Supplementary Information AM-11-047 for

Structural studies of NH_4-exchanged natrolites at ambient conditions and high-temperature

Yongmoon Lee,[1] Donghoon Seoung,[1] Young-Nam Jang,[2] Jianming Bai,[3] Yongjae Lee[1]*

[1]Department of Earth System Sciences, Yonsei University, Seoul 120-749, Korea

[2]Korea Institute of Geoscience and Mineral Resources, Daejeon 305-350, Republic of Korea

[3]National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY, 11973, USA

(office) +82-2-2123-5667, (e-mail) YongjaeLee@yonsei.ac.kr

Supplementary Table 1. EDS chemical composition of the fully and partially NH_4-exchanged natrolites.[a]

Fully NH_4-exchanged natrolite					
Elements		N	K	Al	Si
Atomic percent (%)	*1*	9.77	0.00	9.47	12.88
	2	9.72	0.00	9.33	13.05
	3	9.12	0.00	10.30	14.10
	4	9.46	0.00	9.50	13.21
	5	10.00	0.00	9.73	13.57
	6	10.62	0.00	9.50	13.02
Unit cell composition		$(NH_4)_{16.24}Al_{16}Si_{24}O_{80} \cdot xH_2O$			
Partially NH_4-exchanged natrolite					
Elements		N	K	Al	Si
Atomic percent (%)	*1*	4.30	6.76	10.84	15.90
	2	5.17	6.17	10.34	15.60
	3	2.04	6.64	11.41	18.12
	4	2.46	6.73	11.04	17.89
	5	3.06	6.59	10.42	17.79
	6	3.44	7.40	10.94	16.50
	7	2.33	6.95	11.16	17.85
Unit cell composition		$(NH_4)_{4.78}K_{9.93}Al_{16}Si_{24}O_{80} \cdot xH_2O$			
Atomic ratio of $N^+ : K^+$		0.325 : 0.675			

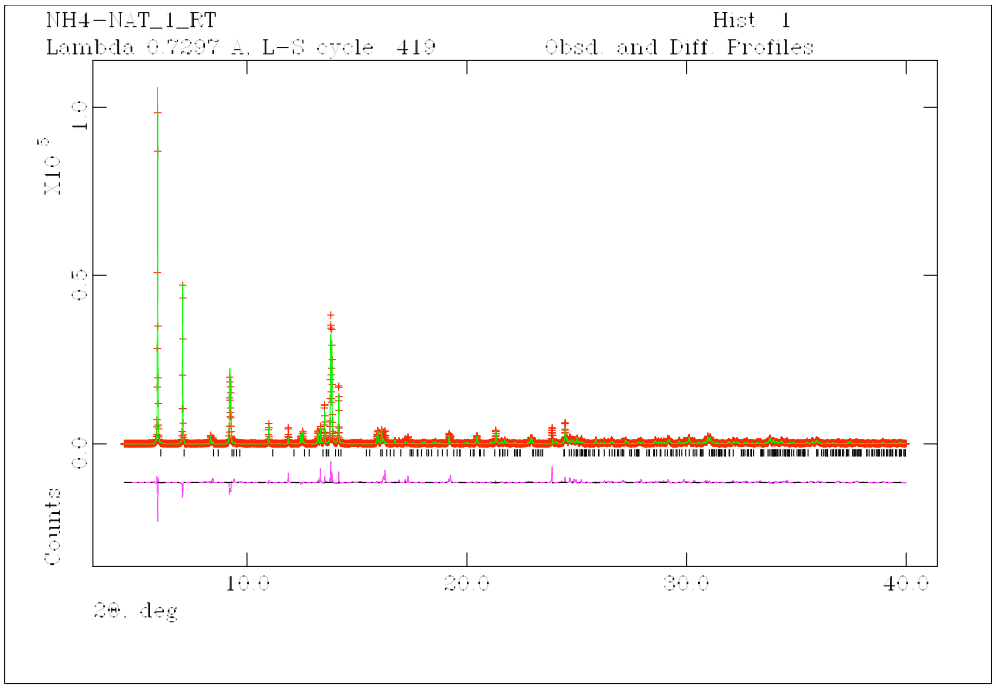
[a]Values are normalized based on 16 aluminum atoms per unit cell.

