**Table S1.** Details pertaining to the structure refinements of scapolite, performed at different temperatures.

| ***T*** **(°C)** | **25** | **150** | **300** | **450** | **600** | **750** | **797** |
|---|---|---|---|---|---|---|---|
| Experiment | SC-HT | SC-HT | SC-HT | SC-HT | SC-HT | SC-HT | SC-HT |
| Space group | *I*4/*m* | *I*4/*m* | *I*4/*m* | *I*4/*m* | *I*4/*m* | *I*4/*m* | *I*4/*m* |
| Unique peaks | 842 | 771 | 770 | 767 | 852 | 753 | 855 |
| Observed peaks $F_o^2/\sigma(F_o^2)>3$ | 786 | 761 | 760 | 758 | 758 | 747 | 763 |
| $R_{int}$ (all) | 0.0301 | 0.0262 | 0.0298 | 0.0261 | 0.0290 | 0.0267 | 0.0312 |
| Refined param. | 61 | 61 | 61 | 61 | 61 | 61 | 61 |
| $R_1$ (obs) | 0.0512 | 0.0494 | 0.0488 | 0.0469 | 0.0469 | 0.0481 | 0.0484 |
| $R_1$ (all) | 0.0531 | 0.0506 | 0.0497 | 0.0478 | 0.0517 | 0.0485 | 0.0525 |
| w$R_1$ (obs) | 0.0700 | 0.0679 | 0.0675 | 0.0644 | 0.0632 | 0.0648 | 0.0641 |
| Residuals ($e^-$/Å$^3$) | +0.88<br>-1.47 | +0.86<br>-1.56 | +0.83<br>-1.54 | +0.73<br>-1.43 | +0.58<br>-1.33 | +0.60<br>-1.19 | +0.51<br>-1.23 |
| *T* (°C) | 25 | -50 | -100 | 25 | 685 | | |
| Experiment | SC-LT | SC-LT | SC-LT | SC-ND | SC-ND | | |
| Space group | *I*4/*m* | *I*4/*m* | *I*4/*m* | *I*4/*m* | *I*4/*m* | | |
| Unique peaks | 922 | 944 | 950 | 5129* | 1308 | | |
| Observed peaks $F_o^2/\sigma(F_o^2)>3$ | 909 | 907 | 912 | 1072 | 800 | | |
| $R_{int}$ (all) | 0.0329 | 0.0236 | 0.0241 | 0.0168 | 0.0893 | | |
| Refined param. | 61 | 61 | 61 | 69 | 65 | | |
| $R_1$ (obs) | 0.0498 | 0.0360 | 0.0370 | 0.0325 | 0.0567 | | |
| $R_1$ (all) | 0.0504 | 0.0381 | 0.0388 | 0.0394 | 0.1097 | | |
| w$R_1$ (obs) | 0.0689 | 0.0594 | 0.0596 | 0.0676 | 0.0957 | | |
| Residuals ($e^-$,fm/Å$^3$) | +0.91<br>-1.92 | +1.17<br>-1.67 | +1.10<br>-1.92 | +1.28<br>-1.55 | +0.68<br>-1.02 | | |

SC-HT: single-crystal XRD high-temperature experiment; SC-LT: single-crystal XRD low-temperature experiment; SC-ND: single-crystal neutron diffraction experiment. *Based on two independent sets of intensity data: the first one with a wavelength of the incident beam of 1.170(1) Å up to $2\theta_{max}$=130° ($\sin(\theta)/\lambda$ = 0.77 Å$^{-1}$) and the second one with a wavelength of the incident beam of 0.7925(5) Å up to $2\theta_{max}$=85° ($\sin(\theta)/\lambda$ = 0.85 Å$^{-1}$).

