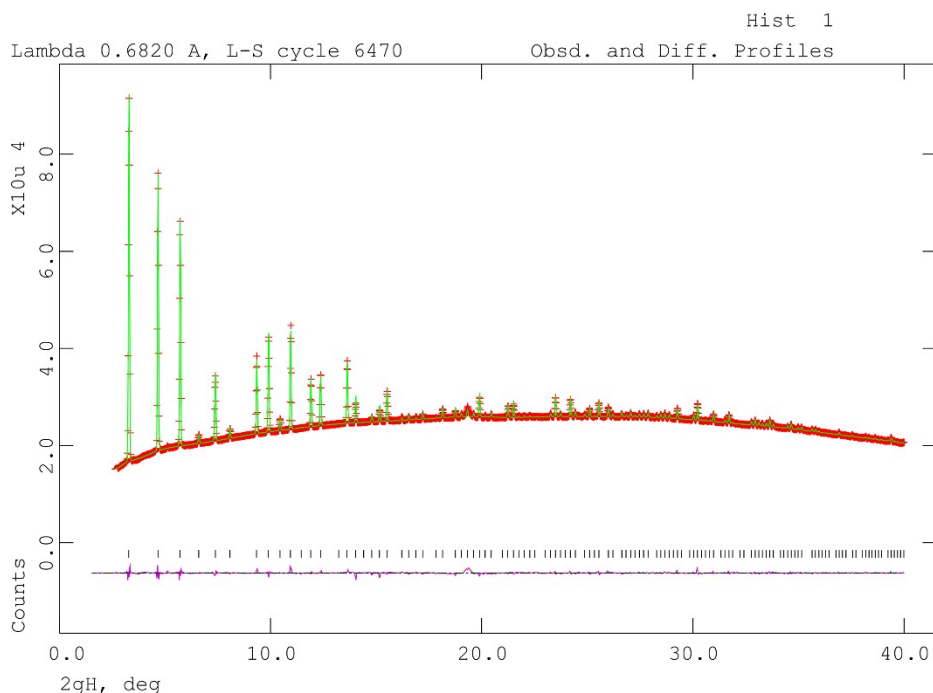


Figure S14. Observed (red dash marks) and calculated (green line) diffraction patterns and final difference curve (purple line) from Rietveld refinements of Si-LTA under intrusion of 3M CaCl₂ aqueous solution at 0.37 GPa.

Table S14. Details of structural refinement parameters of Si-LTA compressed in CaCl₂ 2M and 3M solutions.

	P (GPa)	Rwp (%)	Rp (%)	RF ² (%)	Nobs	Nvar
Si-LTA/CaCl ₂ 2M	0.17	0.7	0.3	13.1	223	53
	0.37	0.7	0.4	18.1	223	53
	0.63	0.6	0.3	18.07	222	57
Si-LTA/CaCl ₂ 3M	0.17	0.6	0.6	14.4	223	54
	0.37	0.7	0.4	17.29	222	54

Contrary to what observed for NaCl solutions, in the case CaCl₂ solutions both ions and H₂O molecules penetrate the LTA cage already at 0.17 GPa (Figure 6 and 7 in the paper), regardless the electrolyte concentration. The structural data obtained for both concentrations are perfectly consistent up to 0.37 GPa. At 0.17 GPa, about 3 H₂O molecules, 0.8 Ca²⁺ cations and 1.7 Cl⁻ anions enter the zeolite pores. Chlorine and calcium ions are bonded each other and located in the main cage. The chlorine anions interact with the framework oxygen atoms, again suggesting, as previously discussed, the presence of silanol defects on zeolite framework. H₂O molecules are spread over two independent sites: W2 molecules coordinate both Ca²⁺ and Cl⁻, while W3 interacts only with Ca²⁺. The number of

ions and H₂O molecules rises with pressure, roughly doubling from 0.17 to 0.37 GPa for both the solution concentrations (Table 4). At 0.37 GPa, for both systems, chlorine anions maintain their bonds with calcium, H₂O molecules and the framework. At this pressure, new bonds are also established between W2 and framework oxygen atoms.

At 0.63 GPa, structural data are available only for Si-LTA/CaCl₂ 2M system. The only differences found with respect to the previous pressure point are: i) the migration of 0.4 H₂O molecules inside sodalite cage (W4b site) and ii) the loss of interaction between W3 and Ca²⁺ cation.

Bibliography

1. Likhacheva, A. Y.; Malyshev, M. E.; Manakov, A. Y.; Goryainov, S. V.; Ancharov, A. I., Non-Hydrostatic Compression of Zeolite Naa in Water Medium: Connection to Anomalous Conductivity. *Z. Kristallogr.* **2009**, *224*, 137-143.