Supporting Information

Cation control of molecular sieving by flexible Li-containing zeolite Rho

Magdalena M. Lozinska, Enzo Mangano, Alex G. Greenaway, Stephen P. Thompson, Claire A. Murray, Robin Fletcher, Stefano Brandani and Paul A. Wright*

S1. Preparation of cation-exchanged forms of Li- and M,Li-Rho

S1.1 Synthesis of Na,Cs-Rho(3.9)

Zeolite Na,Cs-Rho was synthesised from the gel composition: 0.31 NaOH : 0.02 Cs_2O: 1.0 Al_2O_3 : 3.1 SiO_2 : 0.16 (18-crown-6) : 14 H_2O, according to published procedures.[1,2] The starting mixture was prepared by dissolving 1,4,7,10,13,16-hexaoxacy-clooctadecane (4 mmol; Sigma-Aldrich), cesium hydroxide (5 mmol; Sigma-Aldrich) and sodium hydroxide (8 mmol; Fisher Chemicals) in distilled water. Sodium aluminate (26 mmol; BDH Chemicals Ltd.) followed by colloidal silica, Ludox AS-40 (208 mmol; Sigma-Aldrich) was added and the mixture stirred until homogeneous. The gel formed was aged at room temperature for 24 hours in a closed polypropylene bottle under continuous stirring. The crystallization was carried out under static conditions in the same closed polypropylene bottle for 8 days at 383 K. After reaction, the solid obtained was filtered, washed with distilled water then dried at 373 K overnight. The as-prepared Na,Cs-Rho was heated at 823 K under oxygen for 12 hours to remove the template.

S1.2 Synthesis of Na,Cs-Rho(3.2)

Zeolite Na,Cs-Rho was synthesised by modifying a published procedure.[3] The starting mixture was prepared by dissolving aluminium isopropoxide (2.0 mmol; Sigma-Aldrich) in sodium hydroxide (50 wt %; 6.2 mmol; Sigma-Aldrich) at 373 K. After cooling to RT, cesium hydroxide (50 wt %; 1.0 mmol; Sigma-Aldrich) followed by colloidal silica, Ludox AS-30 (100 mmol; Sigma-Aldrich) and distilled water (2.1 mmol) were added and the mixture was stirred until homogeneous. The gel formed was aged at room temperature for 4 days in an autoclave. The crystallisation was carried out under static conditions in the same autoclave for 5 days at 363 K. After reaction, the solid obtained was filtered, washed with distilled water then dried at 373 K overnight. Two batches of 4 g each were prepared.

S1.3 Determination of Si/Al ratio and ion exchange of Na,Cs-Rho samples

The compositions of Li,M-Rho samples were estimated from a combination of MAS NMR spectroscopy and EDX analysis.

Deconvolution of the ^{29}Si MASNMR of the as-prepared Na,Cs-Rho samples, in which all aluminium occupies tetrahedral sites, was used to determine the framework Si/Al ratio of

zeolite Rho. The Si/Al ratio measured in the both as-prepared zeolites Rho was obtained by deconvolution of the ^{29}Si MAS NMR spectrum as 3.9 and 3.2.

Ion exchange of Na,Cs-Rho(3.9) and Na,Cs-Rho(3.2) was conducted according to published procedures.[2,4-7] The calcined Na,Cs-Rho(3.9) and synthesised Na,Cs-Rho(3.2) were fully exchanged with 3M NH_4Cl solution (99.9%; Alfa Aesar), eight times for 5 hours until no cesium or sodium could be observed by EDX analysis. Subsequently the ammonium form was converted to lithium form by additional repeated extended cation exchange treatments with 10% $LiNO_3$ solutions (99.5-99.9%; Sigma-Aldrich) at 353 K in a beaker.

S1.4 Determination of the unit cell composition of M,Li-Rho(3.9) samples

The compositions of M,Li-Rho samples were estimated from a combination of MAS NMR spectroscopy and AAS.

The Li,Na and Li,Cs ion exchange experiments were carried out in a 50 ml beaker held at 333K for 30 mins. Weighed portions (0.20 g) of Li-Rho zeolite were stirred with 10.0 mL of $NaNO_3$ or $CsNO_3$ solution. The concentration of Na^+ and Cs^+ was gradually increased to obtain the required exchange levels and it was in the range of 0.2-50 mg/L Na^+ or Cs^+. Additionally, a high concentration of NH_4^+ (200 mg/L) was used to determine the total amount of Li^+ present in the zeolite. In this case ion exchange was carried out successively until no Li^+ was observed in the solution by atomic absorption spectroscopy (AAS).

To determine the lithium content of the partially cation-exchanged zeolite, the amount of Li^+ ions lost to the solution during ion exchange was calculated and subtracted from the determined total amount of Li. All the solutions were transferred to 50.0 ml volumetric flasks and enough deionised water was added. The calibration curves were provided and were selected according to the expected concentrations of Li in the solution: 5 and 10 ppm. Standard solutions were prepared by diluting the standard Li solution with water. A blank sample contained $NaNO_3$ or $CsNO_3$ solution, and water. The concentrations of Li in the solutions are the average of three measurements. The analytical characteristic of the ion exchange of Li-Rho, including mass of Li in the solution and number of cations per unit cell is summarised in Table S1.1.

Table S1.1 The analytical characteristic of the ion exchange of Li-Rho

Conc. of Li in the solution (ppm)[a)]	Volume of the solution (mL)	Mass of Li in the solution (mg)	Li cations in the solution/ unit cell	Unit cell composition from Rietveld refinement
8.40[b)]	50.0	0.42	9.80	$Li_{9.8}Al_{9.8}Si_{38.2}O_{96}$
6.30	50.0	0.32	7.35	$Li_{7.7}Na_{2.1}Al_{9.8}Si_{38.2}O_{96}$
4.71	50.0	0.24	5.49	$Li_{5.4}Na_{4.3}Al_{9.8}Si_{38.2}O_{96}$
3.00	50.0	0.15	3.50	$Li_{3.4}Na_{6.3}Al_{9.8}Si_{38.2}O_{96}$
7.60	50.0	0.38	8.80	$Li_{8.0}Cs_{0.8}Al_{9.8}Si_{38.2}O_{96}$
7.05	50.0	0.35	8.28	$Li_{8.0}Cs_{1.8}Al_{9.8}Si_{38.2}O_{96}$
6.41	50.0	0.32	7.47	$Li_{7.2}Cs_{2.8}Al_{9.8}Si_{38.2}O_{96}$

a) the average of three measurements b) sum of three successive measurements (1st: 8.0 ppm; 2nd: 0.4 ppm;3rd 0.0 ppm)

S2. Crystallography of Li-Rho, Na,Li-Rho, Cs,Li-Rho and Li-Rho(3.2) materials

S2.1 Refinement of dehydrated structures against laboratory PXRD data

Table S2.1 Crystallographic details of Li,Na-Rho, Li,Cs-Rho and Li-Rho(3.2) materials

	$Cs_{0.8}$Li-Rho	$Cs_{1.8}$Li-Rho	$Cs_{2.8}$Li-Rho
Unit cell	$Li_{8.0}Cs_{0.8}Al_{9.8}Si_{38.2}O_{96}$	$Li_{8.0}Cs_{1.8}Al_{9.8}Si_{38.2}O_{96}$	$Li_{7.2}Cs_{2.8}Al_{9.8}Si_{38.2}O_{96}$
Temp./K	298	298	298
Space group	$I\bar{4}3m$	$I\bar{4}3m$	$I\bar{4}3m$
X-ray source	Cu $K\alpha_1$	Cu $K\alpha_1$	Cu $K\alpha_1$
Diffractometer	Stoe	Stoe	Stoe
Wavelength (Å)	1.54056	1.54056	1.54056
a/ Å	14.3559(6)	14.4113(3)	14.4691(2)
Volume/Å^3	2958.6(4)	2992.99(17)	3029.19(13)
R_p	0.0457	0.0347	0.0332
R_{wp}	0.0638	0.0506	0.0469
χ^2	0.07676	0.08618	0.07095

	$Na_{2.1}$Li-Rho	$Na_{4.3}$Li-Rho	$Na_{6.3}$Li-Rho
Unit cell	$Li_{7.7}Na_{2.1}Al_{9.8}Si_{38.2}O_{96}$	$Li_{5.4}Na_{4.3}Al_{9.8}Si_{38.2}O_{96}$	$Li_{3.4}Na_{6.3}Al_{9.8}Si_{38.2}O_{96}$
Temp./K	298	298	298
Space group	$I\bar{4}3m$	$I\bar{4}3m$	$I\bar{4}3m$
X-ray source	Cu $K\alpha_1$	Cu $K\alpha_1$	Cu $K\alpha_1$
Diffractometer	Stoe	Stoe	Stoe
Wavelength (Å)	1.54056	1.54056	1.54056
a/ Å	14.3017(1)	14.3176(2)	14.3331(3)
Volume/Å^3	2925.25(20)	2935.03(22)	2944.57(15)
R_p	0.0246	0.0316	0.0331
R_{wp}	0.0323	0.0425	0.0435
χ^2	0.03998	0.22346	0.04515

	Li-Rho(3.2)
Unit cell	$Li_{9.4}Al_{11.4}Si_{36.6}O_{96}$
Temp./K	298
Space group	$I\bar{4}3m$
X-ray source	Cu $K\alpha_1$
Diffractometer	Stoe
Wavelength (Å)	1.54056
a/ Å	14.1715(5)
Volume/Å^3	2846.11(11)
R_p	0.0587
R_{wp}	0.0914
χ^2	0.16732

S2.1.1 Cs,Li-Rho series

Table S2.2 Fractional atomic coordinates, occupancies, multiplicities, isotropic displacement parameters (in $Å^2$), Si-O bond lengths, OTO angles of dehydrated Cs,Li-Rho series – laboratory data

$Cs_{0.8}$Li-Rho	x	y	z	Occup.	Mult.	Uiso
Si1	0.27850(33)	0.1208(4)	0.4163(4)	0.8	48	0.025
Al1	0.27850(33)	0.1208(4)	0.4163(4)	0.2	48	0.025
O1	0.2155(6)	0.2155(6)	0.3947(9)	1.0	24	0.025
O2	0.1143(5)	0.1143(5)	0.6304(6)	1.0	24	0.025
O3	0.0284(6)	0.2205(5)	0.3860(6)	1.0	48	0.025
Li (S6R)	0.2754(29)	0.2754(29)	0.2754(29)	1.0	8	0.025
Cs (D8R)	0.0	0.0	0.5	0.1367(27)	6	0.025
Atom 1	**Atom 2**	**Length**				
Si1	O1	1.662(6)				
Si1	O2	1.606(7)				
Si1	O3	1.624(6)				
Si1	O3	1.613(8)				
Atom 1	**Atom 2**	**Atom 3**	**OTO angle**			
O1	Si1	O2	113.6(7)			
O1	Si1	O3	109.8(6)			
O1	Si1	O3	103.9(7)			
O2	Si1	O3	119.2(5)			
O2	Si1	O3	105.7(5)			
O3	Si1	O3	102.8(7)			

$Cs_{1.8}$Li-Rho	x	y	z	Occup.	Mult.	Uiso
Si1	0.27409(21)	0.12268(20)	0.42028(24)	0.8	48	0.0127(9)
Al1	0.27409(21)	0.12268(20)	0.42028(24)	0.2	48	0.0127(9)
O1	0.2236(4)	0.2236(4)	0.3928(6)	1.0	24	0.0127(9)
O2	0.12127(35)	0.12127(35)	0.6333(5)	1.0	24	0.0127(9)
O3	0.0347(4)	0.2073(4)	0.3834(4)	1.0	48	0.0127(9)
Li (S6R)	0.2726(17)	0.2726(17)	0.2726(17)	1.0	8	0.025
Cs (D8R)	0.0	0.0	0.5	0.3077(19)	6	0.025
Atom 1	**Atom 2**	**Length**				
Si1	O1	1.674(5)				
Si1	O2	1.630(4)				
Si1	O3	1.678(4)				
Si1	O3	1.673(5)				
Atom 1	**Atom 2**	**Atom 3**	**OTO angle**			
O1	Si1	O2	103.5(5)			
O1	Si1	O3	109.42(34)			
O1	Si1	O3	110.4(4)			
O2	Si1	O3	119.0(4)			
O2	Si1	O3	102.66(33)			
O3	Si1	O3	111.4(4)			

$Cs_{2.8}$Li-Rho	x	y	z	Occup.	Mult.	Uiso
Si1	0.27200(20)	0.12215(17)	0.42016(21)	0.8	48	0.0087(8)
Al1	0.27200(20)	0.12215(17)	0.42016(21)	0.2	48	0.0087(8)
O1	0.2222(4)	0.2222(4)	0.3907(6)	1.0	24	0.0087(8)
O2	0.12409(32)	0.12409(32)	0.6334(5)	1.0	24	0.0087(8)
O3	0.03157(34)	0.20754(34)	0.3839(4)	1.0	48	0.0087(8)
Li (S6R)	0.2793(15)	0.2793(15)	0.2793(15)	0.9	8	0.025
Cs (D8R)	0.0	0.0	0.5	0.4761(22)	6	0.025

Atom 1	**Atom 2**	**Length**
Si1	O1	1.672(4)
Si1	O2	1.642(4)
Si1	O3	1.692(4)
Si1	O3	1.641(5)

Atom 1	**Atom 2**	**Atom 3**	**OTO angle**
O1	Si1	O2	102.1(4)
O1	Si1	O3	110.71(31)
O1	Si1	O3	112.0(4)
O2	Si1	O3	117.44(34)
O2	Si1	O3	102.89(30)
O3	Si1	O3	111.2(4)

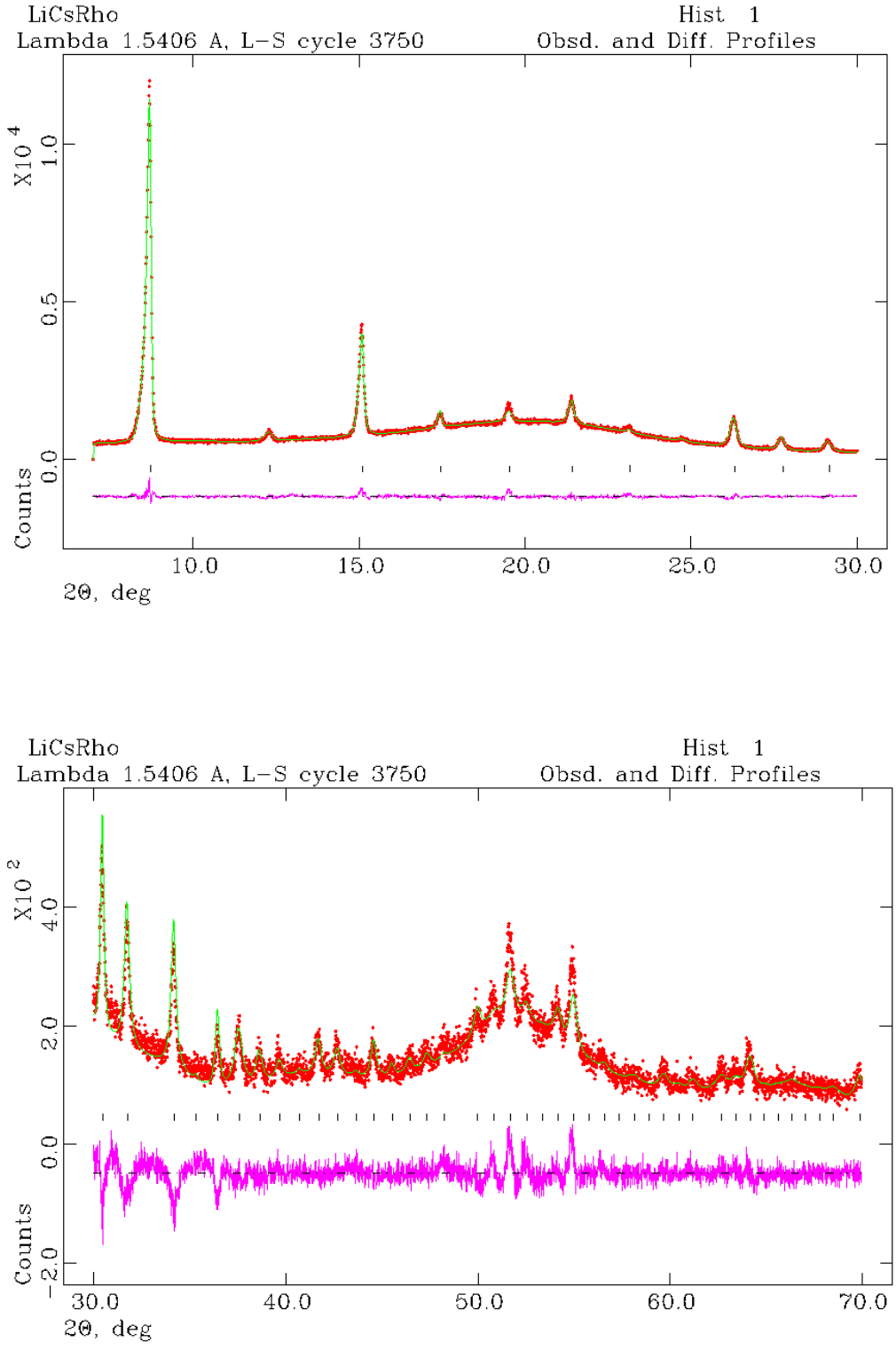
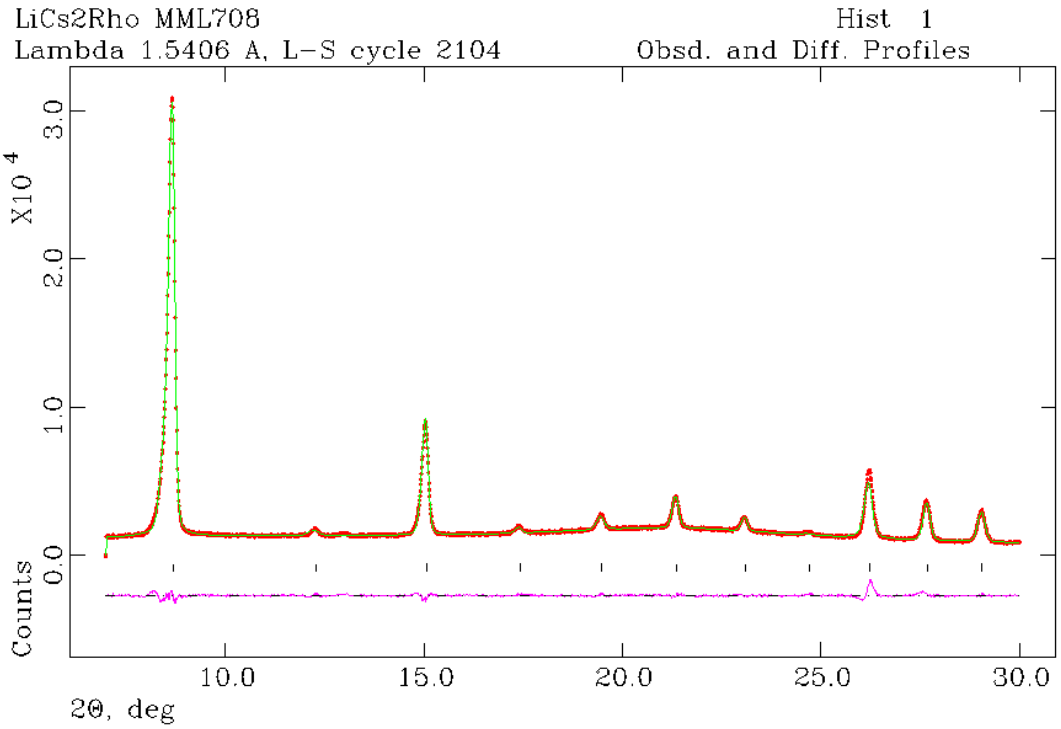