**Table S2.** Selected angles (°), distances (Å) and volumes (Å$^3$) from the refined structure models of scapolite at different temperatures.

| Experiment | *T* (°C) | <T1-O> | V(T1) | <T2-O> | V(T2) | O1-O1 | O3-O3 | M-O2 | M-O3 x2 | M-O4' x2 | M-O4'' x2 | <M-Of> |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SC-HT | 25 | 1.625(3) | 2.202(4) | 1.673(3) | 2.387(4) | 3.776(5) | 3.861(5) | 2.346(4) | 2.519(3) | 2.772(3) | 2.896(3) | 2.674(3) |
| SC-HT | 150 | 1.626(3) | 2.204(4) | 1.672(3) | 2.381(4) | 3.776(8) | 3.861(5) | 2.348(4) | 2.525(3) | 2.781(3) | 2.896(2) | 2.679(3) |
| SC-HT | 300 | 1.626(3) | 2.206(4) | 1.670(3) | 2.376(4) | 3.770(8) | 3.862(5) | 2.353(4) | 2.535(3) | 2.793(3) | 2.898(2) | 2.686(3) |
| SC-HT | 450 | 1.626(3) | 2.203(4) | 1.670(3) | 2.374(4) | 3.764(8) | 3.867(5) | 2.359(4) | 2.544(3) | 2.807(3) | 2.903(2) | 2.695(3) |
| SC-HT | 600 | 1.625(3) | 2.199(4) | 1.669(3) | 2.372(4) | 3.762(8) | 3.875(5) | 2.365(4) | 2.551(3) | 2.820(3) | 2.909(2) | 2.704(3) |
| SC-HT | 750 | 1.625(4) | 2.201(5) | 1.669(3) | 2.373(4) | 3.760(8) | 3.879(5) | 2.371(4) | 2.562(3) | 2.833(3) | 2.915(3) | 2.713(3) |
| SC-HT | 797 | 1.625(3) | 2.199(4) | 1.669(3) | 2.370(4) | 3.758(8) | 3.878(5) | 2.373(4) | 2.565(3) | 2.836(3) | 2.918(3) | 2.716(3) |
| SC-LT | 25 | 1.628(3) | 2.212(4) | 1.676(3) | 2.394(4) | 3.783(5) | 3.867(5) | 2.349(3) | 2.520(2) | 2.773(2) | 2.898(2) | 2.676(2) |
| SC-LT | -50 | 1.629(3) | 2.214(4) | 1.674(2) | 2.393(3) | 3.787(5) | 3.867(4) | 2.350(3) | 2.515(2) | 2.766(2) | 2.897(2) | 2.672(2) |
| SC-LT | -100 | 1.628(3) | 2.214(4) | 1.675(2) | 2.394(3) | 3.788(5) | 3.867(4) | 2.348(3) | 2.512(2) | 2.762(2) | 2.897(2) | 2.670(2) |
| ND | 25 | 1.628(1) | 2.213(1) | 1.672(1) | 2.386(1) | 3.780(1) | 3.862(1) | 2.353(1) | 2.518(1) | 2.773(1) | 2.898(1) | 2.676(1) |
| ND | 685 | 1.627(2) | 2.207(3) | 1.669(2) | 2.372(3) | 3.778(4) | 3.872(3) | 2.369(4) | 2.564(3) | 2.834(3) | 2.913(2) | 2.713(3) |

**Table S3.** Details pertaining to the structure refinements of scapolite, performed at different temperatures and pressures by in-situ single-crystal HTHP.

