

## Supplementary Information for

# In-situ dehydration studies of fully K-, Rb-, and Cs-exchanged natrolite

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Supplementary Table 1. Chemical composition calculated from Energy Dispersive Spectroscopy (EDS) method.

| Energy Dispersive Spectroscopy (EDS) |   |   |       |       |       |
|--------------------------------------|---|---|-------|-------|-------|
| K-NAT                                |   |   |       |       |       |
| Elements                             |   | K   | Al    | Si    | O     |
| Atomic percent (%)                   | 1 | 11.85   | 11.15 | 18.12 | 58.89 |
|                                      | 2 | 11.53   | 11.00 | 18.40 | 59.07 |
|                                      | 3 | 11.68   | 11.58 | 17.84 | 58.90 |
|                                      | 4 | 11.44   | 11.17 | 18.31 | 59.09 |
|                                      | 5 | 11.37   | 11.41 | 18.14 | 59.08 |
| Unit cell composition                |   | $K_{15.69}Al_{15.26}Si_{24.62}O_{80} \cdot xH_2O$ |       |       |       |

Supplementary Table 2. Concentration of elements from samples investigated by Inductively Coupled Plasma (ICP).

| ICP                             |    |            |            |            |
|---------------------------------|----|------------|------------|------------|
|                                 |    | K-NAT      | Rb-NAT     | Cs-NAT     |
| Concentration of elements (ppm) | Al | 155900     | 137960     | 104800     |
|                                 | Na | $\leq 3^*$ |            |            |
|                                 | K  | 162500     | $\leq 1^*$ | $\leq 1^*$ |
|                                 | Rb |            | 273600     |            |
|                                 | Cs |            |            | 224839     |

\*Detection limit: hundreds ppb

Supplementary Table 3. Final refined cell parameters for K-, Rb- and Cs-exchanged natrolite at different temperatures  
(\* dehydrated phases)

| K-NAT           |                  |             |             |                               |
|-----------------|------------------|-------------|-------------|-------------------------------|
| Temperature (□) | cell lengths (Å) |             |             | cell volume (Å <sup>3</sup> ) |
|                 | <i>a</i>         | <i>b</i>    | <i>c</i>    | <i>V</i>                      |
| 25              | 19.2703(2)       | 19.7465(2)  | 6.48245(4)  | 2466.66(4)                    |
| 50              | 19.2821(1)       | 19.7422(2)  | 6.48194(4)  | 2467.48(4)                    |
| 75              | 19.2880(1)       | 19.7257(1)  | 6.48191(3)  | 2466.17(3)                    |
| 100             | 19.2657(1)       | 19.6842(1)  | 6.48045(3)  | 2457.58(3)                    |
| 125             | 19.2593(1)       | 19.6628(1)  | 6.47919(3)  | 2453.62(3)                    |
| 150             | 19.2610(1)       | 19.6515(1)  | 6.47744(3)  | 2451.76(3)                    |
| 175             | 19.2561(2)       | 19.6334(2)  | 6.47282(4)  | 2447.14(3)                    |
|                 | 16.9501(4)*      | 18.0948(4)* | 6.47836(9)* | 1986.96(6)*                   |
| 200             | 19.253(1)        | 19.6357(8)  | 6.4693(4)   | 2445.63(2)                    |
|                 | 16.9658(3)*      | 18.1040(3)* | 6.48236(7)* | 1991.05(7)*                   |
| 225             | 16.9796(3)*      | 18.1169(3)* | 6.48495(7)* | 1994.88(6)*                   |
| 250             | 16.9909(2)*      | 18.1330(3)* | 6.48732(7)* | 1998.71(6)*                   |
| 275             | 17.0087(2)*      | 18.1538(2)* | 6.49101(6)* | 2004.24(5)*                   |
| 300             | 17.0195(3)*      | 18.1697(3)* | 6.49393(7)* | 2008.18(6)*                   |
| 325             | 17.0305(3)*      | 18.1850(3)* | 6.49531(8)* | 2011.59(6)*                   |
| 350             | 17.0456(3)*      | 18.2023(3)* | 6.49911(7)* | 2016.47(6)*                   |
| 375             | 17.0624(3)*      | 18.2230(3)* | 6.50294(7)* | 2021.95(6)*                   |
| 400             | 17.0764(4)*      | 18.2357(4)* | 6.5046(1)*  | 2025.5(1)*                    |
| 425             | 17.0934(3)*      | 18.2579(3)* | 6.50861(8)* | 2031.27(7)*                   |
| 25(cooled down) | 19.2205(6)       | 19.7537(9)  | 6.4860(3)   | 2462.6(1)                     |