Figure S2.1 GSAS plots for dehydrated $Cs_{0.8}Li_{9.0}$-Rho



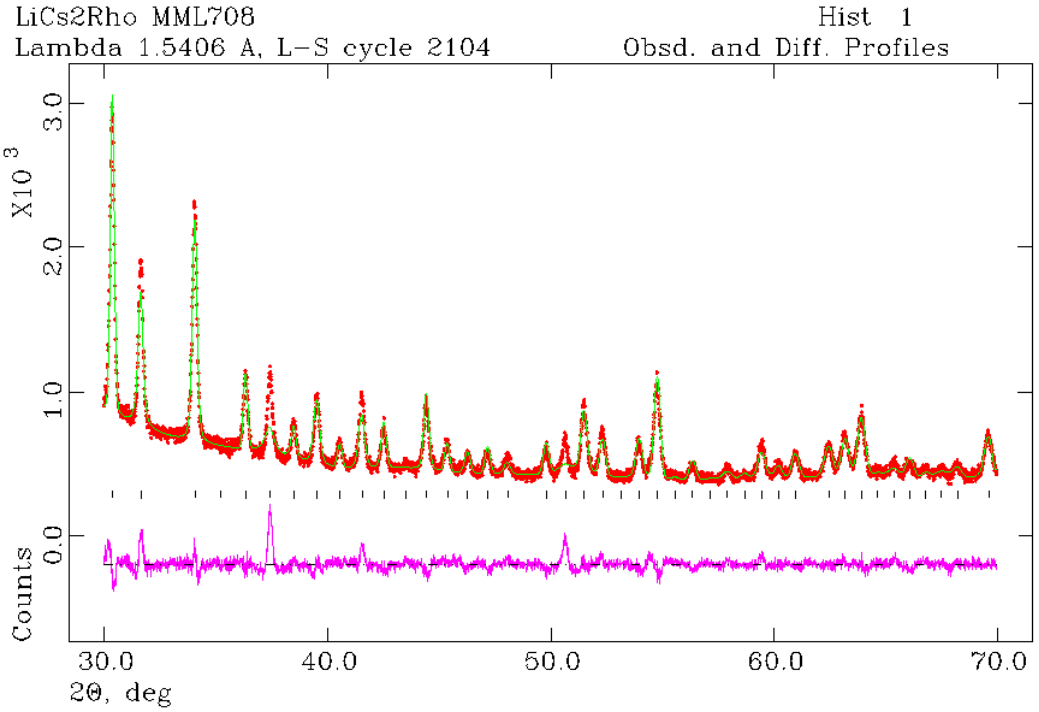


Figure S2.2 GSAS plots for dehydrated $Cs_{1.8}$ $Li_{8.0}$-Rho

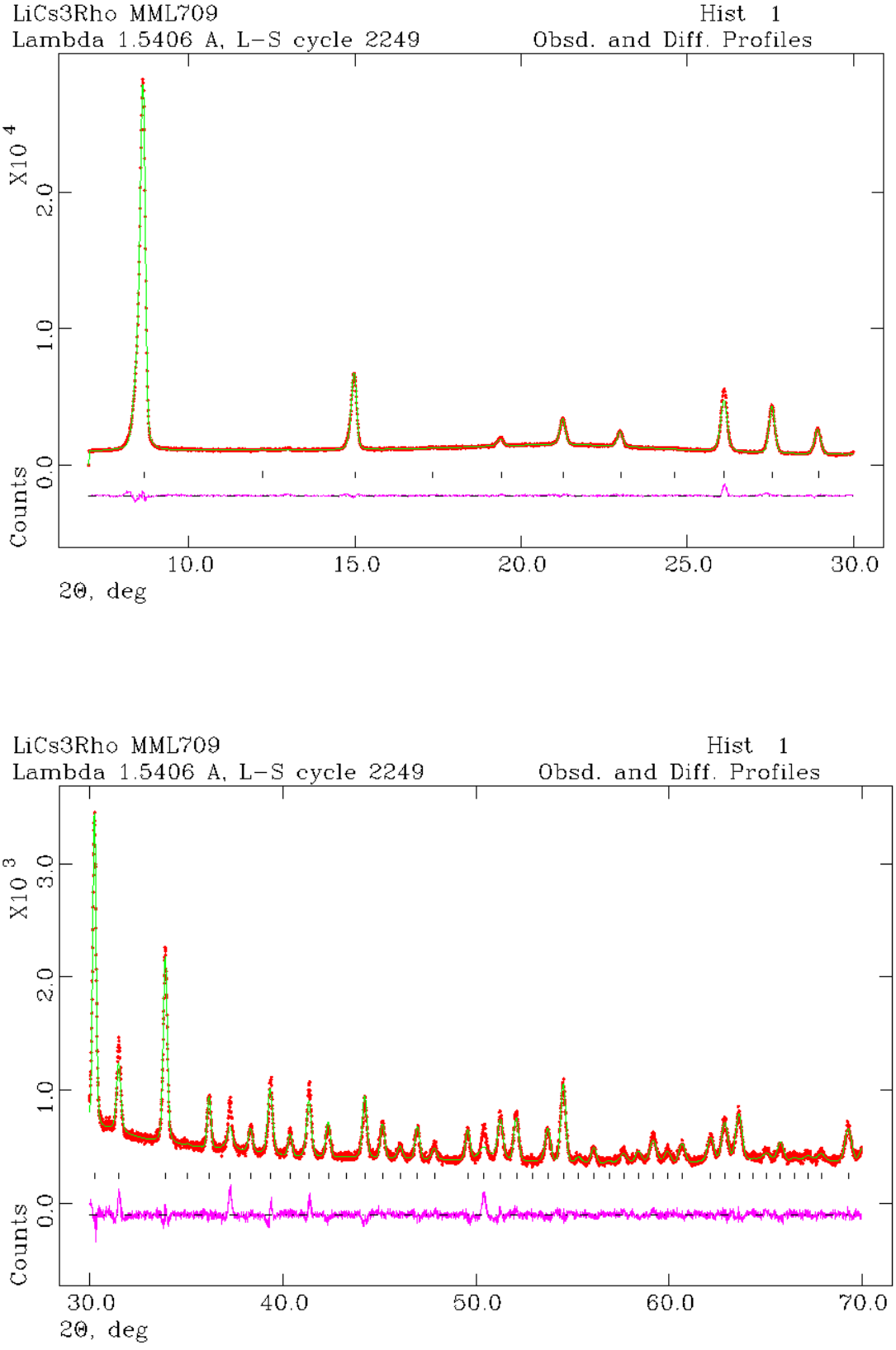


Figure S2.3 GSAS plots for dehydrated $Cs_{2.8}Li_{7.0}$-Rho

S2.1.2 Na,Li-Rho series

Table S2.3 Fractional atomic coordinates, occupancies, multiplicities, isotropic displacement parameters (in $Å^2$), Si-O bond lengths, OTO angles of dehydrated Li,Na-Rho series – laboratory data

Na2.1Li-Rho	**x**	**y**	**z**	**Occup.**	**Mult.**	**Uiso**
Si1	0.27556(24)	0.12456(29)	0.42565(27)	0.8	48	0.00061
Al1	0.27556(24)	0.12456(29)	0.42565(27)	0.2	48	0.00061
O1	0.2192(5)	0.2192(5)	0.3963(7)	1.0	24	0.01
O2	0.1140(4)	0.1140(4)	0.6319(5)	1.0	24	0.01
O3	0.0338(5)	0.2128(4)	0.3895(4)	1.0	48	0.01
Li (S6R)	0.2993(22)	0.2993(22)	0.2993(22)	0.96	8	0.02
Na (S8R)	0.0	0.0	0.631(4)	0.172(9)	12	0.02

Atom 1	**Atom 2**	**Length**
Si1	O1	1.630(5)
Si1	O2	1.681(5)
Si1	O3	1.661(5)
Si1	O3	1.569(7)

Atom 1	**Atom 2**	**Atom 3**	**OTO angle**
O1	Si1	O2	109.0(6)
O1	Si1	O3	107.5(4)
O1	Si1	O3	114.4(5)
O2	Si1	O3	116.8(4)
O2	Si1	O3	103.9(4)
O3	Si1	O3	105.4(5)

$Na_{4.3}$Li-Rho	**x**	**y**	**z**	**Occup.**	**Mult.**	**Uiso**
Si1	0.27518(23)	0.12313(28)	0.42566(28)	0.8	48	0.0185(7)
Al1	0.27518(23)	0.12313(28)	0.42566(28)	0.2	48	0.0185(7)
O1	0.2192(6)	0.2192(6)	0.4045(8)	1.0	24	0.0185(7)
O2	0.1167(5)	0.1167(5)	0.6271(5)	1.0	24	0.0185(7)
O3	0.0385(5)	0.2086(4)	0.3856(4)	1.0	48	0.0185(7)
Li (S6R)	0.2971(30)	0.2971(30)	0.2971(30)	0.67(8)	8	0.02
Na (S8R)	0.0	0.0	0.6090(16)	0.361(11)	12	0.02

Atom 1	**Atom 2**	**Length**
Si1	O1	1.621(5)
Si1	O2	1.664(5)
Si1	O3	1.645(4)
Si1	O3	1.637(5)

Atom 1	**Atom 2**	**Atom 3**	**OTO angle**
O1	Si1	O2	111.3(7)
O1	Si1	O3	105.9(4)
O1	Si1	O3	108.6(6)
O2	Si1	O3	115.9(5)
O2	Si1	O3	103.3(4)
O3	Si1	O3	111.7(5)

$Na_{6.3}$Li-Rho	x	y	z	Occup.	Mult.	Uiso
Si1	0.27488(9)	0.12378(12)	0.42498(11)	0.8	48	0.00809(26)
Al1	0.27488(9)	0.12378(12)	0.42498(11)	0.2	48	0.00809(26)
O1	0.21940(22)	0.21940(22)	0.40349(34)	1.0	24	0.00809(26)
O2	0.11865(22)	0.11865(22)	0.62209(28)	1.0	24	0.00809(26)
O3	0.03913(19)	0.21040(17)	0.38358(20)	1.0	48	0.00809(26)
Li (S6R)	0.2905(11)	0.2905(11)	0.2905(11)	0.45	8	0.035
Na (S6R)	0.2905(11)	0.2905(11)	0.2905(11)	0.090(8)	8	0.035
Na (S8R)	0.0	0.0	0.6081(12)	0.455(5)	12	0.035

Atom 1	Atom 2	Length
Si1	O1	1.6148(21)
Si1	O2	1.6500(20)
Si1	O3	1.6373(21)
Si1	O3	1.6536(23)

Atom 1	Atom 2	Atom 3	OTO angle
O1	Si1	O2	113.32(26)
O1	Si1	O3	106.38(16)
O1	Si1	O3	107.82(24)
O2	Si1	O3	111.97(24)
O2	Si1	O3	104.85(18)
O3	Si1	O3	112.56(23)

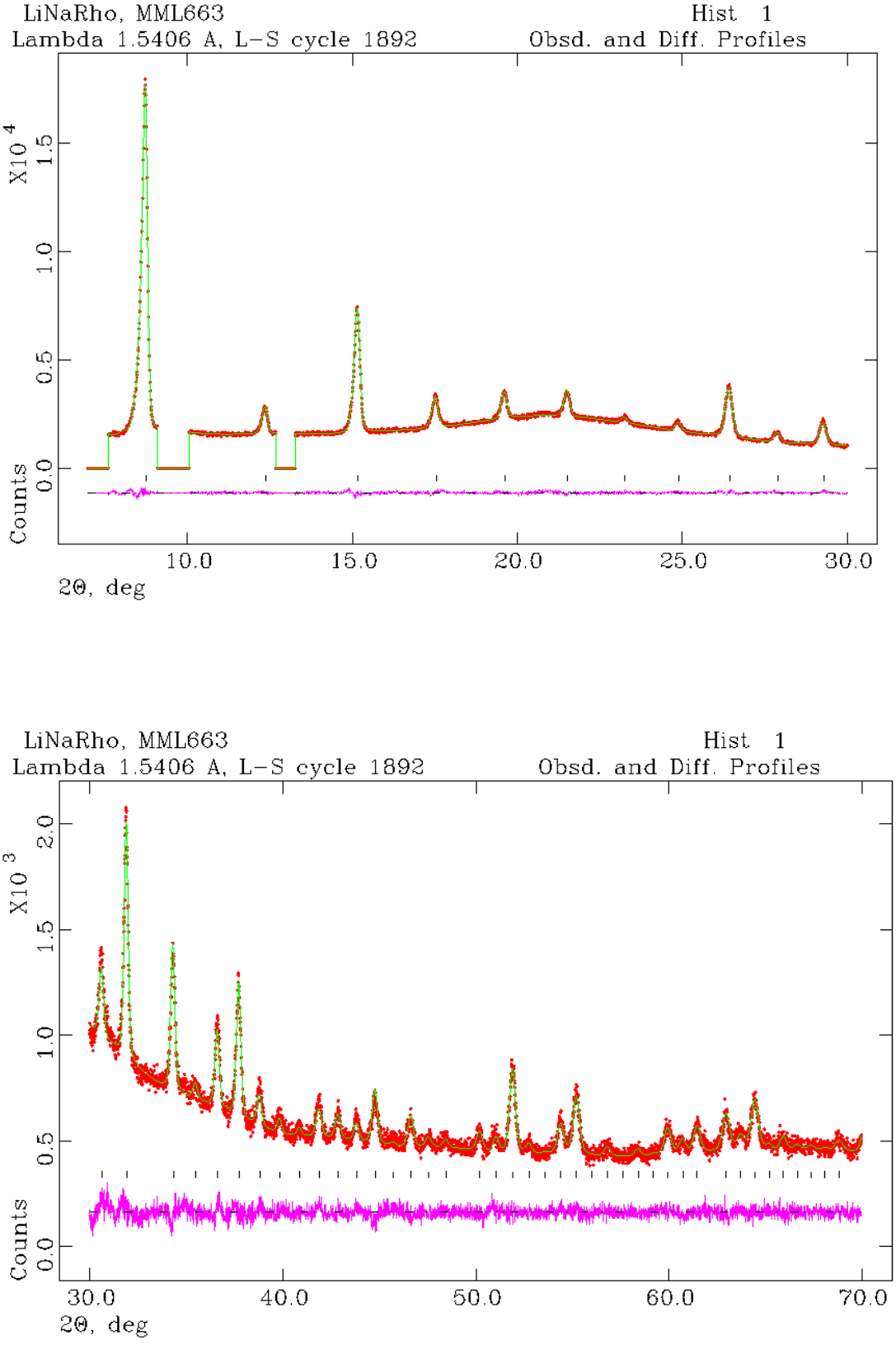
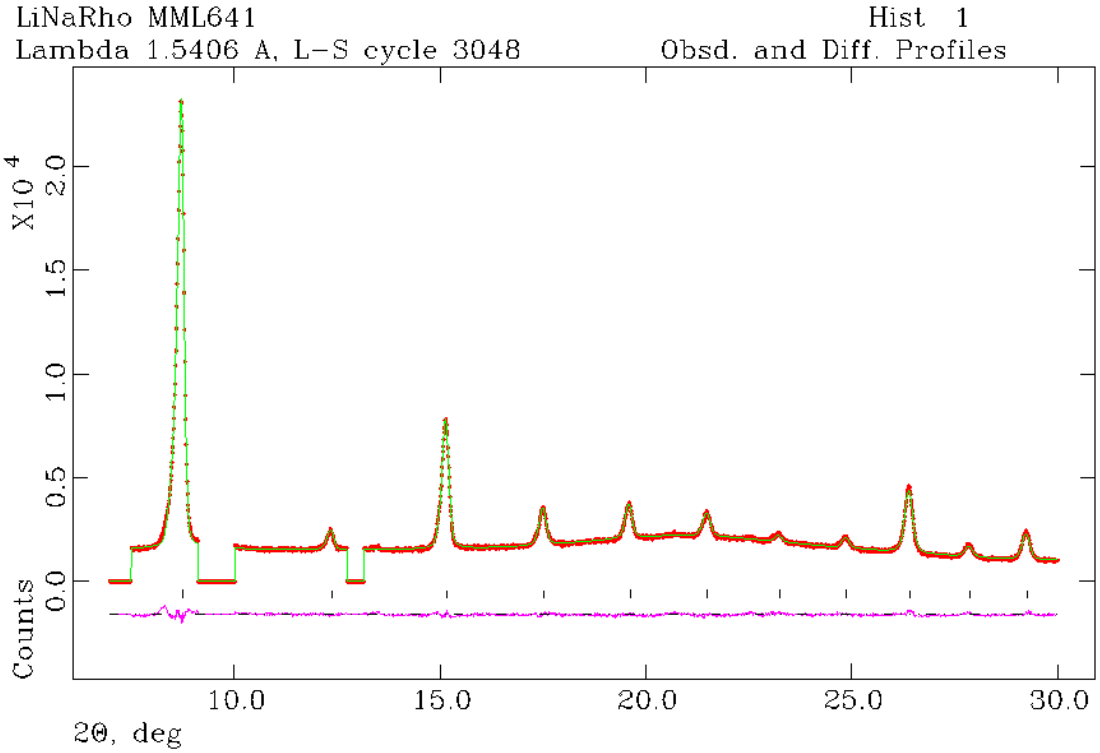