| ***T* (°C)** | **25** | **25** | **100** | **300** | **500** | **650** | **650** | **650** |
|---|---|---|---|---|---|---|---|---|
| ***P* (GPa)** | **0.0001** | **1.27(5)** | **1.92(5)** | **4.67(5)** | **6.35(5)** | **8.98(5)** | **9.41(5)** | **10.30(5)** |
| Experiment | SC-HTHP | SC-HTHP | SC-HTHP | SC-HTHP | SC-HTHP | SC-HTHP | SC-HTHP | SC-HTHP |
| Space group | *I*4/*m* | *I*4/*m* | *I*4/*m* | *I*4/*m* | *I*4/*m* | *I*4/*m* | *I*4/*m* | *I*4/*m* |
| Unique peaks | 466 | 462 | 452 | 436 | 370 | 418 | 418 | 344 |
| Observed peaks $F_o^2/\sigma(F_o^2)>3$ | 431 | 414 | 327 | 407 | 311 | 384 | 376 | 268 |
| $R_{int}$ (all) | 0.0212 | 0.0255 | 0.0673 | 0.0221 | 0.0242 | 0.0250 | 0.0270 | 0.0174 |
| Refined param. | 61 | 61 | 61 | 61 | 61 | 61 | 61 | 61 |
| $R_1$ (obs) | 0.0461 | 0.0433 | 0.0752 | 0.0669 | 0.0640 | 0.0733 | 0.0756 | 0.0806 |
| $R_1$ (all) | 0.0479 | 0.0467 | 0.0859 | 0.0692 | 0.0701 | 0.0772 | 0.0803 | 0.0916 |
| w$R_1$ (obs) | 0.0658 | 0.0596 | 0.0834 | 0.0947 | 0.0773 | 0.0890 | 0.0941 | 0.0972 |
| Residuals ($e^-$/Å$^3$) | +0.70<br>-1.34 | +0.63<br>-0.92 | +0.80<br>-0.72 | +0.72<br>-0.92 | +0.68<br>-0.75 | +1.05<br>-0.88 | +0.97<br>-0.64 | +0.62<br>-0.73 |

SC-HTHP: In situ single-crystal experiment at high-temperature and high-pressure with the resistive-heated diamond anvil cell

**Table S4.** Selected angles (°), distances (Å) and volumes (Å$^3$) from the refined structure models of scapolite at different temperatures and pressures from the in situ HTHP experiment.

| Ramp | *T* (°C) | *P* (GPa) | <T1-O> | V(T1) | <T2-O> | V(T2) | O1-O1 | O3-O3 | M-O2 | M-O3 x2 | M-O4' x2 | M-O4'' x2 | <M-Of> |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 25 | 0.0001 | 1.628(4) | 2.103(5) | 1.671(4) | 2.379(6) | 3.792(10) | 3.862(8) | 2.347(5) | 2.501(4) | 2.746(4) | 2.891(3) | 2.660(4) |
| 2 | 25 | 1.27 | 1.623(4) | 2.191(5) | 1.666(4) | 2.354(6) | 3.779(10) | 3.847(8) | 2.329(5) | 2.479(4) | 2.724(4) | 2.863(3) | 2.637(4) |
| 2 | 100 | 1.92 | 1.621(5) | 2.182(7) | 1.662(4) | 2.342(6) | 3.779(10) | 3.817(8) | 2.325(5) | 2.481(4) | 2.732(4) | 2.845(4) | 2.634(4) |
| 2 | 300 | 4.67 | 1.610(7) | 2.141(9) | 1.657(5) | 2.317(7) | 3.75(2) | 3.796(12) | 2.296(7) | 2.432(5) | 2.693(5) | 2.798(4) | 2.592(5) |
| 2 | 500 | 6.35 | 1.609(7) | 2.136(9) | 1.655(6) | 2.308(8) | 3.74(2) | 3.833(12) | 2.302(8) | 2.418(6) | 2.707(6) | 2.788(5) | 2.590(6) |
| 2 | 650 | 8.48 | 1.595(9) | 2.081(12) | 1.643(6) | 2.261(8) | 3.70(2) | 3.783(12) | 2.297(9) | 2.406(8) | 2.689(8) | 2.772(9) | 2.576(8) |
| 2 | 650 | 9.41 | 1.590(10) | 2.060(13) | 1.641(7) | 2.250(8) | 3.70(2) | 3.781(12) | 2.304(10) | 2.394(9) | 2.698(8) | 2.751(11) | 2.570(9) |
| 2 | 650 | 10.30 | 1.60(2) | 2.08(2) | 1.640(11) | 2.25(2) | 3.71(3) | 3.79(2) | 2.287(14) | 2.40(2) | 2.683(13) | 2.73(2) | 2.56(2) |