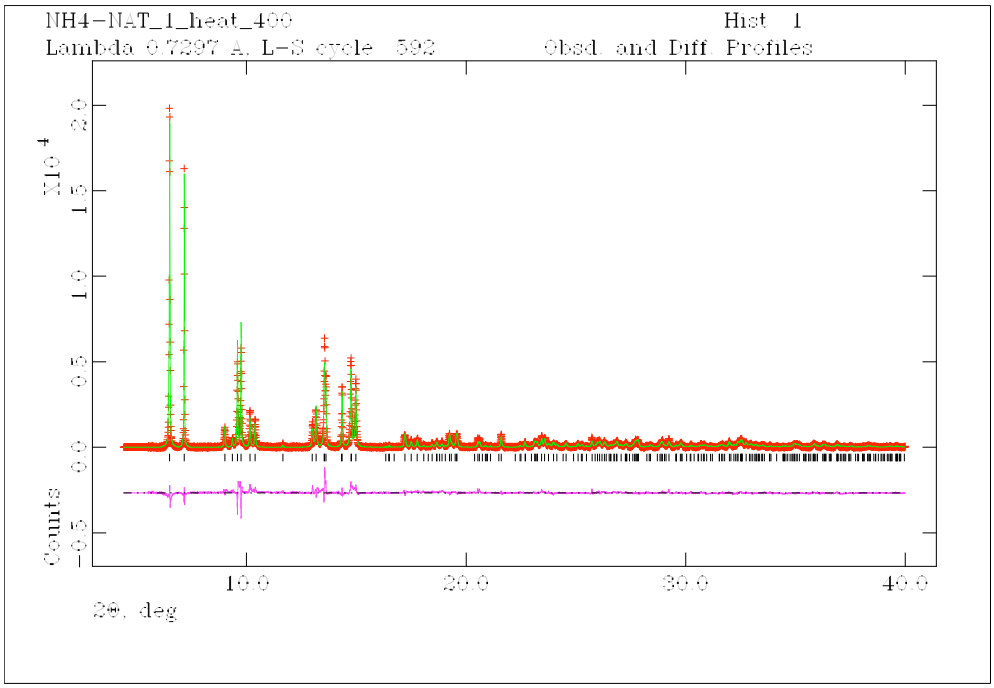
Supplementary Table 2. Unit cell parameters of NH_4- and partially NH_4-exchanged natrolites at different temperatures.[a]