Figure S2.4 GSAS plots for dehydrated $Li_{7.7}Na_{2.1}Al_{9.8}Si_{38.2}O_{96}$



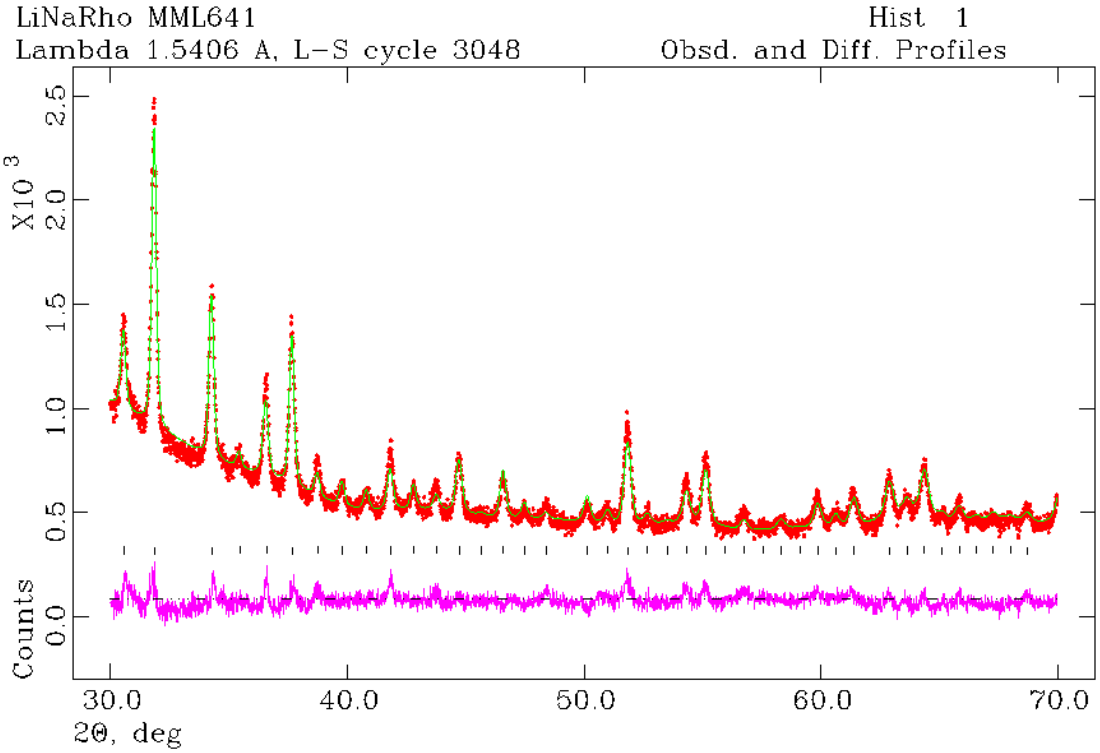


Figure S2.5 GSAS plots for dehydrated $Li_{5.5}Na_{4.3}Al_{9.8}Si_{38.2}O_{96}$

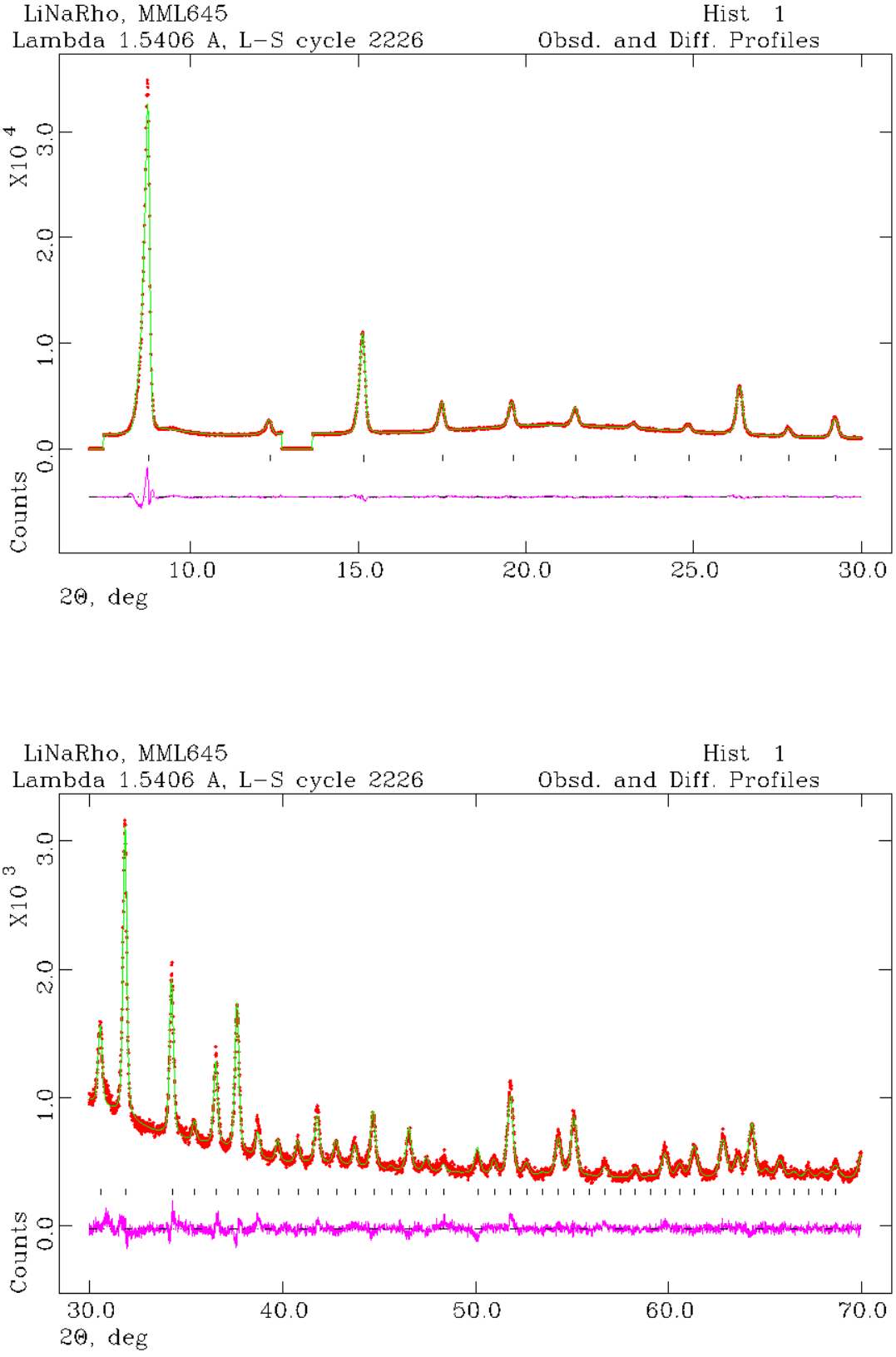


Figure S2.6 GSAS plots for dehydrated $Na_{6.3}Li_{3.5}Al_{9.8}Si_{38.2}O_{96}$

Table S2.4 Fractional atomic coordinates, occupancies, multiplicities, isotropic displacement parameters (in $Å^2$), Si-O bond lengths, OTO angles of dehydrated Li-Rho(3.2) – laboratory data

Li-Rho	**x**	**y**	**z**	**Occup.**	**Mult.**	**Uiso**
Si1	0.27957(18)	0.12865(20)	0.42966(20)	0.8	48	0.0149(8)
Al1	0.27957(18)	0.12865(20)	0.42966(20)	0.2	48	0.0149(8)
O1	0.2299(4)	0.2299(4)	0.4024(6)	1.0	24	0.0114(12)
O2	0.11270(31)	0.11270(31)	0.6281(4)	1.0	24	0.0114(12)
O3	0.0449(4)	0.21539(29)	0.38333(34)	1.0	48	0.0114(12)
Li (S6R)	0.2942(19)	0.2942(19)	0.2942(19)	0.88(6)	8	0.03
Li (S8R)	0.0	0.0	0.625(10)	0.19(4)	12	0.03

Atom 1	**Atom 2**	**Length**
Si1	O1	1.644(5)
Si1	O2	1.6405(32)
Si1	O3	1.633(4)
Si1	O3	1.643(4)

Atom 1	**Atom 2**	**Atom 3**	**OTO angle**
O1	Si1	O2	108.4(4)
O1	Si1	O3	107.56(29)
O1	Si1	O3	110.0(4)
O2	Si1	O3	111.58(33)
O2	Si1	O3	108.83(28)
O3	Si1	O3	110.4(4)

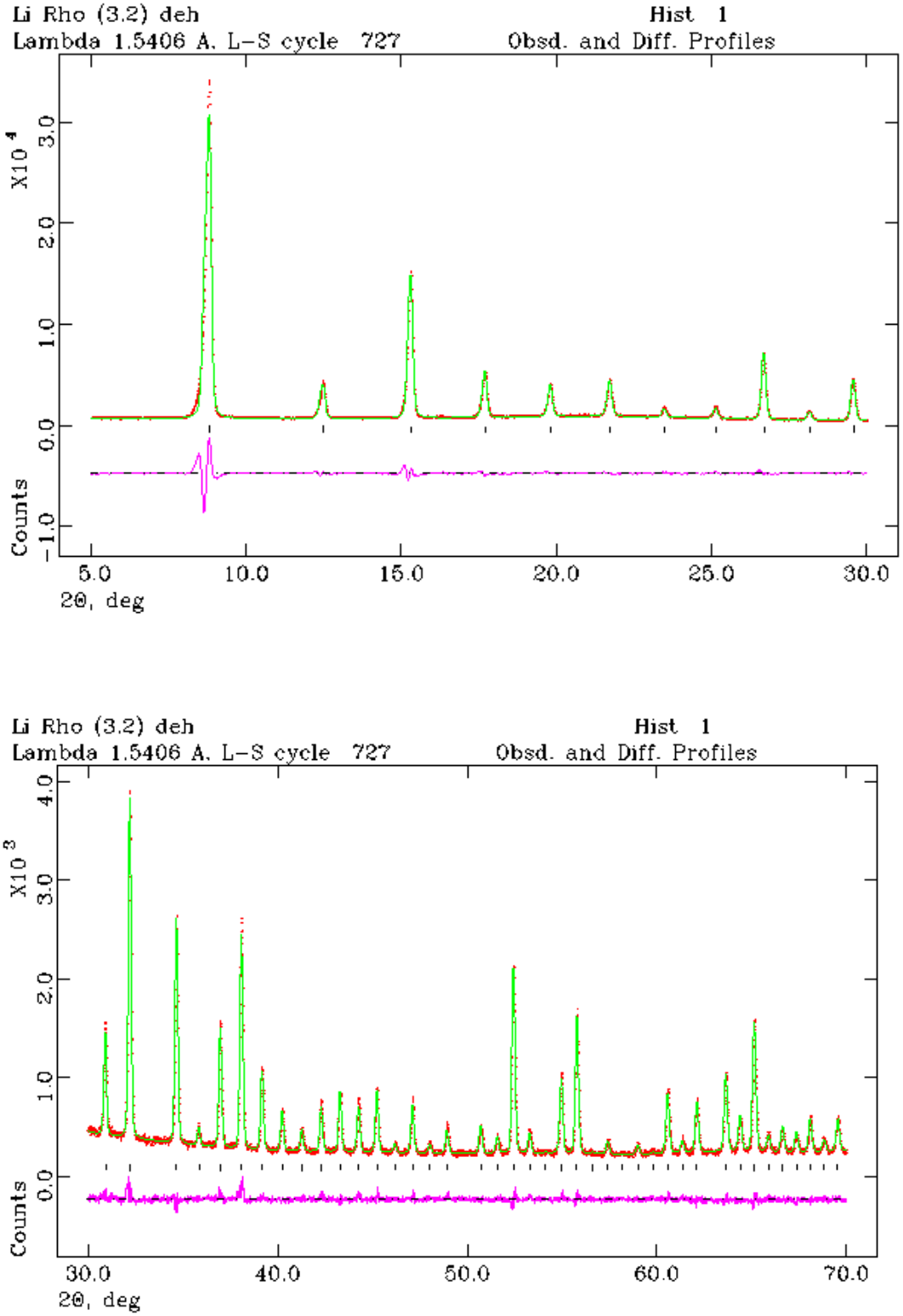


Figure S2.7 GSAS plots for dehydrated Li-Rho(3.2)

2.2 Refinement of structures during CO_2 adsorption against synchrotron data

Table S2.5 Crystallographic details of Li-Rho, $Na_{6.2}$Li-Rho and $Cs_{2.5}$Li-Rho materials

	Li-Rho	Li-Rho (0.10 bar CO_2)	Li-Rho (0.62 bar CO_2)
Unit cell	$Li_{10.4}Al_{9.8}Si_{38.2}O_{96}$ x 3.7 H_2O	$Li_{10.4}Al_{9.8}Si_{38.2}O_{96}$ x 5.7 CO_2	$Li_{10.4}Al_{9.8}Si_{38.2}O_{96}$ x 11.0 CO_2
Temperature/K	298	298	298
Space group	$I\bar{4}3m$	$I\bar{4}3m$	$I\bar{4}3m$
X-ray source	Beamline I11	Beamline I11	Beamline I11
Diffractometer	Synchrotron	Synchrotron	Synchrotron
Wavelength (Å)	0.826163	0.826163	0.826163
a/ Å	14.3446(1)	14.4281(1)	14.5604(2)
Volume/Å^3	2951.65(8)	3003.49(9)	3086.86(15)
R_p	0.0067	0.0085	0.0110
R_{wp}	0.0104	0.0141	0.0184
χ^2	0.02490	0.05149	0.07014

	Li,Na-Rho	Li,Na-Rho (0.1 bar CO_2)	Li,Na-Rho (0.2 bar CO_2)
Unit cell	$Li_{3.6}Na_{6.2}Al_{9.8}Si_{38.2}O_{96}$	$Li_{3.6}Na_{6.2}Al_{9.8}Si_{38.2}O_{96}$ x 0.9 CO_2	$Li_{3.6}Na_{6.2}Al_{9.8}Si_{38.2}O_{96}$ x 1.6 CO_2
Temperature/K	298	298	298
Space group	$I\bar{4}3m$	$I\bar{4}3m$	$I\bar{4}3m$
X-ray source	Beamline I11	Beamline I11	Beamline I11
Diffractometer	Synchrotron	Synchrotron	Synchrotron
Wavelength (Å)	0.826956	0.826956	0.826956
a/ Å	14.3384(3)	14.3513(3)	14.3651(2)
Volume/Å^3	2947.85(8)	2955.80(15)	2964.34(20)
R_p	0.0325	0.0413	0.0443
R_{wp}	0.0424	0.0602	0.0630
χ^2	0.05865	0.04197	0.04527

	Li,Na-Rho (10 bar CO_2)
Unit cell	$Li_{3.6}Na_{6.2}Al_{9.8}Si_{38.2}O_{96}$ x 15 CO_2
Temperature/K	298
Space group	$I\bar{4}3m$
X-ray source	Beamline I11
Diffractometer	Synchrotron
Wavelength (Å)	0.826956
a/ Å	14.6133(8)
Volume/Å^3	3120.69(12)
R_p	0.0378
R_{wp}	0.0523
χ^2	0.08235

	Cs,Li-Rho	Cs,Li-Rho (0.19 bar CO_2)	Li,Cs-Rho (1.2 bar CO_2)
Unit cell	$Cs_{2.5}Li_7Al_{9.8}Si_{38.2}O_{96}$	$Cs_{2.5}Li_7Al_{9.8}Si_{38.2}O_{96}$ x CO_2	$Cs_{2.5}$ $Li_7Al_{9.8}Si_{38.2}O_{96}$ x CO_2
Temperature/K	298	298	298
Space group	$I\bar{4}3m$	$I\bar{4}3m$	$I\bar{4}3m$
X-ray source	Beamline I11	Beamline I11	Beamline I11
Diffractometer	Synchrotron	Synchrotron	Synchrotron
Wavelength (Å)	0.826163	0.826163	0.826163
a/ Å	14.4789(1)	14.5303(2)	14.5846(9)
Volume/Å^3	3035.33(5)	3067.780(35)	3102.35(5)
R_p	0.0208	0.0170	0.0173
R_{wp}	0.0313	0.0249	0.0261
χ^2	0.05440	0.05368	0.04541

2.2.1 Li-Rho

Table S2.6 Cubic unit cell parameter, *a*, of zeolite Li-Rho (*I* -43*m*) upon adsorption and desorption of CO_2, measured by one or two phase Le Bail structureless refinement, together with goodness of fit parameters (Synchrotron data).

pCO_2 / mbar	***a*, phase I / Å**	***a*, phase II / Å**	**wRp; Rp**
Dehydrated*	14.3396(1)	-	0.0122 ; 0.0074
52 mbar	14.3753(3)	-	0.0122 ; 0.0074
97 mbar	14.4268(3)	-	0.0116 ; 0.0076
150 mbar	14.4653(2)	-	0.0197 ; 0.0107
220 mbar	14.5029(3)	-	0.0125 ; 0.0076
287 mbar	14.5206(5)	-	0.0130 ; 0.0081
387 mbar	14.5344(4)	-	0.0131 ; 0.0081
617 mbar	14.5562(7)	-	0.0145 ; 0.0086
888 mbar	14.5875(3)	-	0.0202 ; 0.0122
1174 mbar	14.6136(1)	14.6330(2)	0.0177 ; 0.0116
2530 mbar	14.6517(4)	14.6676(1)	0.0280 ; 0.0158
4900 mbar	14.7321(2)	14.7412(2)	0.0350 ; 0.0180
9000 mbar	-	14.7561(8)	0.0078; 0.0058
4250 mbar	14.7397(9)	14.7300(2)	0.0348; 0.0181
1400 mbar	14.7008(5)	14.6830(5)	0.0345; 0.0182
0 mbar	14.4953(1)	-	0.0285; 0.0192