**Table S5.** Reflection conditions for the space group *I*4/*m* and number of violating reflections.

| **Reflection conditions** | ***T* (°C)** | **Total number of reflections** | **Violating reflections with *I*/sig(*I*) ≥ 3** | **Violating reflections with *I*/sig(*I*) ≥ 6** |
|---|---|---|---|---|
| *hkl*: *h*+*k*+*l* = 2*n* | 25 °C | 5860 | 9 | 0 |
| | -25 °C | 5837 | 12 | 0 |
| | -50 °C | 5841 | 45 | 7 |
| | -75 °C | 5869 | 32 | 7 |
| | -100 °C | 5861 | 34 | 5 |
| *hk*0: *h* + *k* = 2*n* | 25 °C | 494 | 6 | 0 |
| | -25 °C | 493 | 11 | 0 |
| | -50 °C | 498 | 13 | 2 |
| | -75 °C | 494 | 10 | 1 |
| | -100 °C | 494 | 7 | 2 |
| 0*kl*: *k* + *l* = 2*n* | 25 °C | 254 | 1 | 0 |
| | -25 °C | 253 | 0 | 0 |
| | -50 °C | 251 | 3 | 1 |
| | -75 °C | 255 | 1 | 0 |
| | -100 °C | 257 | 1 | 1 |
| *hhl*: *l* = 2*n* | 25 °C | 200 | 0 | 0 |
| | -25 °C | 198 | 0 | 0 |
| | -50 °C | 197 | 0 | 0 |
| | -75 °C | 200 | 1 | 0 |

| | | | | |
|---|---|---|---|---|
| | -100 °C | 200 | 2 | 0 |
| 00*l*: *l* = 2*n* | 25 °C | 24 | 3 | 0 |
| | -25 °C | 24 | 3 | 0 |
| | -50 °C | 25 | 1 | 0 |
| | -75 °C | 25 | 1 | 0 |
| | -100 °C | 25 | 2 | 0 |
| *h*00: *h* = 2*n* | 25 °C | 51 | 2 | 0 |
| | -25 °C | 51 | 3 | 0 |
| | -50 °C | 51 | 1 | 0 |
| | -75 °C | 50 | 2 | 0 |
| | -100 °C | 53 | 2 | 0 |

Reflection conditions for s.g. $P4_2/n$ – *hk*0: *h* + *k* = 2*n*; 00*l*: *l* = 2*n*; *h*00: *h* = 2*n*

**Table S6.** Refined atomic site coordinates and isotropic/equivalent displacement parameters (Å$^2$) from selected structure refinements.

| ***I*4/*m* scapolite – L*T* experiment at 25 °C** | | | | | |
|---|---|---|---|---|---|
| **Site** | ***s.o.f.*** | ***x*** | ***y*** | ***z*** | $U_{iso/eq}$ |
| Ca | 0.465 | 0.3603(1) | 0.28512(9) | 0 | 0.0260(4) |
| K | 0.0576 | " | " | " | " |
| Na | 0.465 | " | " | " | " |
| T1 | 1 | 0.16127(7) | 0.09042(7) | 0 | 0.0043(2) |
| T2 | 1 | 0.16112(5) | 0.41428(5) | 0.20688(9) | 0.0069(2) |
| O1 | 1 | 0.0420(2) | 0.1500(2) | 0 | 0.0123(7) |
| O2 | 1 | 0.1900(2) | 0.3769(2) | 0 | 0.0137(7) |
| O3 | 1 | 0.1506(2) | 0.5517(2) | 0.2103(3) | 0.0163(6) |
| O4 | 1 | 0.2310(2) | 0.1311(2) | 0.1733(2) | 0.0157(5) |
| Cl | 0.48 | 0.5 | 0.5 | 0 | 0.053(2) |
| C | 0.12 | 0.534(4) | 0.491(5) | 0 | " |
| Oc1 | 0.12 | 0.448(3) | 0.563(4) | 0 | " |
| Oc2 | 0.12 | 0.390(5) | 0.489(6) | 0 | " |
| Oc3 | 0.12 | 0.481(5) | 0.618(6) | 0 | " |
| ***I*4/*m* scapolite – L*T* experiment at -100 °C** | | | | | |
| **Site** | ***s.o.f.*** | ***x*** | ***y*** | ***z*** | $U_{iso/eq}$ |
| Ca | 0.465 | 0.36047(8) | 0.28468(8) | 0 | 0.0228(3) |