| Rb-NAT          |                  |             |            |                               |
|-----------------|------------------|-------------|------------|-------------------------------|
| Temperature (□) | cell lengths (Å) |             |            | cell volume (Å <sup>3</sup> ) |
|                 | <i>a</i>         | <i>b</i>    | <i>c</i>   | <i>V</i>                      |
| 25              | 19.8234(3)       | 19.9871(3)  | 6.5283(1)  | 2586.58(8)                    |
| 50              | 19.8326(3)       | 19.9837(3)  | 6.5286(1)  | 2587.48(7)                    |
| 75              | 19.8373(4)       | 19.9728(4)  | 6.5268(1)  | 2586.0(1)                     |
| 100             | 19.8340(3)       | 19.9628(3)  | 6.5228(1)  | 2582.62(9)                    |
| 125             | 19.8301(4)       | 19.9556(4)  | 6.5205(1)  | 2580.30(9)                    |
| 150             | 19.8179(4)       | 19.9504(4)  | 6.5174(1)  | 2576.8(3)                     |
|                 | 17.418(2)*       | 18.511(2)*  | 6.5158(5)* | 2100.8(2)*                    |
| 175             | 19.809(1)        | 19.968(1)   | 6.5163(4)  | 2577.6(3)                     |
|                 | 17.428(1)*       | 18.527(1)*  | 6.5172(3)* | 2104.3(3)*                    |
| 200             | 17.436(1)*       | 18.541(1)*  | 6.5206(3)* | 2107.9(3)*                    |
| 225             | 17.449(1)*       | 18.552(1)*  | 6.5232(3)* | 2111.6(3)*                    |
| 250             | 17.4629(9)*      | 18.565(1)*  | 6.5262(3)* | 2115.7(3)*                    |
| 275             | 17.478(1)*       | 18.569(1)*  | 6.5291(4)* | 2119.0(4)*                    |
| 300             | 17.5013(9)*      | 18.595(1)*  | 6.5339(3)* | 2126.3(3)*                    |
| 325             | 17.519(1)*       | 18.604(1)*  | 6.5367(4)* | 2130.4(4)*                    |
| 350             | 17.542(1)*       | 18.626(1)*  | 6.5414(4)* | 2137.3(4)*                    |
| 375             | 17.562(1)*       | 18.645(1)*  | 6.5453(4)* | 2143.2(4)*                    |
| 400             | 17.608(1)*       | 18.687(2)*  | 6.5544(5)* | 2156.7(5)*                    |
| 425             | 17.625(1)*       | 18.706(1)*  | 6.5580(3)* | 2162.1(3)*                    |
| 25(cooled down) | 17.3364(8)*      | 18.4601(9)* | 6.5053(2)* | 2081.9(2)*                    |

| Cs-NAT          |                  |             |            |                               |
|-----------------|------------------|-------------|------------|-------------------------------|
| Temperature (□) | cell lengths (Å) |             |            | cell volume (Å <sup>3</sup> ) |
|                 | <i>a</i>         | <i>b</i>    | <i>c</i>   | <i>V</i>                      |
| 25              | 20.2894(1)       | 19.9982(1)  | 6.5574(1)  | 2660.67(3)                    |
| 50              | 20.2802(1)       | 20.0051(1)  | 6.5581(1)  | 2660.66(3)                    |
| 75              | 20.2621(1)       | 20.0193(1)  | 6.5593(1)  | 2660.68(4)                    |
| 100             | 20.2874(9)       | 19.9866(7)  | 6.5634(3)  | 2661.3(2)                     |
|                 | 18.0872(5)*      | 18.9867(5)* | 6.5722(1)* | 2257.0(1)*                    |
| 125             | 18.1018(4)*      | 19.0019(4)* | 6.5843(1)* | 2264.8(1)*                    |
| 150             | 18.1208(4)*      | 19.0102(4)* | 6.5921(1)* | 2270.8(1)*                    |
| 175             | 18.1365(4)*      | 19.0133(4)* | 6.5943(1)* | 2273.9(1)*                    |
| 200             | 18.1495(3)*      | 19.0148(4)* | 6.5954(1)* | 2276.1(1)*                    |
| 225             | 18.1652(3)*      | 19.0188(4)* | 6.5966(1)* | 2279.0(1)*                    |
| 250             | 18.1792(3)*      | 19.0218(4)* | 6.5970(1)* | 2281.2(1)*                    |
| 275             | 18.1954(5)*      | 19.0295(5)* | 6.5983(2)* | 2284.7(2)*                    |
| 300             | 18.2074(4)*      | 19.0318(4)* | 6.5984(1)* | 2286.4(1)*                    |
| 325             | 18.2218(3)*      | 19.0374(4)* | 6.5988(1)* | 2289.1(1)*                    |
| 350             | 18.2338(4)*      | 19.0412(4)* | 6.5986(1)* | 2291.0(1)*                    |
| 375             | 18.2436(4)*      | 19.0481(4)* | 6.5994(1)* | 2293.3(1)*                    |
| 400             | 18.2685(5)*      | 19.0488(5)* | 6.6020(1)* | 2297.4(2)*                    |
| 425             | 18.2802(4)*      | 19.0653(4)* | 6.6031(1)* | 2301.3(1)*                    |
| 25(cooled down) | 18.0095(3)*      | 18.9510(4)* | 6.5658(1)* | 2240.90(8)*                   |

Supplementary Figure 1. Results of Rietveld refinements of the structural models of K-, Rb-, and Cs-NAT at 400 °C 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 lower curves represents the differences between observed and calculated profiles ( $I_{\text{obs}} - I_{\text{calc}}$ ) plotted on the same scale as the observed data.