Table S2.7 Fractional atomic coordinates, occupancies, multiplicities, isotropic displacement parameters (in $Å^2$), Si-O bond lengths, OTO angles of dehydrated Li-Rho and in equilibrium with 0.10 bar and 0.62 bar CO_2 – synchrotron data

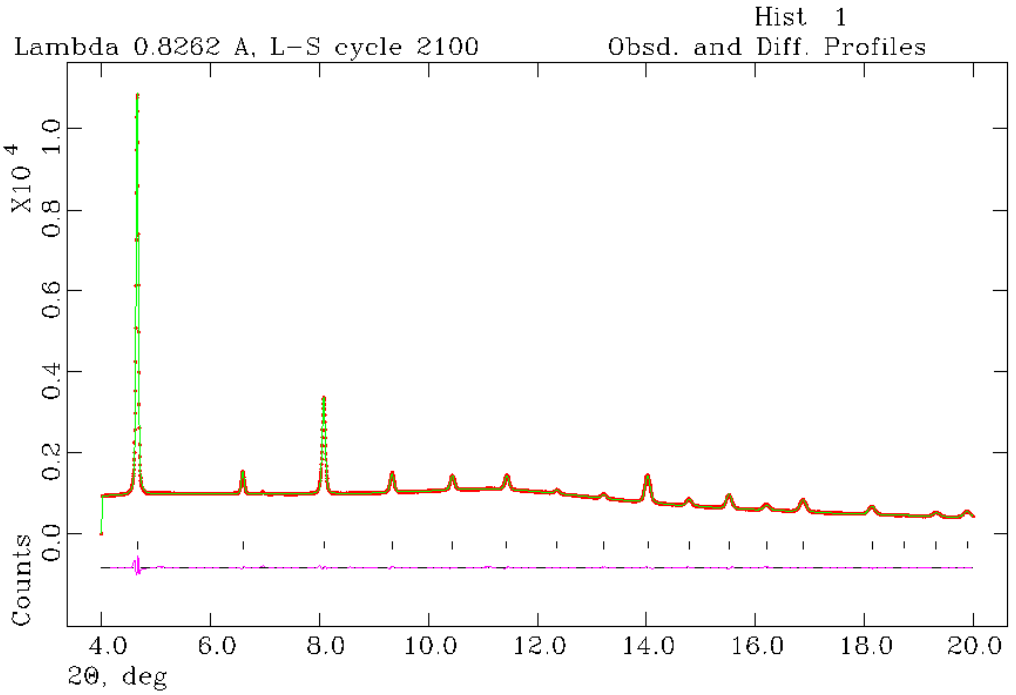
Li-Rho	x	y	z	Occup.	Mult.	Uiso
Si1	0.27486(8)	0.12337(9)	0.42446(10)	0.8	48	0.0096(4)
Al1	0.27486(8)	0.12337(9)	0.42446(10)	0.2	48	0.0096(4)
O1	0.22025(18)	0.22025(18)	0.39985(25)	1.0	24	0.0093(8)
O2	0.12079(18)	0.12079(18)	0.62994(15)	1.0	24	0.0093(8)
O3	0.03645(15)	0.21441(12)	0.38355(17)	1.0	48	0.0093(8)
Li (S6R)	0.2978(9)	0.2978(9)	0.2978(9)	1.0	8	0.025
Li (S8R)	0.5	0.10794	0.5	0.2	12	0.025
OW (D8R)	0.0	0.5	0.0	0.212(9)	6	0.05
OW2 (S8R)	0.5	0.1133(22)	0.5	0.204(7)	12	0.05
Atom 1	**Atom 2**	**Length**				
Si1	O1	1.6338(15)				
Si1	O2	1.6342(17)				
Si1	O3	1.6281(14)				
Si1	O3	1.6170(19)				
Atom 1	**Atom 2**	**Atom 3**	**OTO angle**			
O1	Si1	O2	107.72(18)			
O1	Si1	O3	108.55(15)			
O1	Si1	O3	108.21(18)			
O2	Si1	O3	112.88(15)			
O2	Si1	O3	108.12(15)			
O3	Si1	O3	111.21(21)			

Li-Rho (0.10 bar)	x	y	z	Occup.	Mult.	Uiso
Si1	0.22678(9)	0.07532(10)	0.37708(11)	0.8	48	0.0005(5)
Al1	0.22678(9)	0.07532(10)	0.37708(11)	0.2	48	0.0005(5)
O1	0.12639(16)	0.12639(16)	0.37542(25)	1.0	24	0.0071(9)
O2	0.21670(13)	0.21670(13)	0.59867(20)	1.0	24	0.0071(9)
O3	-0.03693(10)	0.21292(16)	0.38478(16)	1.0	48	0.0071(9)
Li (S6R)	0.26	0.26	0.26	1.0	8	0.025
Li (S8R)	0.0	0.607	0.0	0.2	12	0.025
OC1	0.4267(12)	0.0	0.0	0.2450(28)	12	0.025
OC2	0.2603(12)	0.0	0.0	0.2450(28)	12	0.025
CO1	0.3435(12)	0.0	0.0	0.2450(28)	12	0.025
OC3	0.3492(12)	0.3492(12)	0.3492(12)	0.343(4)	8	0.025
OC4	0.3849(11)	0.5073(20)	0.3849(11)	0.1144(14)	24	0.025
CO2	0.3628(10)	0.4302(16)	0.3628(10)	0.1144(14)	24	0.025
Atom 1	**Atom 2**	**Length**				
Si1	O1	1.6252(13)				
Si1	O2	1.6154(18)				
Si1	O3	1.6357(13)				
Si1	O3	1.6210(20)				
Atom 1	**Atom 2**	**Atom 3**	**OTO angle**			
O1	Si1	O2	110.06(20)			
O1	Si1	O3	109.94(14)			
O1	Si1	O3	109.19(17)			
O2	Si1	O3	108.97(13)			
O2	Si1	O3	107.22(16)			
O3	Si1	O3	111.43(20)			

Li-Rho (0.62 bar)	x	y	z	Occup.	Mult.	Uiso
Si1	0.22946(11)	0.07712(13)	0.38080(14)	0.8	48	0.001
Al1	0.22946(11)	0.07712(13)	0.38080(14)	0.2	48	0.001
O1	0.13506(22)	0.13506(22)	0.37450(32)	1.0	24	0.00362
O2	0.21105(17)	0.21105(17)	0.59636(26)	1.0	24	0.00362
O3	-0.03337(14)	0.21044(19)	0.38662(20)	1.0	48	0.00362
Li (S6R)	0.26	0.26	0.26	1.0	8	0.025
Li (S8R)	0.0	0.607	0.0	0.2	12	0.025
OC1	0.4197(7)	0.0	0.0	0.554(4)	12	0.025
OC2	0.2548(7)	0.0	0.0	0.554(4)	12	0.025
CO1	0.3372(7)	0.0	0.0	0.554(4)	12	0.025
OC3	0.3496(8)	0.3496(8)	0.3496(8)	0.638(5)	8	0.025
OC4	0.3957(8)	0.5009(16)	0.3957(8)	0.2127(16)	24	0.025
CO2	0.3690(6)	0.4275(12)	0.3690(6)	0.2127(16)	24	0.025

Atom 1	Atom 2	Length
Si1	O1	1.6155(17)
Si1	O2	1.6178(23)
Si1	O3	1.6346(17)
Si1	O3	1.6143(26)

Atom 1	Atom 2	Atom 3	OTO angle
O1	Si1	O2	108.55(25)
O1	Si1	O3	111.88(19)
O1	Si1	O3	109.53(21)
O2	Si1	O3	107.70(17)
O2	Si1	O3	107.04(21)
O3	Si1	O3	111.94(24)



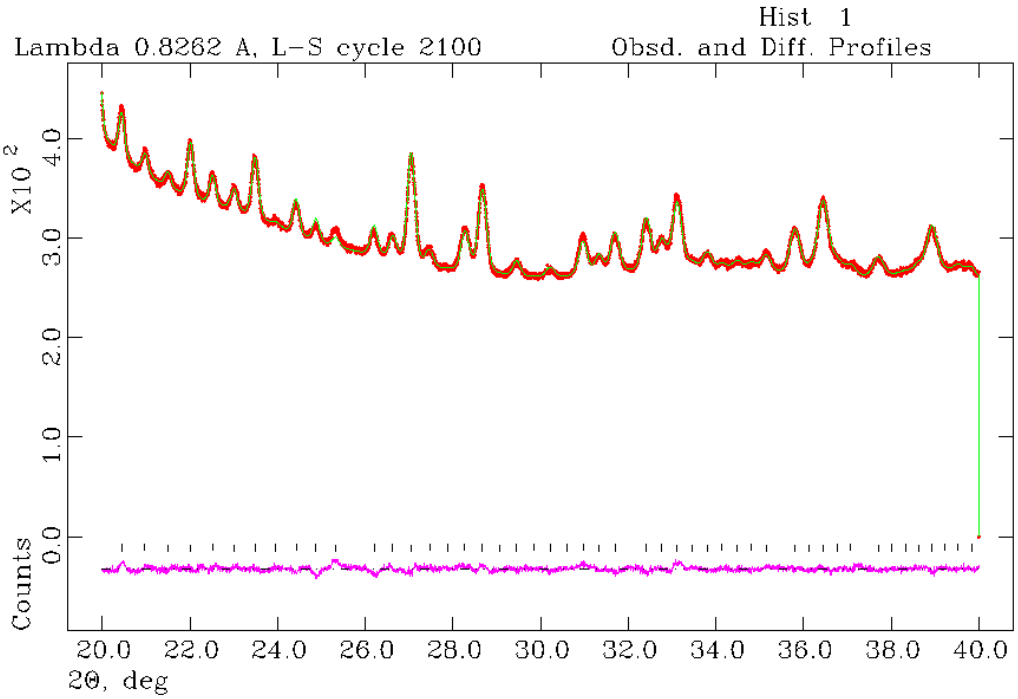


Figure S2.8 GSAS plots for dehydrated Li-Rho

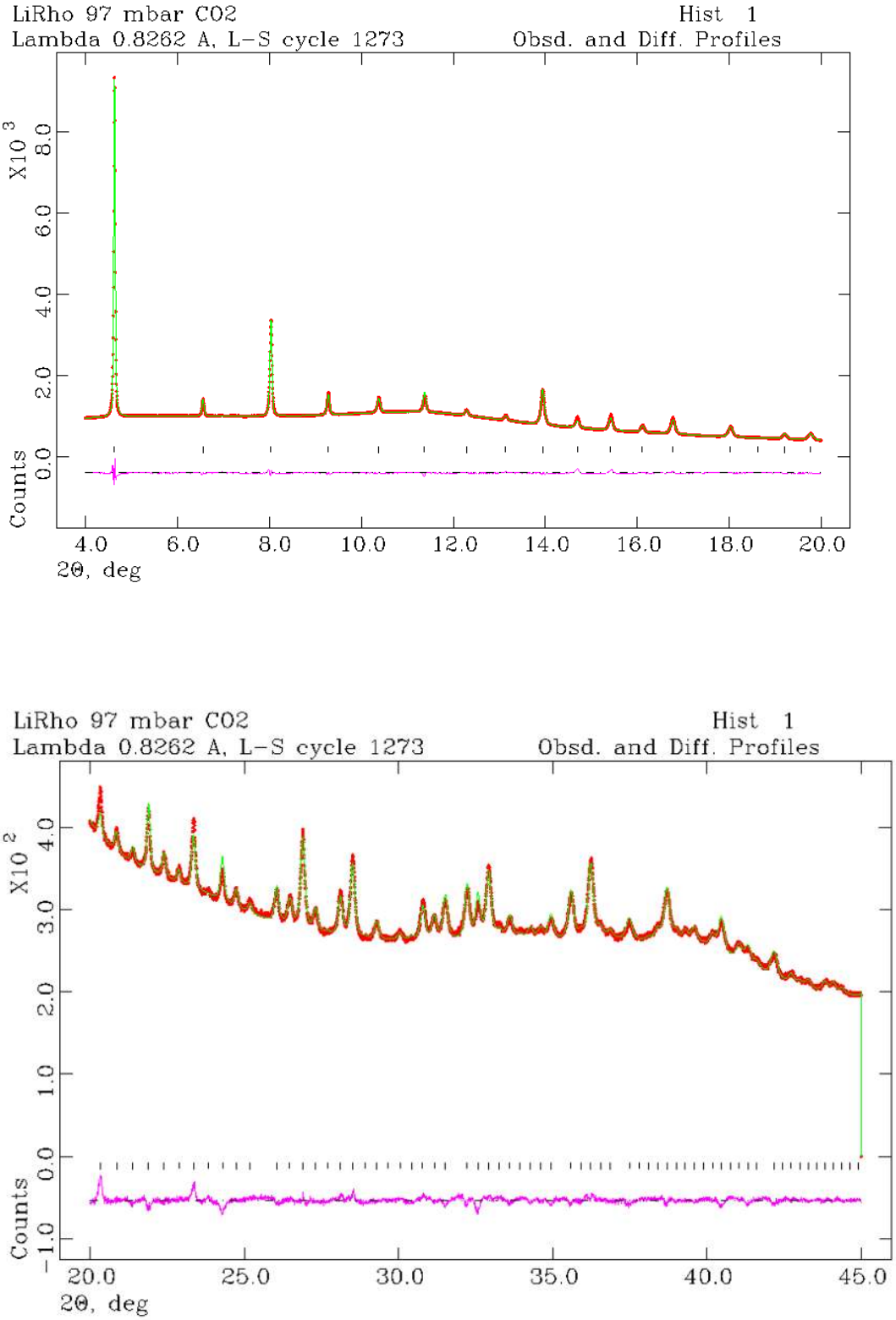
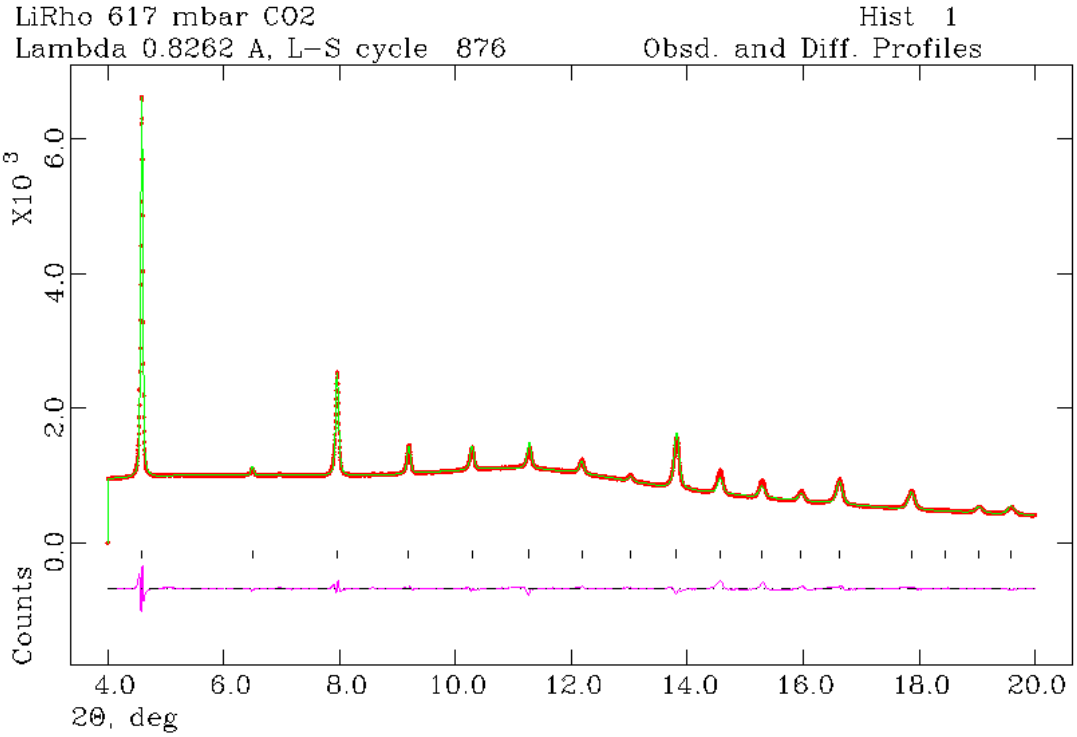


Figure S2.9 GSAS plots for Li-Rho in equilibrium with 0.10 bar of CO_2 ($Li_{10}Al_{9.8}Si_{38.2}O_{96}$. 5.7 CO_2)