| | | | | | |
|---|---|---|---|---|---|
| K | 0.0576 | “ | “ | “ | “ |
| Na | 0.465 | “ | “ | “ | “ |
| T1 | 1 | 0.16121(6) | 0.09109(6) | 0 | 0.0047(2) |
| T2 | 1 | 0.16109(5) | 0.41382(5) | 0.20673(8) | 0.0072(2) |
| O1 | 1 | 0.0420(2) | 0.1504(2) | 0 | 0.0106(6) |
| O2 | 1 | 0.1898(2) | 0.3760(2) | 0 | 0.0123(6) |
| O3 | 1 | 0.1509(1) | 0.5515(1) | 0.2101(2) | 0.0144(5) |
| O4 | 1 | 0.2311(1) | 0.1318(1) | 0.1733(2) | 0.0147(5) |
| Cl | 0.48 | 0.5 | 0.5 | 0 | 0.046(2) |
| C | 0.12 | 0.538(4) | 0.492(4) | 0 | “ |
| Oc1 | 0.12 | 0.444(3) | 0.545(3) | 0 | “ |
| Oc2 | 0.12 | 0.394(5) | 0.486(5) | 0 | “ |
| Oc3 | 0.12 | 0.480(5) | 0.614(5) | 0 | “ |

**_I_4/_m_ scapolite – H_T_ experiment at 797 °C**

| **Site** | ***s.o.f.*** | ***x*** | ***y*** | ***z*** | $U_{iso/eq}$ |
|---|---|---|---|---|---|
| Ca | 0.465 | 0.3602(1) | 0.2869(1) | 0 | 0.0651(7) |
| K | 0.0576 | “ | “ | “ | “ |
| Na | 0.465 | “ | “ | “ | “ |
| T1 | 1 | 0.16137(8) | 0.08638(8) | 0 | 0.0179(3) |
| T2 | 1 | 0.16127(6) | 0.41793(6) | 0.2074(1) | 0.0217(2) |
| O1 | 1 | 0.0439(2) | 0.1473(3) | 0 | 0.039(1) |