	Fully NH_4-exchanged natrolite				Partially NH_4-exchanged natrolite			
Temperature (□)	a	b	c	volume	a	b	c	volume
25	19.8368(2)	20.0574(2)	6.5165(1)	2592.74(4)	19.5511(2)	19.9342(2)	6.4923(1)	2530.27(4)
50	19.8424(1)	20.0516(1)	6.5168(1)	2592.85(3)	19.5535(2)	19.9269(2)	6.4925(1)	2529.75(4)
75	19.8465(2)	20.0404(2)	6.5161(1)	2591.65(4)	19.5437(2)	19.9050(2)	6.4906(1)	2524.96(4)
100	19.8482(2)	20.0308(2)	6.5146(1)	2590.04(5)	19.5258(2)	19.8799(2)	6.4876(1)	2518.29(5)
125	19.8464(2)	20.0289(2)	6.5140(1)	2589.31(5)	19.5203(2)	19.8674(2)	6.4867(1)	2515.66(5)
150	17.8927(4)	18.4934(5)	6.5466(1)	2166.2(1)	19.5185(2)	19.8600(1)	6.4871(1)	2514.64(5)
175	17.8881(5)	18.5015(5)	6.5464(1)	2166.6(1)	19.4938(3)^{h} 17.657(5)^{d}	19.8367(2)^{h} 18.527(5)^{d}	6.4808(1)^{h} 6.523(1)^{d}	2506.08(6)^{h} 2134.0(7)^{d}
200	17.8845(5)	18.5090(5)	6.5463(1)	2167.0(1)	19.484(1)^{h} 17.628(1)^{d} 16.969(7)^{K}	19.827(1)^{h} 18.533(1)^{d} 18.155(8)^{K}	6.4774(2)^{h} 6.5252(4)^{d} 6.486(2)^{K}	2502.3(2)^{h} 2131.8(2)^{d} 1998.1(8)^{K}
225	17.8842(4)	18.5194(5)	6.5479(1)	2168.7(1)	17.5869(9)^{d} 16.943(3)^{K}	18.513(1)^{d} 18.121(5)^{K}	6.5227(3)^{d} 6.489(2)^{K}	2123.7(1)^{d} 1992.3(6)^{K}
250	17.8826(5)	18.5278(5)	6.5485(1)	2169.7(1)	17.5741(7)^{d} 16.9860(9)^{K}	18.5348(8)^{d} 18.131(1)^{K}	6.5321(2)^{d} 6.4889(5)^{K}	2127.7(2)^{d} 1998.5(2)^{K}
275	17.8806(5)	18.5377(5)	6.5494(1)	2170.9(1)	17.5585(8)^{d} 16.9996(8)^{K}	18.5354(6)^{d} 18.1538(9)^{K}	6.5361(2)^{d} 6.4899(6)^{K}	2127.2(2)^{d} 2002.8(2)^{K}
300	17.8779(5)	18.5441(5)	6.5493(1)	2171.3(1)	17.534(1)^{d} 17.008(1)^{K}	18.524(1)^{d} 18.164(1)^{K}	6.5346(3)^{d} 6.4928(5)^{K}	2122.4(2)^{d} 2005.8(2)^{K}
325	17.8792(5)	18.5528(5)	6.5504(1)	2172.8(1)	17.5129(8)^{d} 17.029(1)^{K}	18.5233(6)^{d} 18.173(1)^{K}	6.5373(2)^{d} 6.4928(7)^{K}	2120.7(2)^{d} 2009.3(2)^{K}
350	17.8797(5)	18.5620(5)	6.5512(1)	2174.2(1)	17.4947(8)^{d} 17.071(2)^{K}	18.5247(6)^{d} 18.199(3)^{K}	6.5365(3)^{d} 6.49(1)^{K}	2118.4(2)^{d} 2016.2(5)^{K}
375	17.8806(5)	18.5698(5)	6.5519(1)	2175.5(1)	17.4702(7)^{d} 17.076(2)^{K}	18.5141(6)^{d} 18.207(2)^{K}	6.5388(2)^{d} 6.491(1)^{K}	2114.9(2)^{d} 2018.2(4)^{K}
400	17.8820(5)	18.5781(5)	6.5527(1)	2176.9(1)	17.4722(5)^{d} 17.095(2)^{K}	18.5303(4)^{d} 18.2219(2)^{K}	6.5430(1)^{d} 6.484(1)^{K}	2118.4(1)^{d} 2019.8(4)^{K}
425	17.8770(5)	18.5896(5)	6.5530(1)	2177.7(1)	17.4481(7)^{d} 17.149(2)^{K}	18.5104(6)^{d} 18.269(2)^{K}	6.5428(2)^{d} 6.478(1)^{K}	2113.1(2)^{d} 2029.5(4)^{K}
450					17.4335(5)^{d} 17.263(2)^{K}	18.5056(4)^{d} 18.306(3)^{K}	6.5468(2)^{d} 6.502(1)^{K}	2112.1(1)^{d} 2054.9(5)^{K}
475					17.4196(4)^{d} 17.344(2)^{K}	18.5118(4)^{d} 18.455(2)^{K}	6.5420(1)^{d} 6.5137(9)^{K}	2109.6(1)^{d} 2085.0(1)^{K}
Cooled down to RT					16.9152(6)^{K}	18.0634(7)^{K}	6.4703(2)^{K}	1977.0(1)^{K}