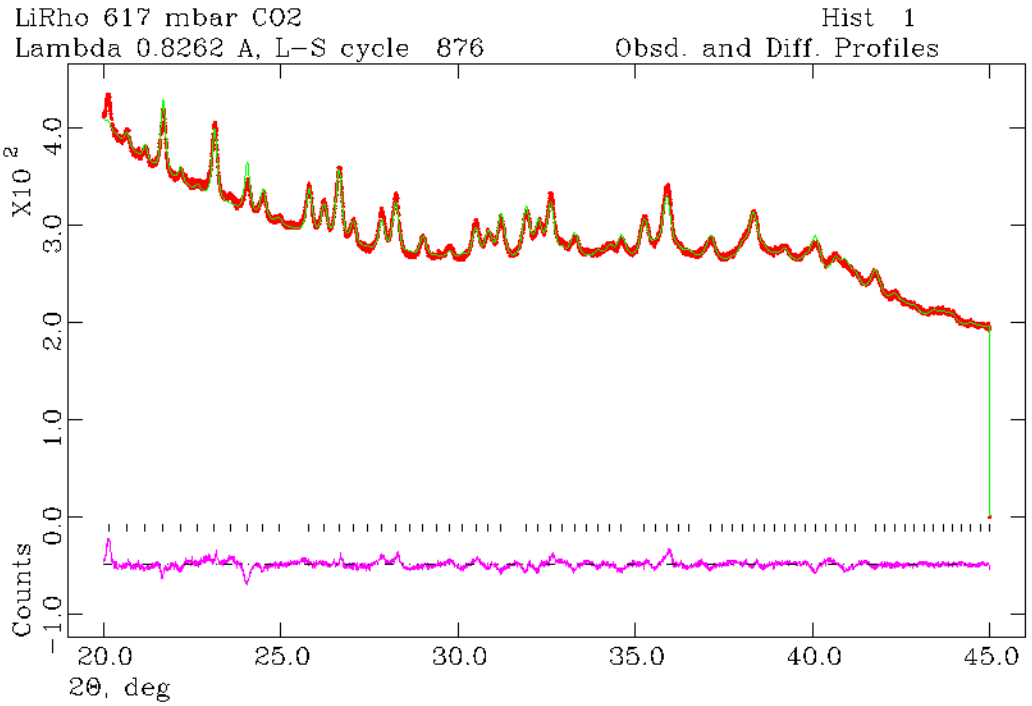


Figure S2.10 GSAS plots for Li-Rho in equilibrium with 0.62 bar of CO_2 ($Li_{10}Al_{9.8}Si_{38.2}O_{96}$ 11.0 CO_2)

2.2.2 $Na_{6.2}$ Li-Rho

Tabel S2.8 Cubic unit cell parameter, *a*, of zeolite $Na_{6.2}$ $Li_{3.6}$-Rho (*I*-43*m*) upon adsorption and desorption of CO_2, measured by one or two phase Le Bail structureless refinement, together with goodness of fit parameters

Sample of Li,Na-Rho	Unit cell parameter Phase I (Å)	Unit cell parameter Phase II (Å)	wRp; Rp
Dehydrated*	14.3384(3)	0	0.0425; 0.0325
40 mbar of CO_2	14.3414(7)	0	0.0449; 0.0301
110 mbar of CO_2*	14.3512(4)	0	0.0604; 0.0413
200 mbar of CO_2	14.3607(7)	14.4523(7)	0.0214; 0.0147
300 mbar of CO_2	14.3610(7)	14.4561(3)	0.0213; 0.0142
400 mbar of CO_2	14.3704(3)	14.4686(8)	0.0265; 0.0174
500 mbar of CO_2	14.4190(5)	14.5764(5)	0.0243; 0.0169
1050 mbar of CO_2	14.4350(7)	14.5901(3)	0.0264; 0.0184
5050 mbar of CO_2	14.4615(8)	14.6066(7)	0.0262; 0.0188
10000 mbar of CO_2*	14.5220(3)	14.6139(3)	0.0480; 0.0331
0 mbar of CO_2	0	14.5683(2)	0.0270; 0.0196

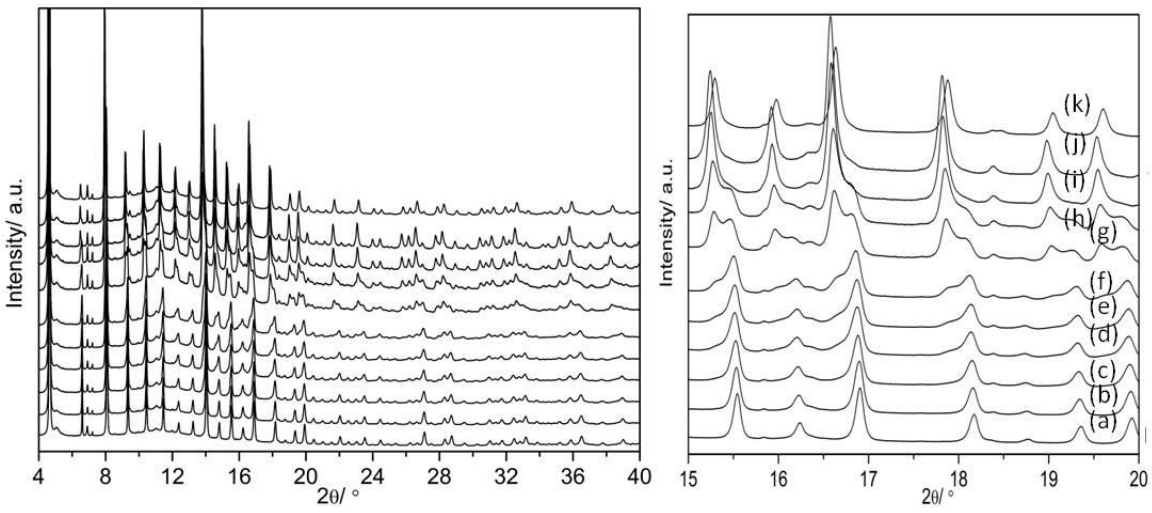


Figure S2.11 PXRD of $Li_{3.6}Na_{6.2}$-Rho (a) dehydrated and measured with CO_2 adsorbed at different pressures (given in mbar): (b) 40, (c) 110, (d) 200, (e) 300, (f) 400, (g) 500, (h) 1050, (i) 5050, (j) 10000 and (k) subsequently evacuated.

Table S2.9 Fractional atomic coordinates, occupancies, multiplicities, isotropic displacement parameters (in $Å^2$), Si-O bond lengths, OTO angles of dehydrated $Li_{3.6}Na_{6.2}$-Rho and in equilibrium with 0.10, 0.20 and 10 bar CO_2 – synchrotron data

Li,Na-Rho	x	y	z	Occup.	Mult.	Uiso
Si1	0.27488(9)	0.12376(11)	0.42501(11)	0.8	48	0.00831(17)
Al1	0.27488(9)	0.12376(11)	0.42501(11)	0.2	48	0.00831(17)
O1	0.21939(21)	0.21939(21)	0.40337(33)	1.0	24	0.00831(17)
O2	0.11859(21)	0.11859(21)	0.62211(27)	1.0	24	0.00831(17)
O3	0.03916(18)	0.21027(16)	0.38356(20)	1.0	48	0.00831(17)
Li (S6R)	0.290011)	0.2900(11)	0.2900(11)	0.45	8	0.03
Na (S6R)	0.2900(11)	0.2900(11)	0.2900(11)	0.086(7)	8	0.03
Na (S8R)	0.0	0.0	0.6074(6)	0.448(5)	12	0.03
Atom 1	**Atom 2**	**Length**				
Si1	O1	1.6154(21)				
Si1	O2	1.6506(19)				
Si1	O3	1.6380(20)				
Si1	O3	1.6538(22)				
Atom 1	**Atom 2**	**Atom 3**	**OTO angle**			
O1	Si1	O2	113.28(25)			
O1	Si1	O3	106.28(16)			
O1	Si1	O3	107.90(23)			
O2	Si1	O3	112.05(22)			
O2	Si1	O3	104.76(17)			
O3	Si1	O3	112.64(22)			

Li,Na-Rho (0.1 bar)	x	y	z	Occup.	Mult.	Uiso
Si1	0.27341(18)	0.12320(21)	0.42520(21)	0.8	48	0.0034(7)
Al1	0.27341(18)	0.12320(21)	0.42520(21)	0.2	48	0.0034(7)
O1	0.2192(4)	0.2192(4)	0.4031(5)	1.0	24	0.0034(7)
O2	0.1197(4)	0.1197(4)	0.6243(5)	1.0	24	0.0034(7)
O3	0.0388(4)	0.21036(33)	0.3833(4)	1.0	48	0.0034(7)
Li (S6R)	0.2976(19)	0.2976(19)	0.2976(19)	0.45	8	0.025
Na (S6R)	0.2976(19)	0.2976(19)	0.2976(19)	0.1	8	0.025
Na (S8R)	0.0	0.0	0.6008(11)	0.45	12	0.025
O(CO2)1a	0.78134	0.0	0.0	0.062(6)	12	0.025
O(CO2)1b	0.60116	0.0	0.0	0.062(6)	12	0.025
C(CO2)1	0.68978	0.0	0.0	0.062(6)	12	0.025
O(CO2)2a	0.34947	0.56421	0.34947	0.0086(24)	24	0.025
O(CO2)2b	0.38299	0.38299	0.38299	0.026(7)	8	0.025
C(CO2)2	0.36623	0.4736	0.36623	0.0086(24)	24	0.025
Atom 1	**Atom 2**	**Length**				
Si1	O1	1.614(4)				
Si1	O2	1.664(4)				
Si1	O3	1.627(4)				
Si1	O3	1.650(5)				
Atom 1	**Atom 2**	**Atom 3**	**OTO angle**			
O1	Si1	O2	111.1(5)			
O1	Si1	O3	107.14(27)			
O1	Si1	O3	108.1(4)			
O2	Si1	O3	112.1(4)			
O2	Si1	O3	104.66(33)			
O3	Si1	O3	113.7(4)			

Li,Na-Rho (0.2 bar)	x	y	z	Occup.	Mult.	Uiso
Si1	0.27162(19)	0.12247(23)	0.42377(24)	0.8	48	0.005
Al1	0.27162(19)	0.12247(23)	0.42377(24)	0.2	48	0.005
O1	0.2203(4)	0.2203(4)	0.4020(6)	1.0	24	0.005

O2	0.1209(4)	0.1209(4)	0.6226(7)	1.0	24	0.005
O3	0.0394(4)	0.2081(4)	0.3824(5)	1.0	48	0.005
Li (S6R)	0.28935	0.28935	0.28935	0.45	8	0.025
Na (S6R)	0.28935	0.28935	0.28935	0.1	8	0.025
Na (S8R)	0.0	0.0	0.59411	0.45	12	0.025
O(CO2)1a	0.784(8)	0.0	0.0	0.093(5)	12	0.025
O(CO2)1b	0.618(8)	0.0	0.0	0.093(5)	12	0.025
C(CO2)1	0.698(8)	0.0	0.0	0.093(5)	12	0.025
O(CO2)2a	0.364(15)	0.5576(27)	0.364(15)	0.0200(27)	24	0.025
O(CO2)2b	0.388(5)	0.388(5)	0.388(5)	0.060(8)	8	0.025
C(CO2)2	0.36623	0.4736	0.36623	0.0200(27)	24	0.025

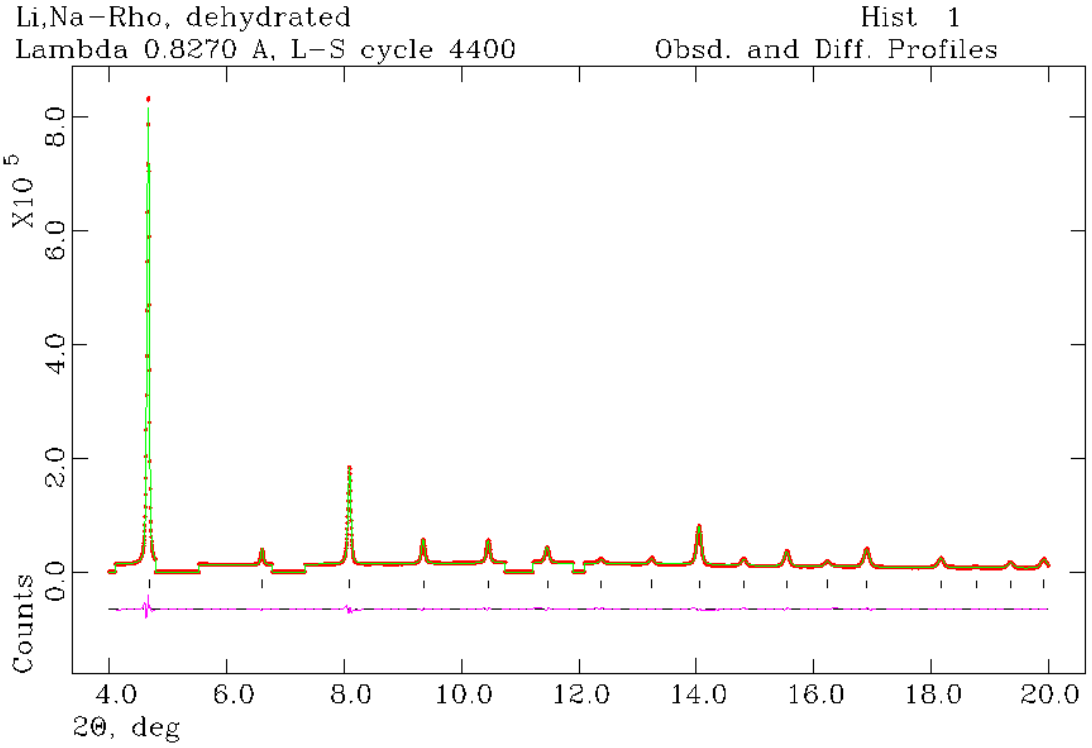
Atom 1	**Atom 2**	**Length**
Si1	O1	1.617(5)
Si1	O2	1.672(4)
Si1	O3	1.615(4)
Si1	O3	1.688(5)

Atom 1	**Atom 2**	**Atom 3**	**OTO angle**
O1	Si1	O2	110.2(6)
O1	Si1	O3	108.23(34)
O1	Si1	O3	107.8(5)
O2	Si1	O3	112.4(5)
O2	Si1	O3	102.7(4)
O3	Si1	O3	115.4(5)

Li,Na-Rho (10 bar)	**x**	**y**	**z**	**Occup.**	**Mult.**	**Uiso**
Si1	0.27227(14)	0.11661(15)	0.41802(13)	0.8	48	0.0058(4)
Al1	0.27227(14)	0.11661(15)	0.41802(13)	0.2	48	0.0058(4)
O1	0.20931(26)	0.20931(26)	0.3907(4)	1.0	24	0.0037(6)
O2	0.12416(27)	0.12416(27)	0.62574(31)	1.0	24	0.0037(6)
O3	0.03092(23)	0.21057(21)	0.38980(26)	1.0	48	0.0037(6)
Li (S6R)	0.29	0.29	0.29	0.45	8	0.025
Na (S6R)	0.29	0.29	0.29	0.1	8	0.025
Na (S8R)	0.0	0.0	0.5531(7)	0.45	12	0.025
O(CO2)1a	0.7656(6)	0.0	0.0	0.746(4)	12	0.03
O(CO2)1b	0.5995(6)	0.0	0.0	0.746(4)	12	0.03
C(CO2)1	0.6816(6)	0.0	0.0	0.746(4)	12	0.03
O(CO2)2a	0.3452(9)	0.5432(6)	0.3452(9)	0.2828(17)	24	0.03
O(CO2)2b	0.3880(5)	0.3880(5)	0.3880(5)	0.848(5)	8	0.03
C(CO2)2	0.3563(10)	0.4600(8)	0.3563(10)	0.2828(17)	24	0.03

Atom 1	**Atom 2**	**Length**
Si1	O1	1.6857(23)
Si1	O2	1.6396(31)
Si1	O3	1.5972(31)
Si1	O3	1.6714(32)

Atom 1	**Atom 2**	**Atom 3**	**OTO angle**
O1	Si1	O2	110.44(28)
O1	Si1	O3	105.12(23)
O1	Si1	O3	111.16(32)
O2	Si1	O3	119.20(25)
O2	Si1	O3	103.72(24)
O3	Si1	O3	107.19(30)



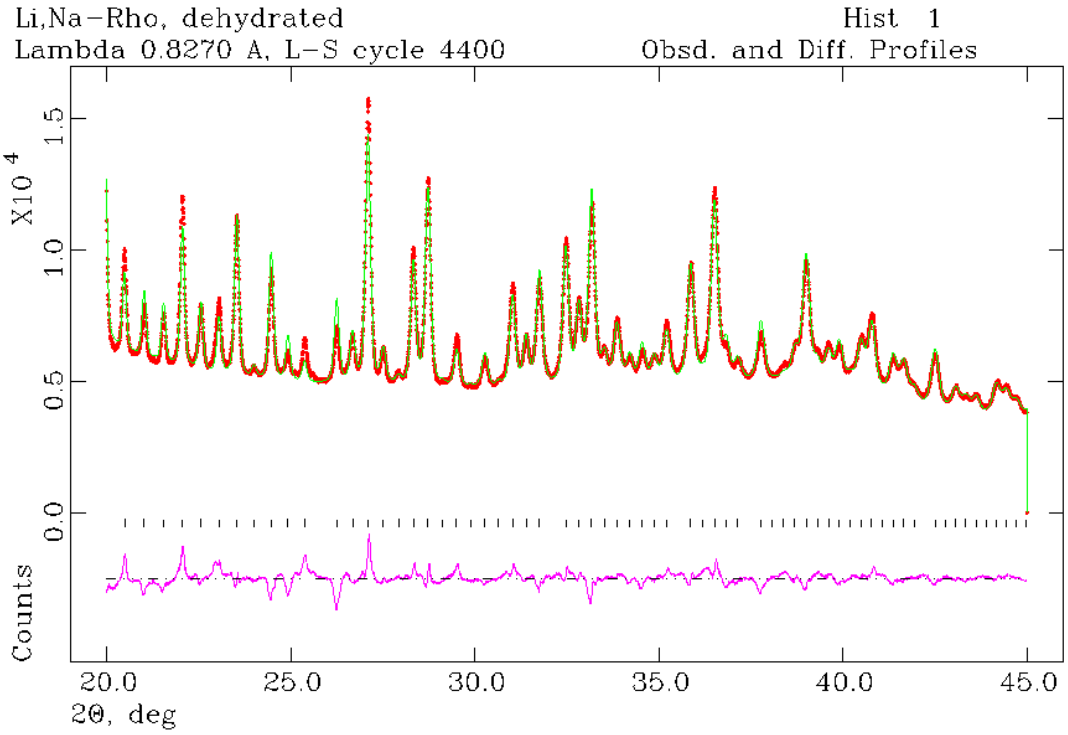
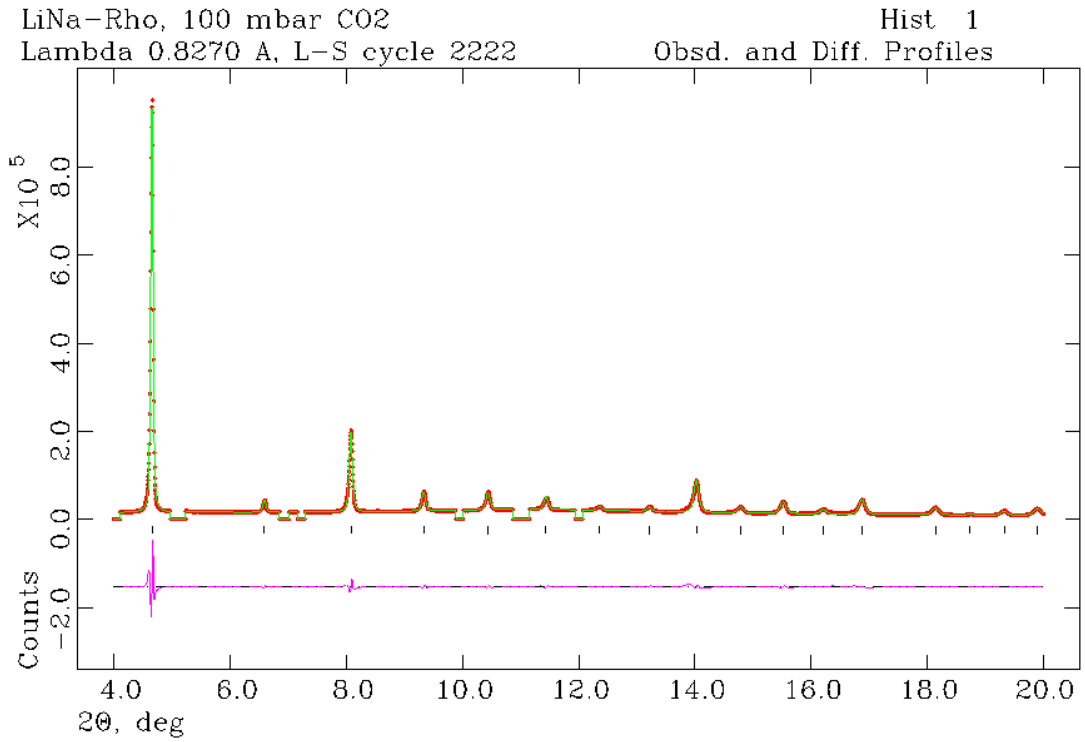