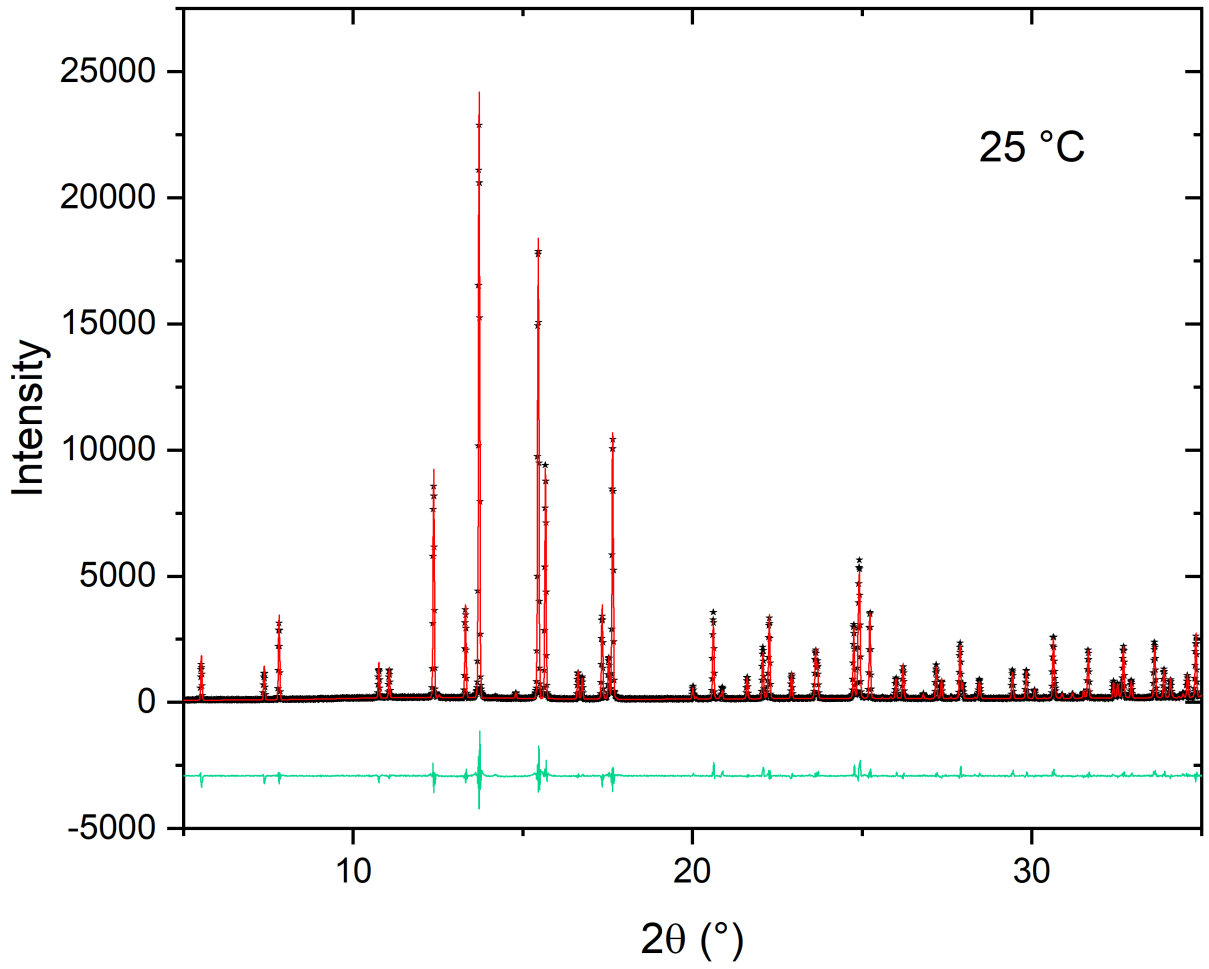
| | | | | | |
|---|---|---|---|---|---|
| O2 | 1 | 0.1917(3) | 0.3833(3) | 0 | 0.036(1) |
| O3 | 1 | 0.1494(2) | 0.5533(2) | 0.2144(4) | 0.0437(9) |
| O4 | 1 | 0.2317(2) | 0.1262(2) | 0.1730(3) | 0.0374(7) |
| Cl | 0.48 | 0.5 | 0 | 0 | 0.122(3) |
| C | 0.12 | 0.518(3) | 0.499(5) | 0 | “ |
| Oc1 | 0.12 | 0.442(7) | 0.576(11) | 0 | “ |
| Oc2 | 0.12 | 0.395(7) | 0.508(9) | 0 | “ |
| Oc3 | 0.12 | 0.474(5) | 0.621(4) | 0 | “ |