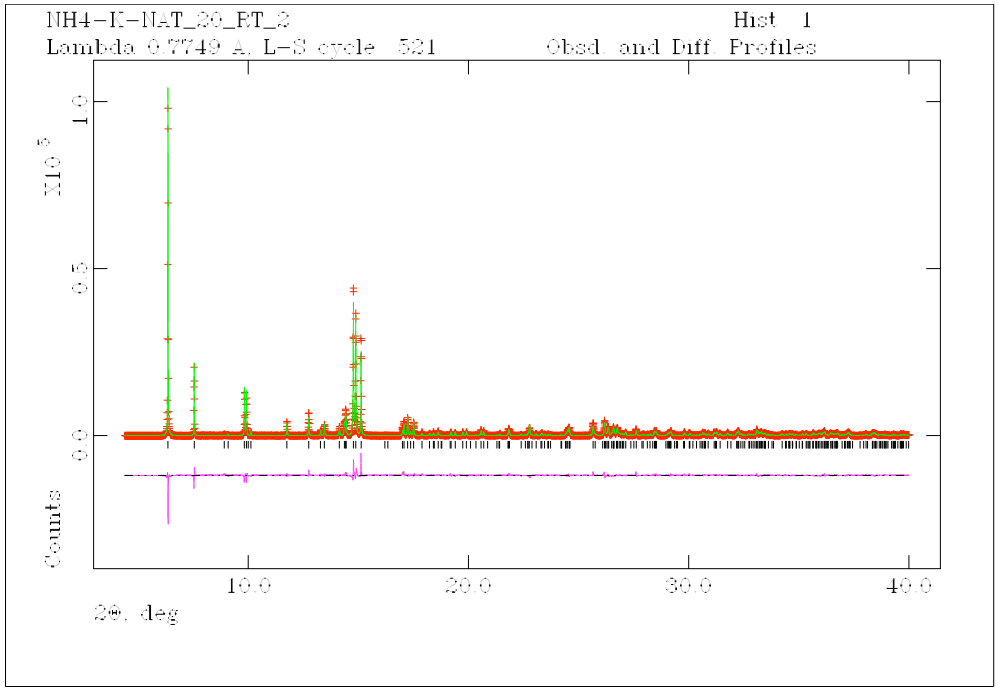
[a]Esd's are in parentheses. In the case of the partially NH_4-exchanged natrolite, three or two different phases coexist from 175°C; [h]the original hydrated phase, [d]the partially NH_4-exchanged natrolite in the dehydrated state, and [K]the K-rich phase separated from the partially NH_4-exchanged natrolite.

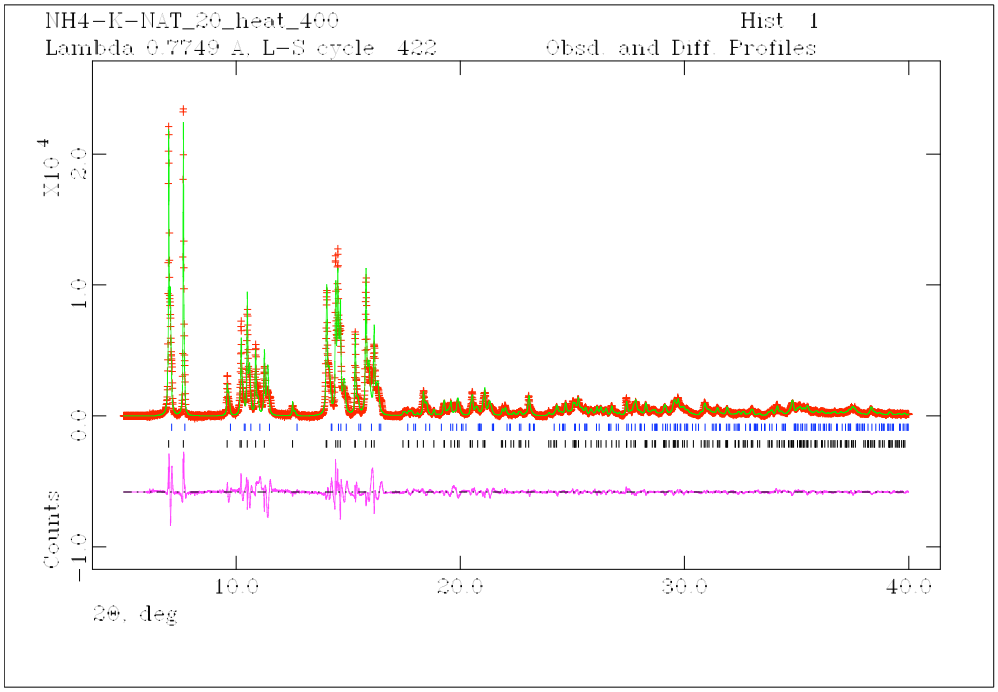
Supplementary Figure 1. Rietveld refinement fits of the structural models of the fully NH_4-exchanged natrolite at RT (upper) and at 400˚C (lower) using synchrotron X-ray powder diffraction data. Points shown represent the observed data. The continuous lines through the sets of points are the calculated profiles from the structure refinements summarized in Tables 1-2. The sets of tic marks below the data indicate the positions of the allowed reflections. The lower curves represent the differences between observed and calculated profiles (I_{obs} - I_{calc}) plotted on the same scale as the observed data.