Figure S2.12 GSAS plots for dehydrated $Na_{6.2}$Li-Rho ($Li_{3.6}Na_{6.2}Al_{9.8}Si_{38.2}O_{96}$)



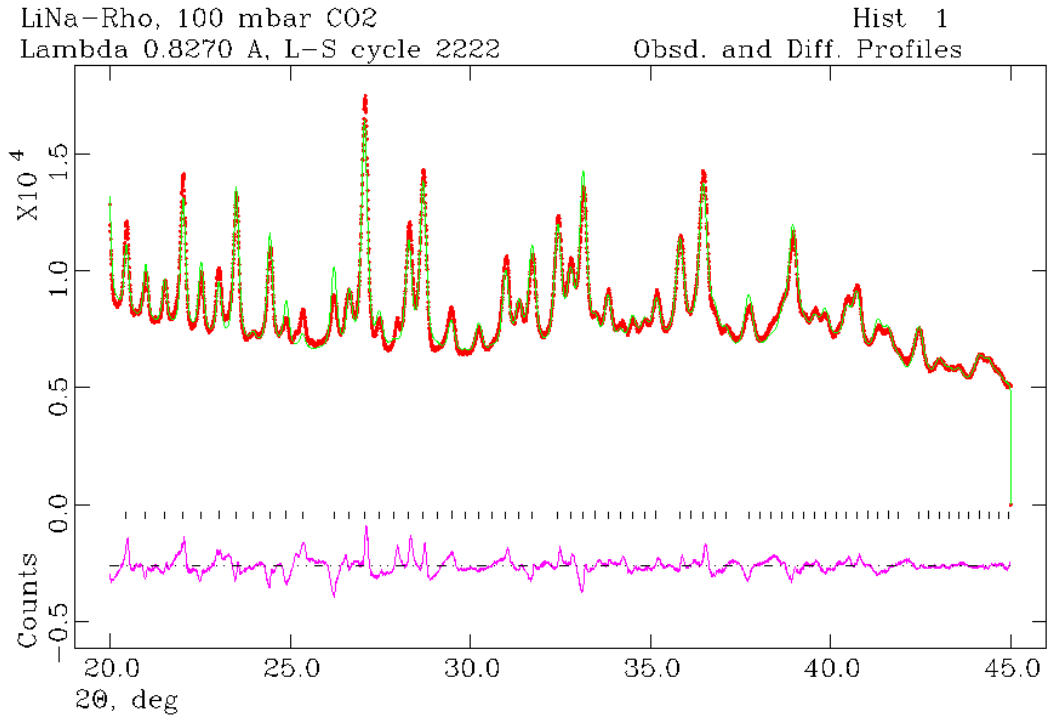


Figure S2.13 GSAS plots for $Na_{6.2}Li$-Rho in equilibrium with 0.1 bar of CO_2 ($Li_{3.6}Na_{6.2}Al_{9.8}Si_{38.2}O_{96}$. 0.9 CO_2)

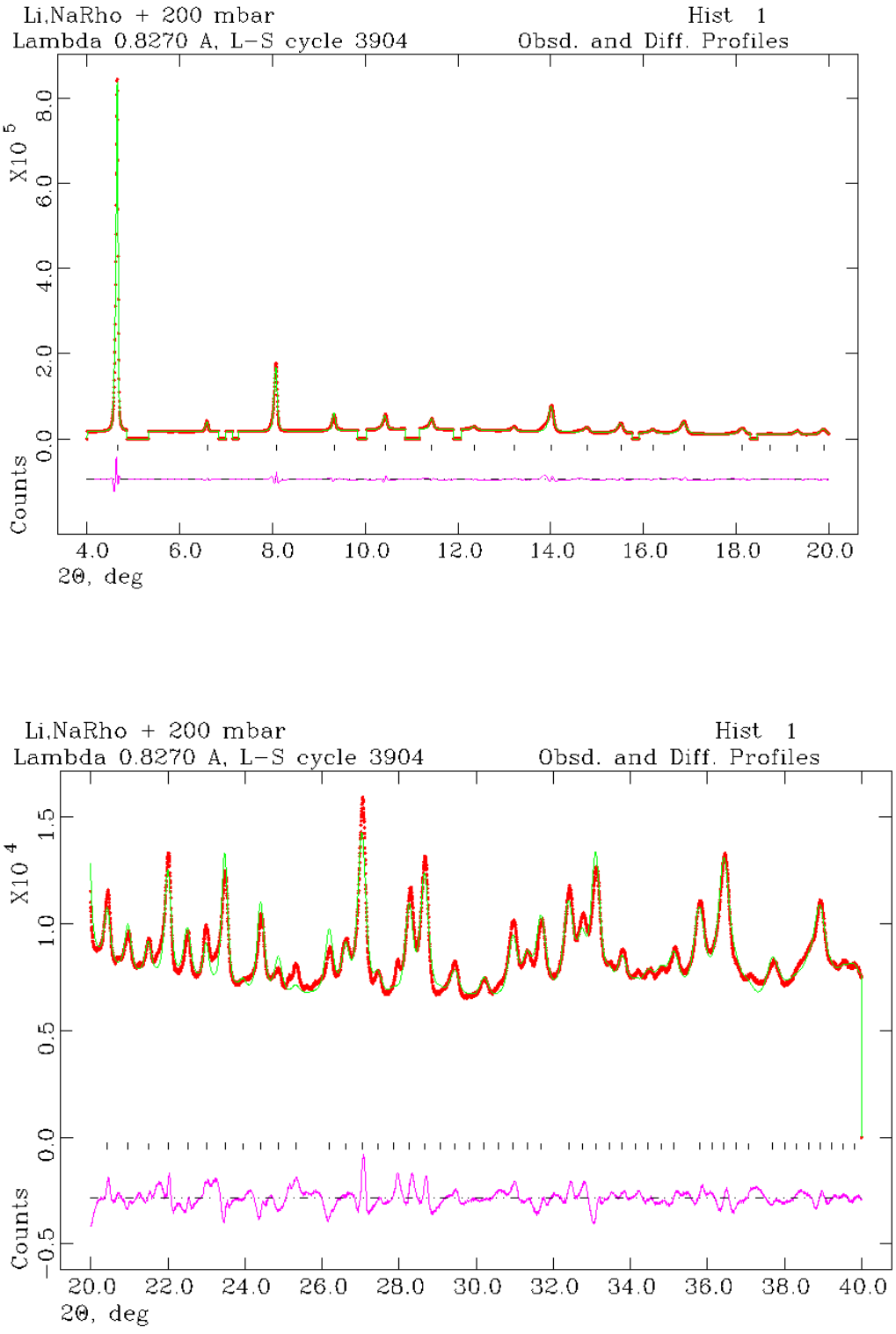
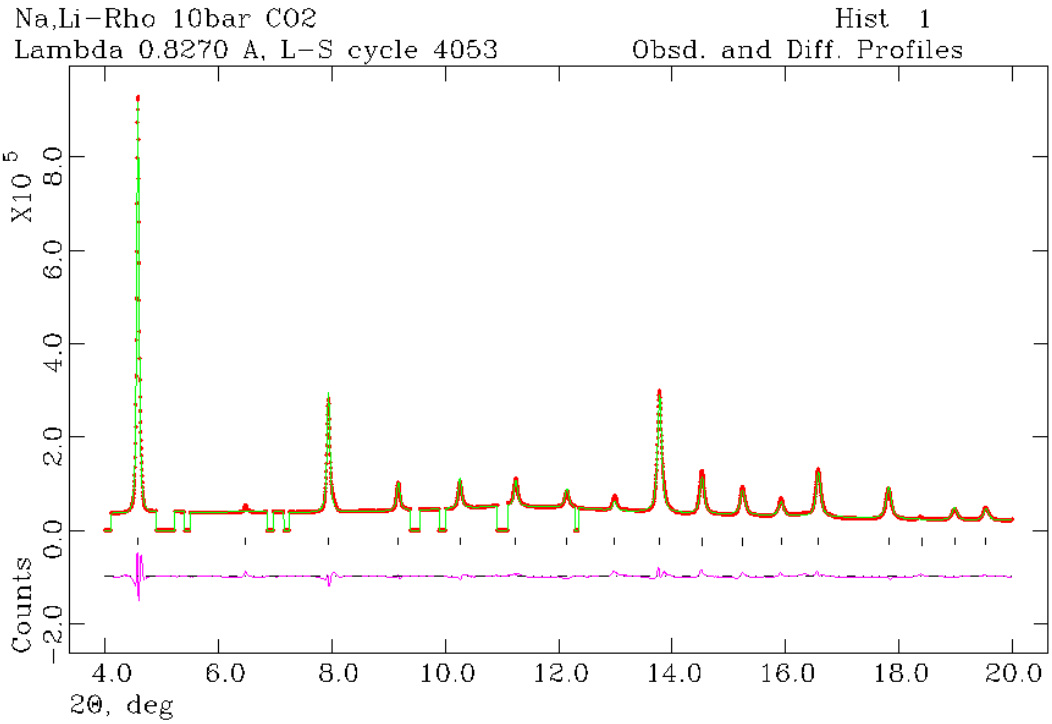


Figure S2.14 GSAS plots for $Na_{6.2}$Li-Rho in equilibrium with 0.2 bar of CO_2 ($Li_{3.6}Na_{6.2}Al_{9.8}Si_{38.2}O_{96}$. 1.6 CO_2)



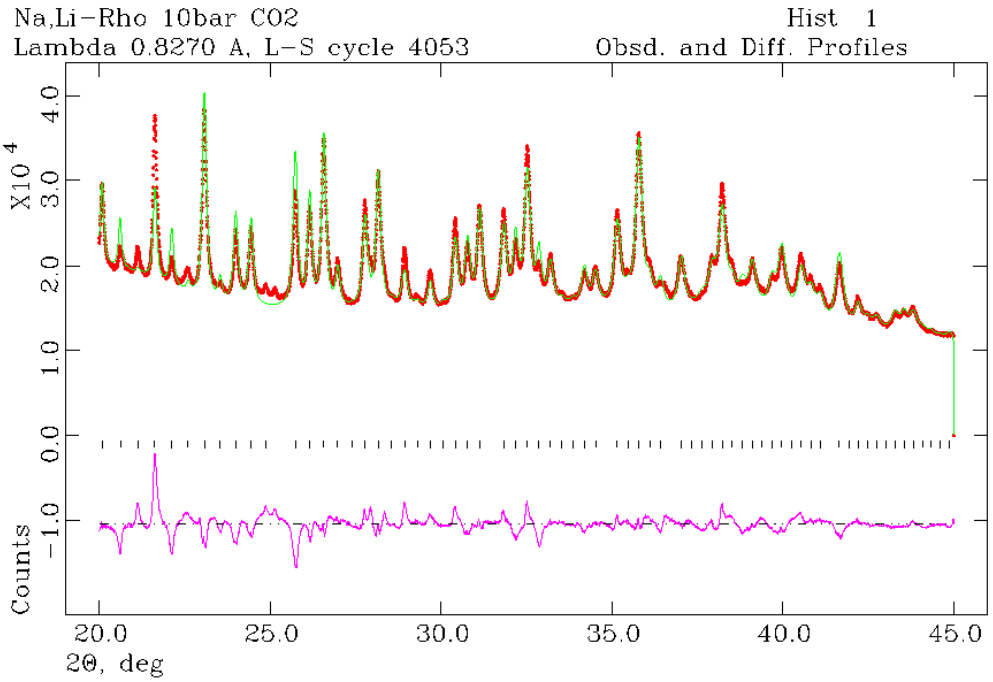


Figure S2.15 GSAS plots for Li,Na-Rho in equilibrium with 10 bar of CO_2 ($Li_{3.6}Na_{6.2}Al_{9.8}Si_{38.2}O_{96}$ x 15 CO_2)

2.2.3 $Cs_{2.5}$Li-Rho

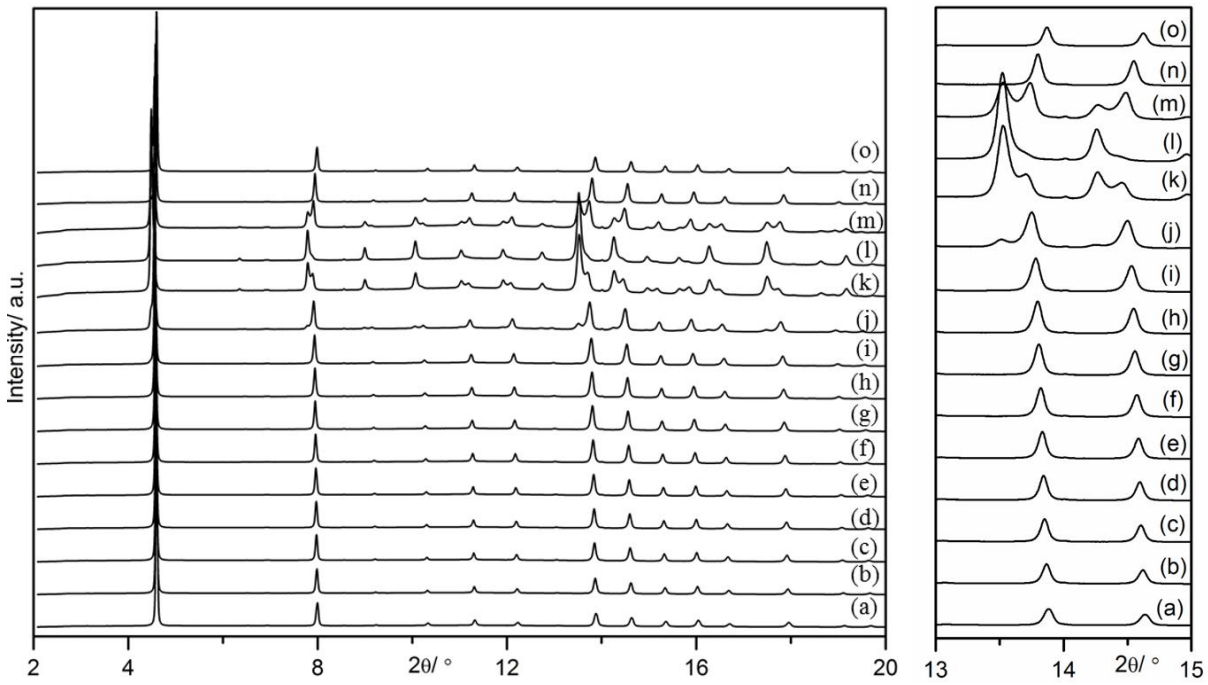


Figure S2.16. In situ PXRD patterns as a function of CO_2 pressure for $Cs_{2.5}$Li-Rho: (a) dehydrated and measured with CO_2 adsorbed at different pressures (given in mbar): (b) 29, (c) 63, (d) 108, (e) 190, (f) 352, (g) 622, (h) 838, (i) 1200, (j) 3900, (k) 10500, (l) 19200, (m) 5200, (n) 660 mbar and (o) evacuated.

Table S2.10 Cubic unit cell parameter, *a*, of zeolite $Li_{8.0}Cs_{2.5}$-Rho (*I*-43*m*) upon adsorption and desorption of CO_2, measured by one or two phase Le Bail structureless refinement, together with goodness of fit parameters

p_{CO2}	***a*, Phase I (Å)**	***a*, Phase II (Å)**	**wRp ; Rp**
Dehydrated	14.4826(2)	-	0.0269 ; 0.0181
29 mbar of CO_2	14.4989(3)	-	0.0350 ; 0.0179
63 mbar of CO_2	14.5144(4)	-	0.0376 ; 0.0217
108 mbar of CO_2	14.5221(5)	-	0.0311 ; 0.0206
190 mbar of CO_2	14.5331(6)	-	0.0390 ; 0.0230
352 mbar of CO_2	14.5460(1)	-	0.0336 ; 0.0205
622 mbar of CO_2	14.5613(3)	-	0.0348 ; 0.0207
838 mbar of CO_2	14.5715(8)	-	0.0344 ; 0.0211
1200 mbar of CO_2	14.5871(9)	-	0.0368 ; 0.0231
3900 mbar of CO_2	14.6279(7)	14.8205(9)	0.0283 ; 0.0191
10500 mbar of CO_2	14.6780(9)	14.8660(2)	0.0241 ; 0.0165
19200 mbar of CO_2	14.7122(7)	14.8671(4)	0.0157 ; 0.0110
5200 mbar of CO_2	14.6374(5)	14.8420(8)	0.0335 ; 0.0217
660 mbar of CO_2	14.5696(8)	-	0.0373 ; 0.0225
0 mbar of CO_2	14.4958(8)	-	0.0300 ; 0.0170

Table S2.11 Fractional atomic coordinates, occupancies, multiplicities, isotropic displacement parameters (in $Å^2$), Si-O bond lengths, OTO angles of dehydrated Li,Cs-Rho and in equilibrium with 0.19 bar and 1.20 bar CO_2 – synchrotron data

Li,Cs-Rho	x	y	z	Occup.	Mult.	Uiso
Si1	0.27247(8)	0.12233(8)	0.42144(8)	0.8	48	0.00750(25)
Al1	0.27247(8)	0.12233(8)	0.42144(8)	0.2	48	0.00750(25)
O1	0.21459(16)	0.21459(16)	0.39456(24)	1	24	0.0139(5)
O2	0.12446(14)	0.12446(14)	0.62565(21)	1	24	0.0139(5)
O3	0.03270(14)	0.21138(14)	0.38878(15)	1	48	0.0139(5)
Li (S6R)	0.247	0.247	0.247	1	8	0.025
Cs (D8R)	0	0	0.5	0.4195(9)	6	0.025
Atom 1	**Atom 2**	**Length**				
Si1	O1	1.6242(15)				
Si1	O2	1.6343(15)				
Si1	O3	1.6402(19)				
Si1	O3	1.6358(22)				
Atom 1	**Atom 2**	**Atom 3**	**OTO angle**			
O1	Si1	O2	110.46(19)			
O1	Si1	O3	107.66(13)			
O1	Si1	O3	112.99(18)			
O2	Si1	O3	113.48(16)			
O2	Si1	O3	105.83(13)			
O3	Si1	O3	106.45(18)			

Li,Cs-Rho (0.19 bar)	x	y	z	Occup.	Mult.	Uiso
Si1	0.27042(6)	0.12135(6)	0.42014(7)	0.8	48	0.00947(20)
Al1	0.27042(6)	0.12135(6)	0.42014(7)	0.2	48	0.00947(20)
O1	0.21243(13)	0.21243(13)	0.39522(19)	1	24	0.0155(4)
O2	0.12649(12)	0.12649(12)	0.62728(18)	1	24	0.0155(4)
O3	0.03041(12)	0.20881(11)	0.38787(13)	1	48	0.0155(4)
Li (S6R)	0.2266	0.2266	0.2266	1	8	0.025
Cs (D8R)	0	0	0.5	0.4227(8)	6	0.025
OC1	0.7648(6)	0	0	0.82184	12	0.286(5)
OC2	0.1423(5)	0.1423(5)	0.1423(5)	0.80924	8	0.358(11)
OC3	0.3989(13)	0.3989(13)	0.3989(13)	0.40973	8	0.520(27)
Atom 1	**Atom 2**	**Length**				
Si1	O1	1.6101(12)				
Si1	O2	1.6463(13)				
Si1	O3	1.6635(16)				
Si1	O3	1.6360(19)				
Atom 1	**Atom 2**	**Atom 3**	**OTO angle**			
O1	Si1	O2	109.91(16)			
O1	Si1	O3	107.93(12)			
O1	Si1	O3	112.59(15)			
O2	Si1	O3	114.53(14)			
O2	Si1	O3	103.86(11)			
O3	Si1	O3	108.07(14)			

Li,Cs-Rho (1.20 bar)	x	y	z	Occup.	Mult.	Uiso
Si1	0.26930(6)	0.11977(7)	0.41834(7)	0.8	48	0.01036(23)
Al1	0.26930(6)	0.11977(7)	0.41834(7)	0.2	48	0.01036(23)

O1	0.21168(14)	0.21168(14)	0.39250(21)	1	24	0.0181(4)
O2	0.12892(17)	0.12892(17)	0.62456(15)	1	24	0.0181(4)
O3	0.02756(12)	0.21017(9)	0.38908(15)	1	48	0.0181(4)
Li (S6R)	0.2266	0.2266	0.2266	1	8	0.025
Cs (D8R)	0	0	0.5	0.4565(14)	6	0.0569(9)
OC1	0.7990(7)	0	0	1	12	0.503(5)
OC2	0.1412(7)	0.1412(7)	0.1412(7)	1	8	0.503(5)
OC3	0.3702(10)	0.3702(10)	0.3702(10)	1	8	0.503(5)
OC4	0.6914(7)	0	0	1	12	0.503(5)

Atom 1	**Atom 2**	**Length**
Si1	O1	1.6263(11)
Si1	O2	1.6382(16)
Si1	O3	1.6536(13)
Si1	O3	1.6260(17)

Atom 1	**Atom 2**	**Atom 3**	**OTO angle**
O1	Si1	O2	109.61(14)
O1	Si1	O3	109.94(13)
O1	Si1	O3	112.81(17)
O2	Si1	O3	113.49(11)
O2	Si1	O3	104.40(13)
O3	Si1	O3	106.52(16)

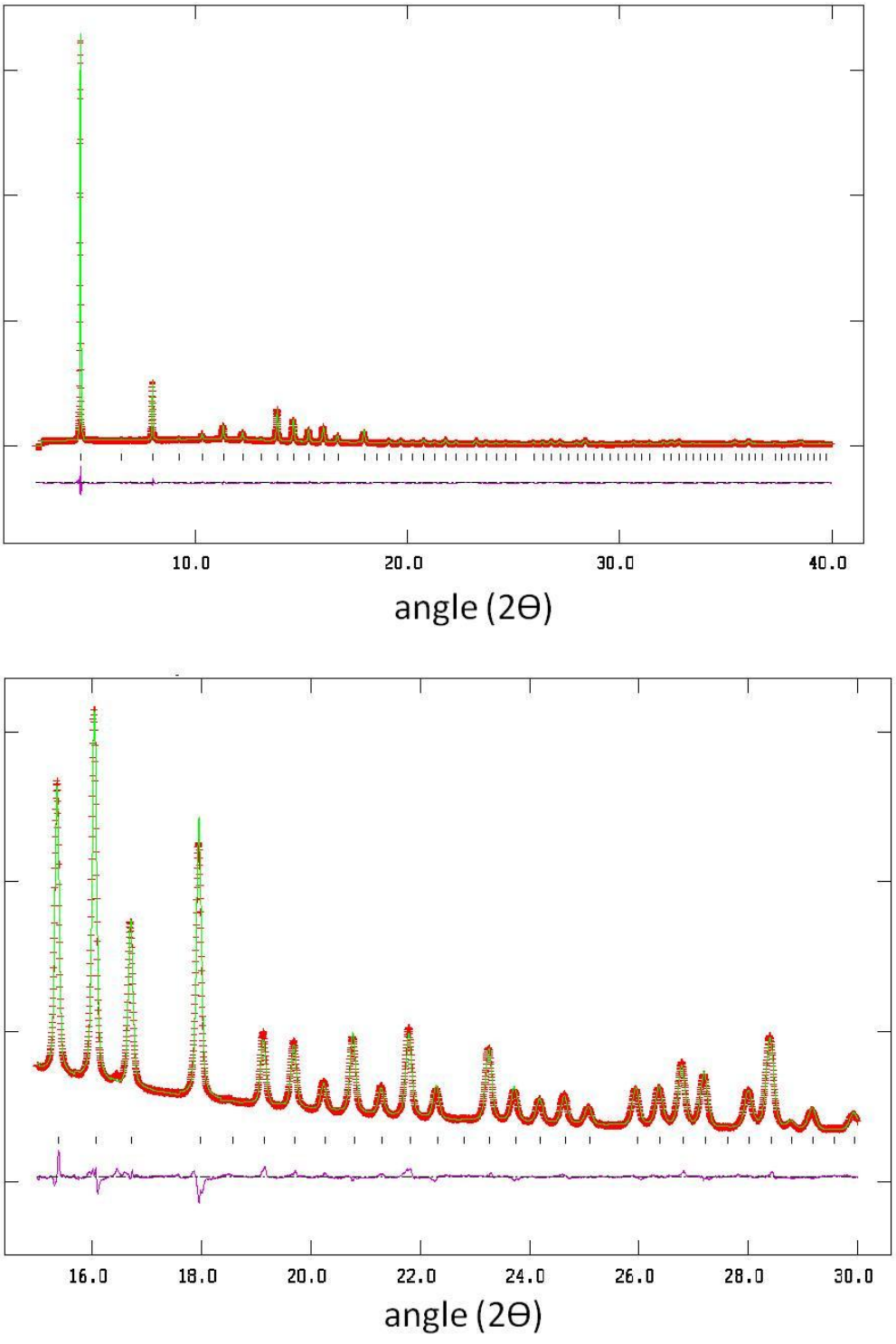
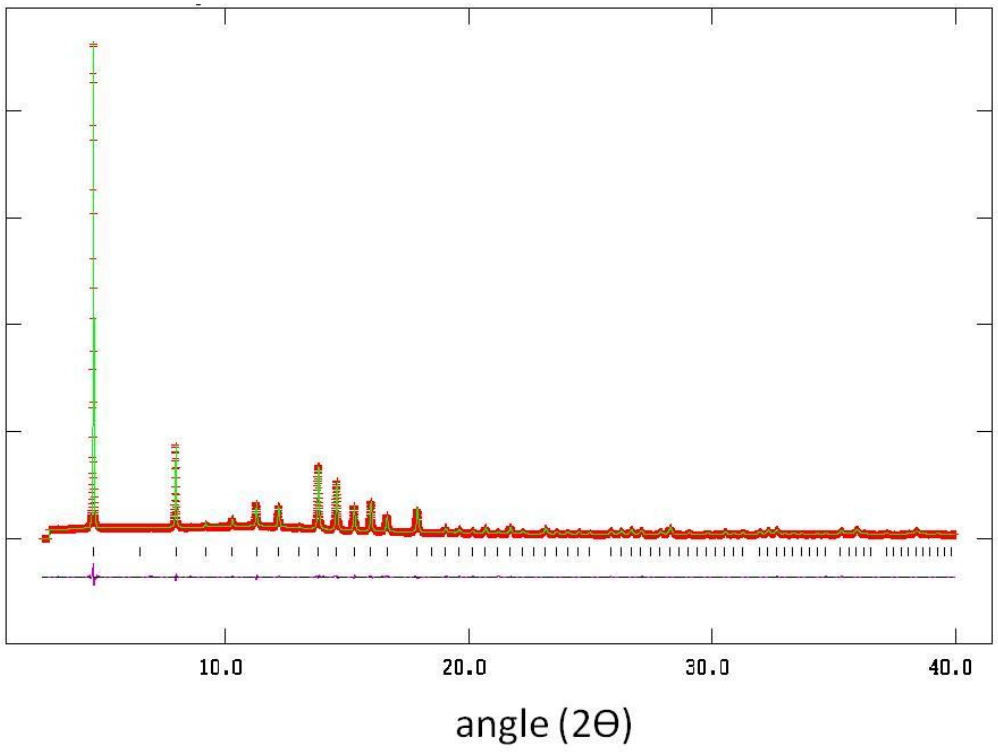


Figure S2.17 GSAS plots for dehydrated $Cs_{2.5}$Li-Rho



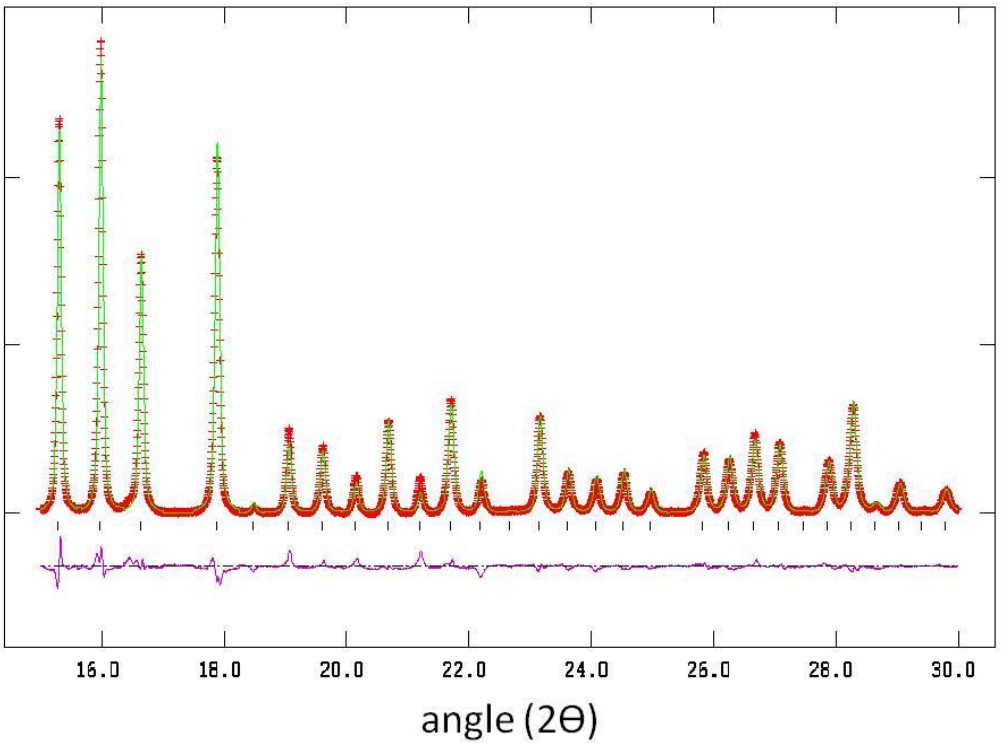
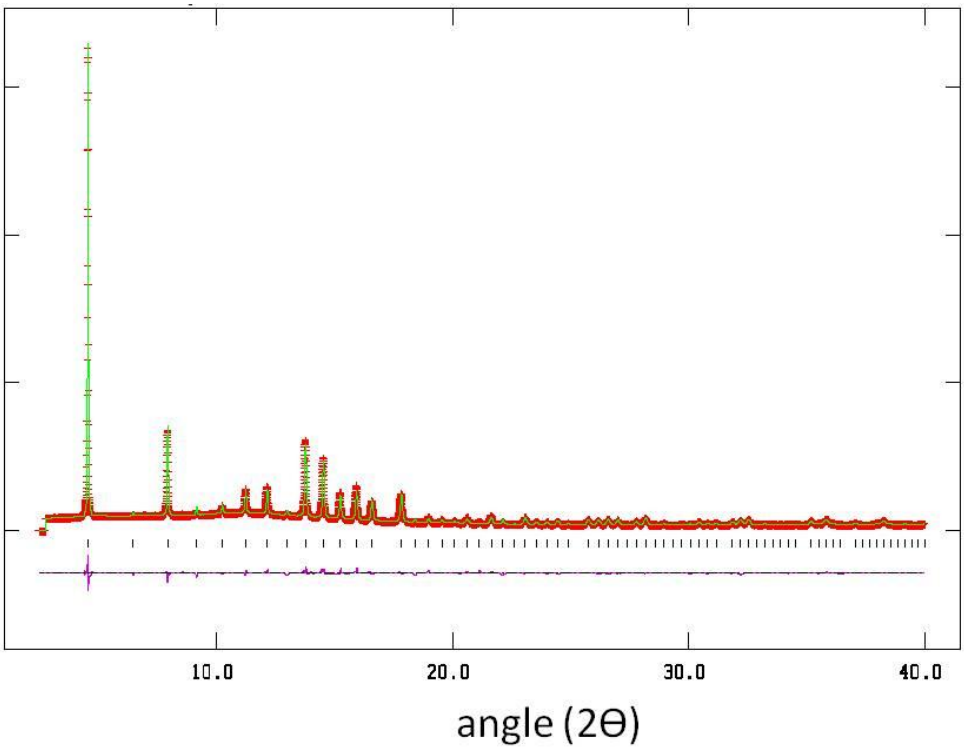


Figure S2.18 GSAS plots for $Cs_{2.5}$Li-Rho in equilibrium with 0.19 bar of CO_2



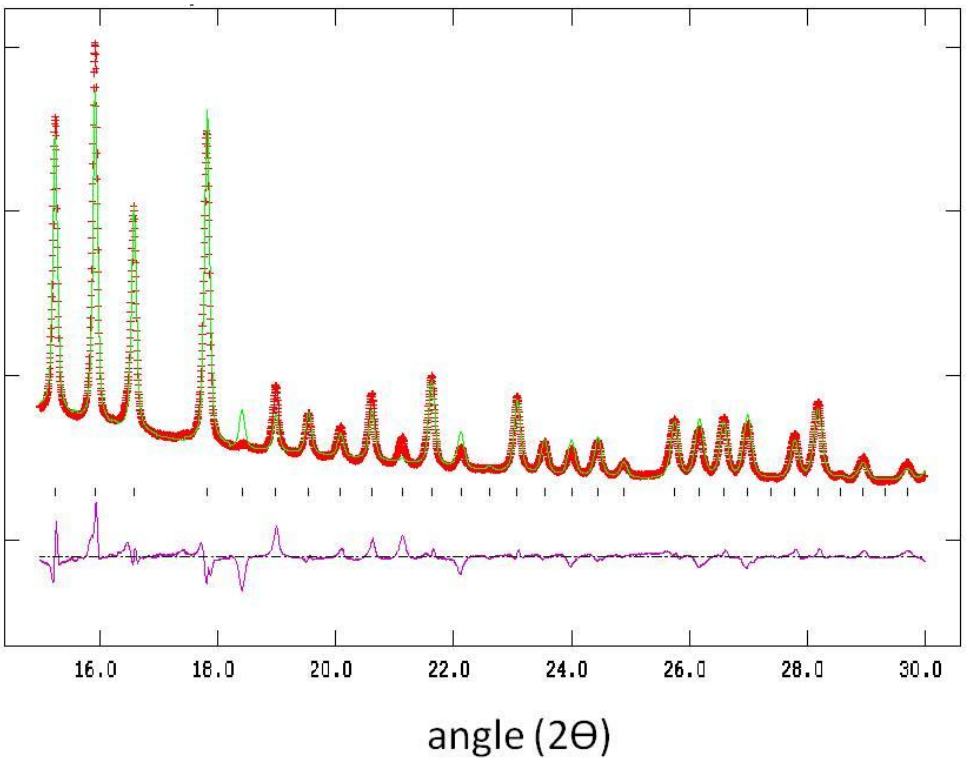


Figure S2.19 GSAS plots for $Cs_{2.5}$Li-Rho in equilibrium with 1.20 bar of CO_2