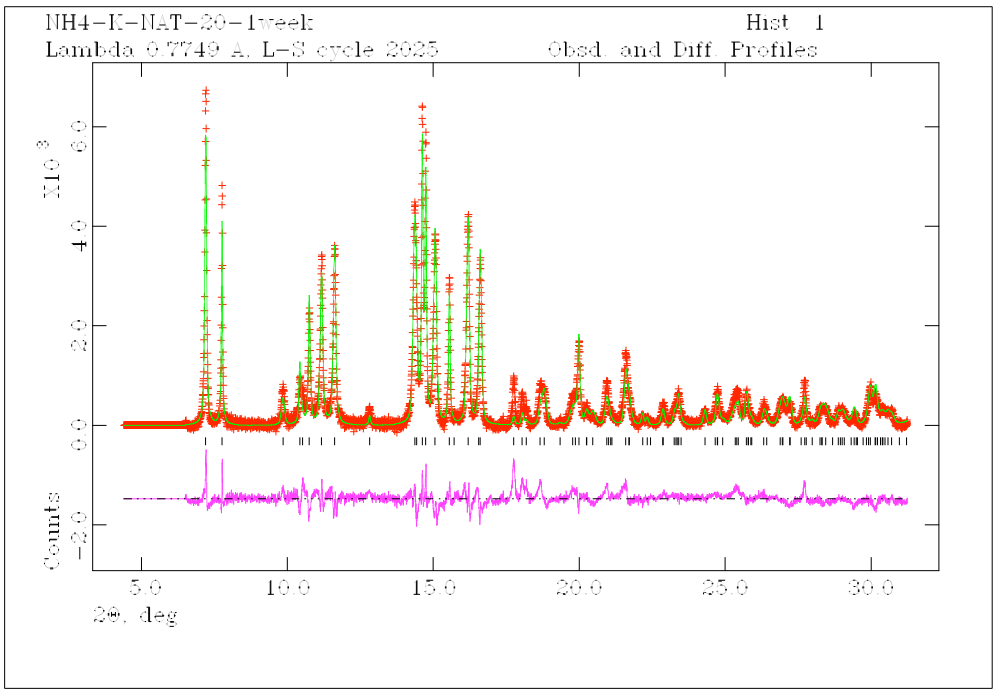




Supplementary Figure 2. Rietveld refinement fits of the structural models of the partially NH_4-exchanged natrolite at RT (upper), at 400˚C (middle), and after one week of exposure to atmospheric conditions (lower) using synchrotron X-ray powder diffraction data. Points shown represent the observed data. The continuous lines through the sets of points are the calculated profiles from the structure refinements summarized in Tables 1-2. The sets of tic marks below the data indicate the positions of the allowed reflections. In the case of the fit to the 400˚C data, the K-rich phase is included as a minor secondary phase. The lower curves represent the differences between observed and calculated profiles (I_{obs} - I_{calc}) plotted on the same scale as the observed data.






NH4-K-NAT-20-1week
Hist 1
Lambda 0.7749 A, L-S cycle 2025
Obsd and Diff Profiles
X10^3
6.0
4.0
2.0
0.0
-2.0
Counts
5.0
10.0
15.0
20.0
25.0
30.0
2θ, deg