3. Gas adsorption on Li- and H-Rho and Li-Rho(3.2)

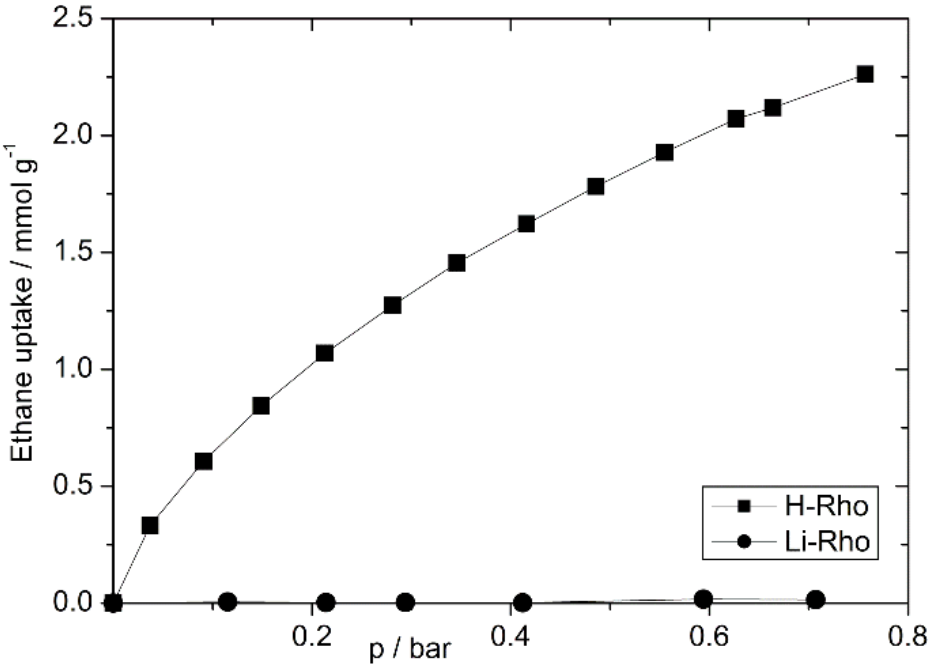


Figure S3.1 Ethane adsorption isotherms at 298 K on H-Rho and Li-Rho

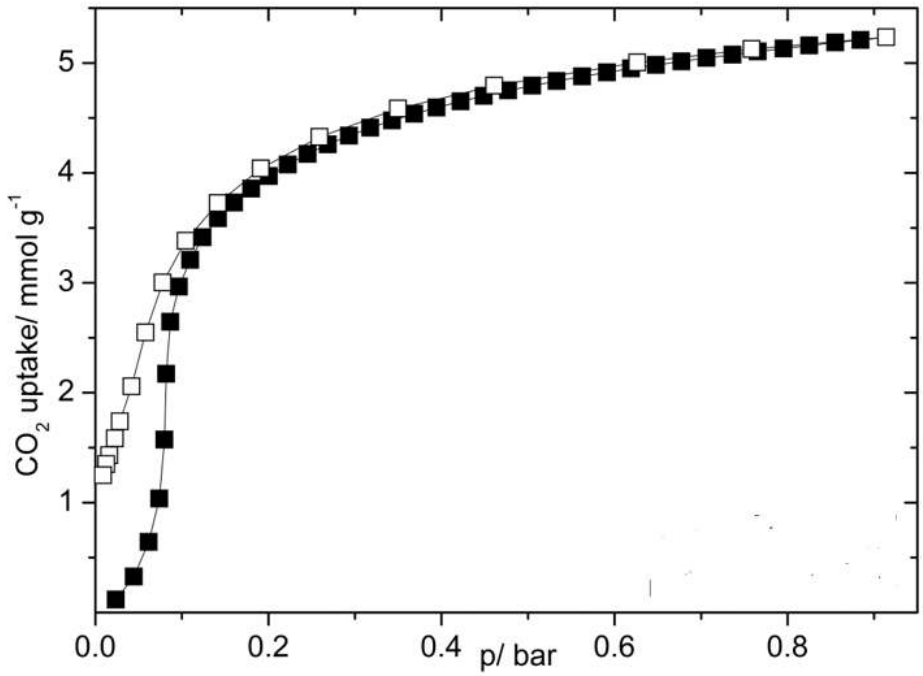


Figure S3.2 CO_2 adsorption isotherm at 298 K on Li-Rho(3.2)

4. Adsorption on $Na_{2.1}Li$-Rho

4.1 CO_2 adsorption

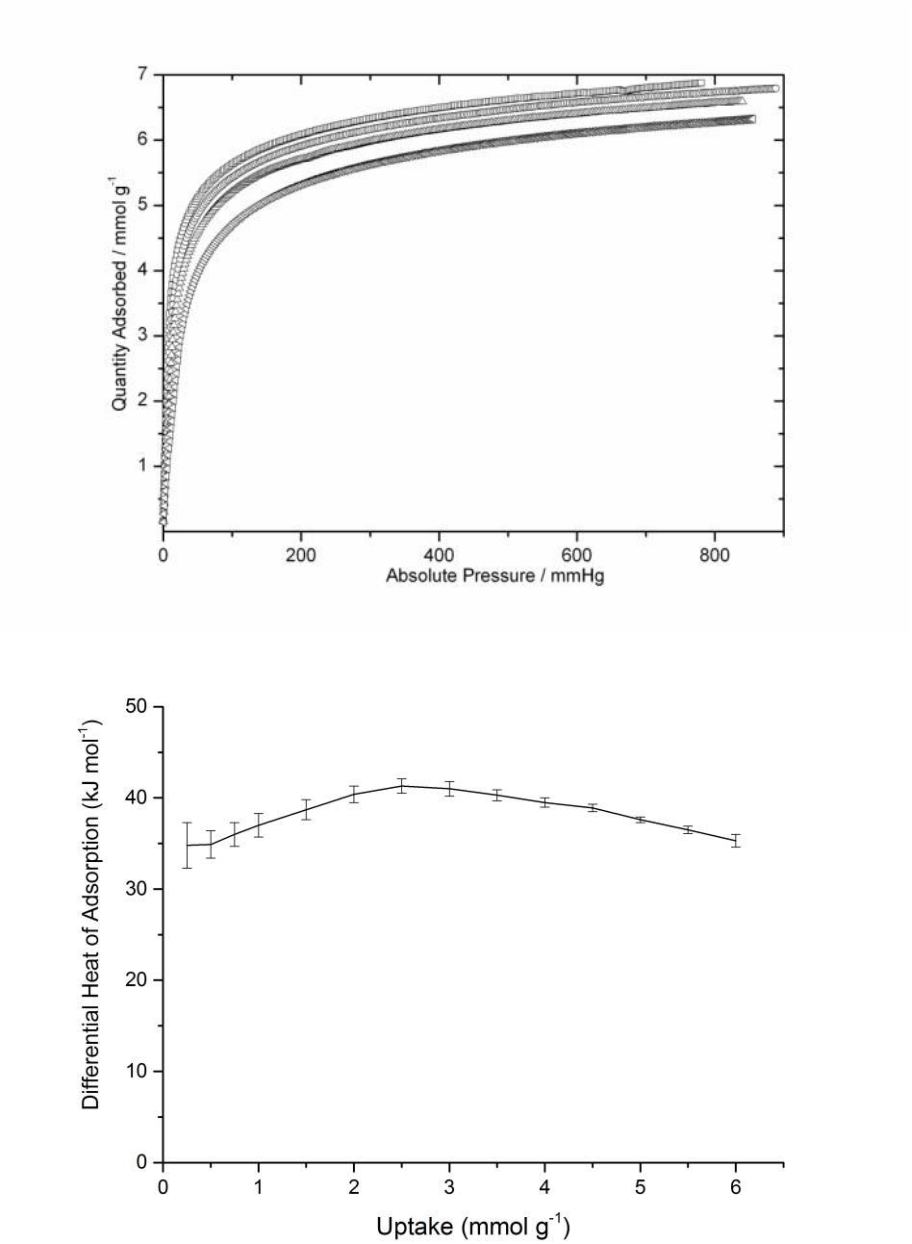


Figure S4.1 (Above) CO_2 adsorption isotherms on $Na_{2.1}Li$-Rho at 273, 278, 283 and 293 K (uptake increasing at lower temperatures) and (below) the isosteric heats of adsorption as a function of uptake.

4.2 CH_4 adsorption

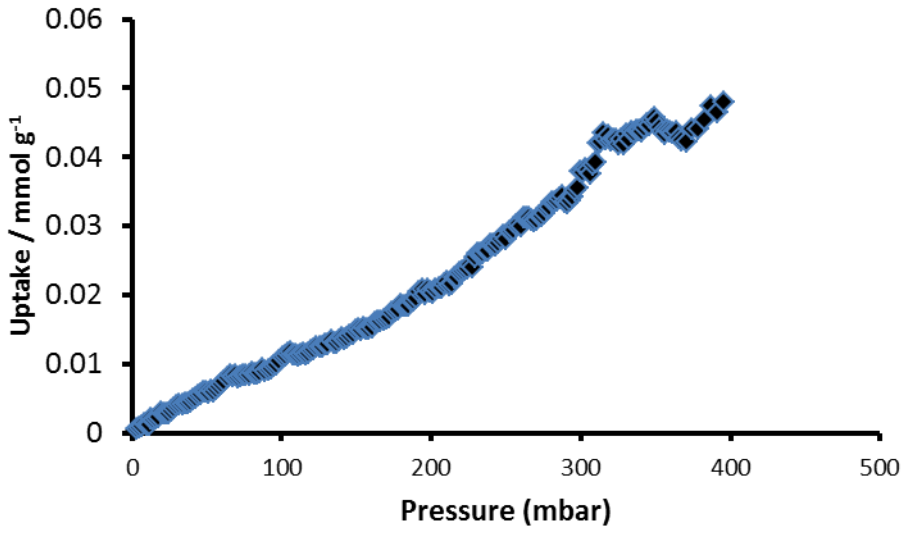


Figure S4.2 CH_4 adsorption isotherm on $Na_{2.1}Li$-Rho, measured at 298 K

5. Adsorption on LiCs-Rho

5.1 CH_4 adsorption

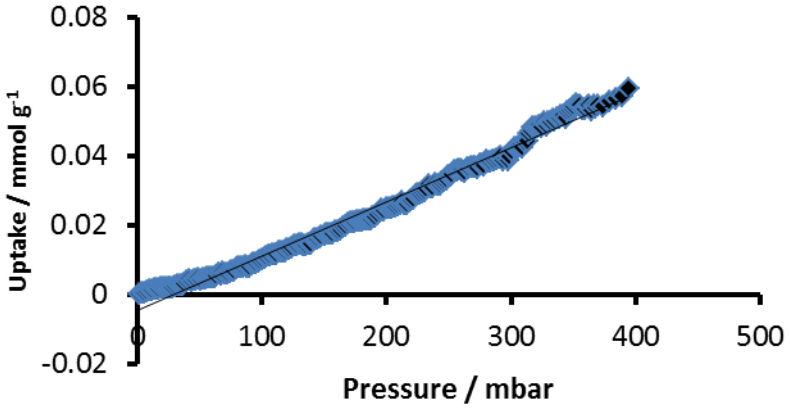


Figure S5.1 CH_4 adsorption isotherm on $Cs_{1.8}Li$-Rho at 298 K.

5.2 CO_2 adsorption

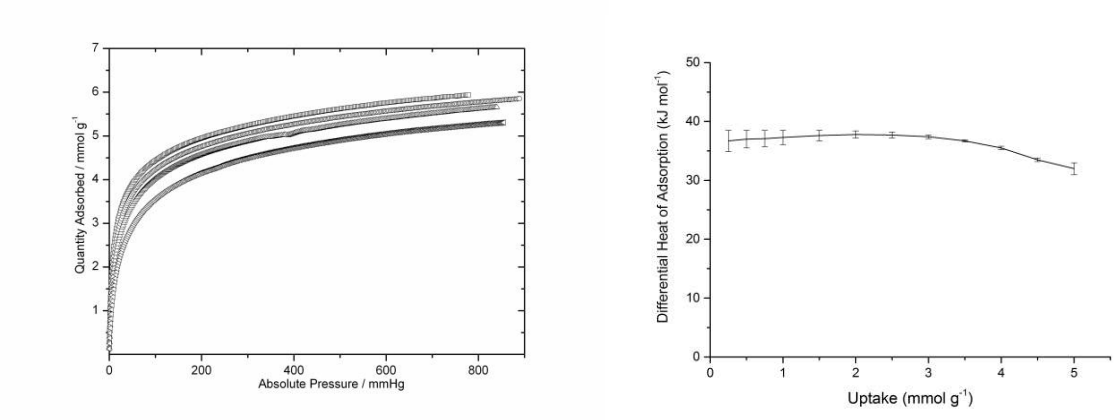


Figure S5.2 (Left) CO_2 adsorption isotherms on $Cs_{2.5}Li$-Rho at 273, 278, 283 and 293 K (uptake increasing at lower temperatures) and (right) isosteric heats of adsorption as a function of uptake.

6. Breakthrough and desorption curves for Zeolite 13X

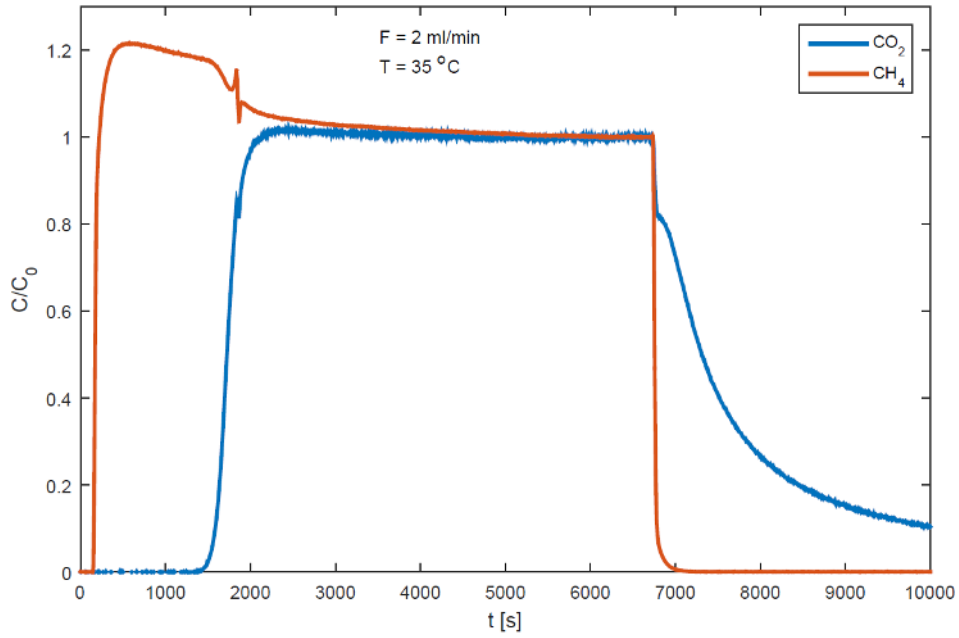


Figure S6.1 Experimental breakthrough curves for 13X with 5% CO_2 and 40% CH_4 in He. Feed conditions: flowrate = 2 ml/min, CO_2/CH_4/He = 5/40/55, P = 1 bar, T = 35 °C.

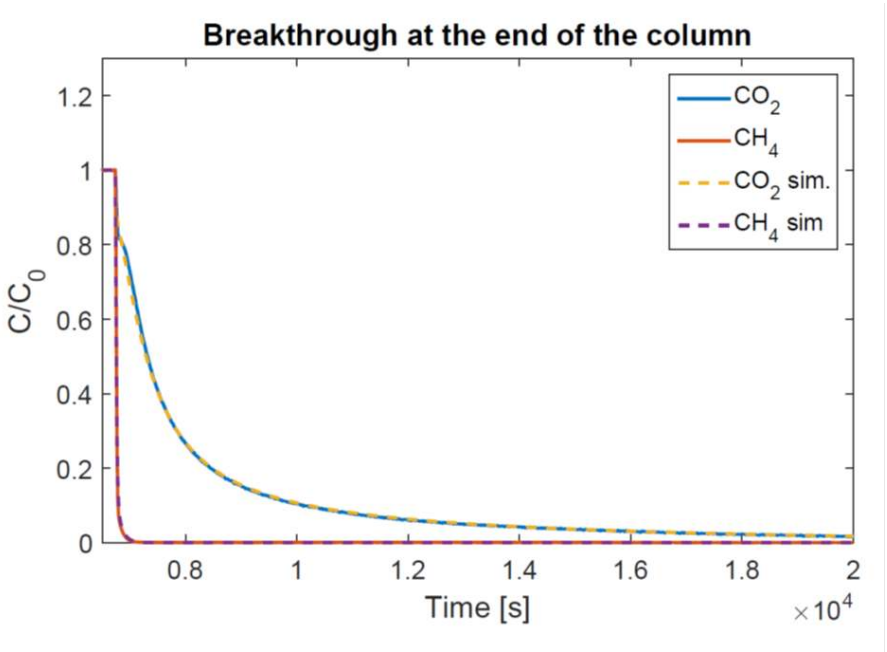


Figure S6.2 Experimental and predicted breakthrough curves for 13X with 5% CO_2 and 40% CH_4 in He. Feed conditions: flowrate = 2 ml/min, CO_2/CH_4/He = 5/40/55, P = 1 bar, T = 35 °C.

7. References

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