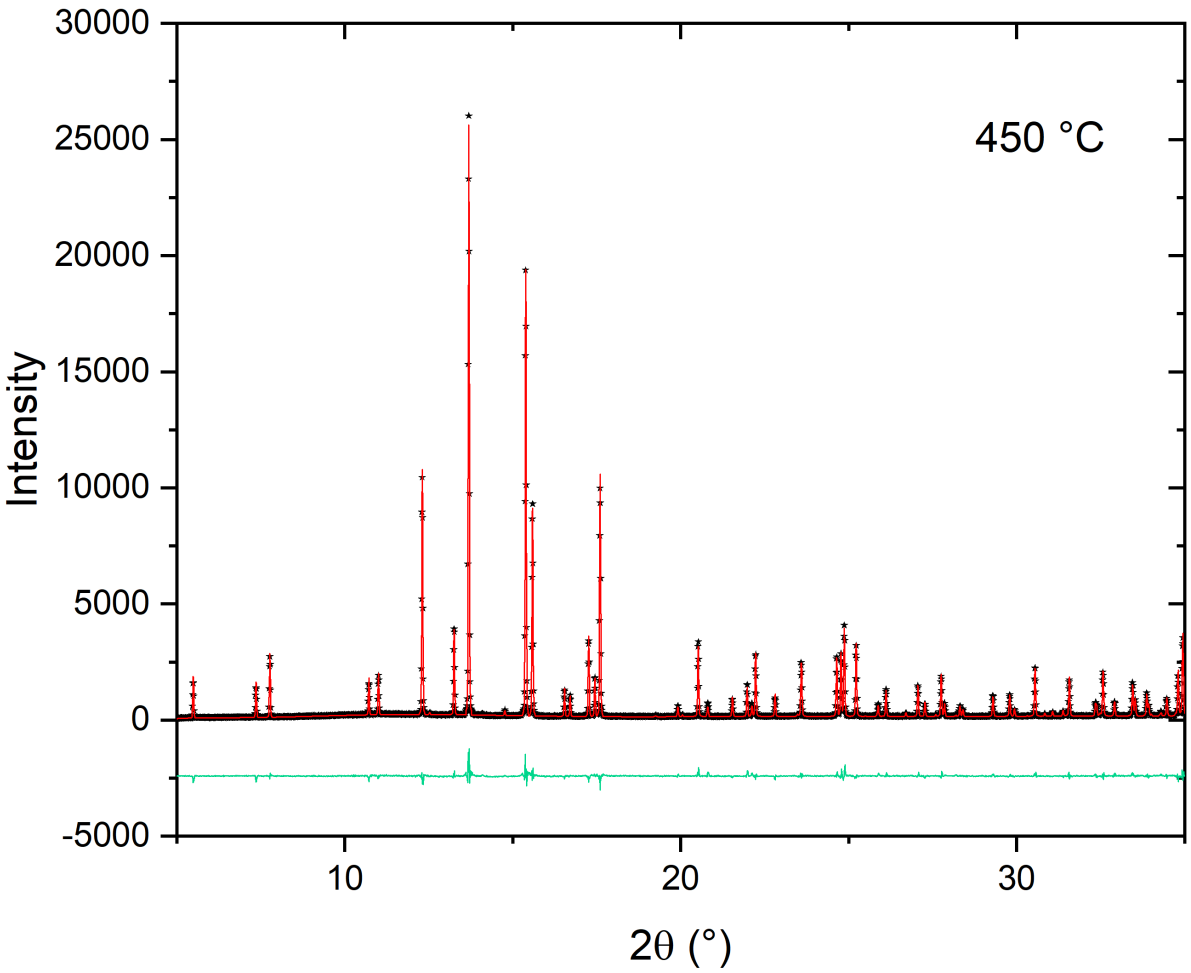
***I*4/*m* scapolite – H*T*H*P* experiment at 650 °C and 10.30 GPa**

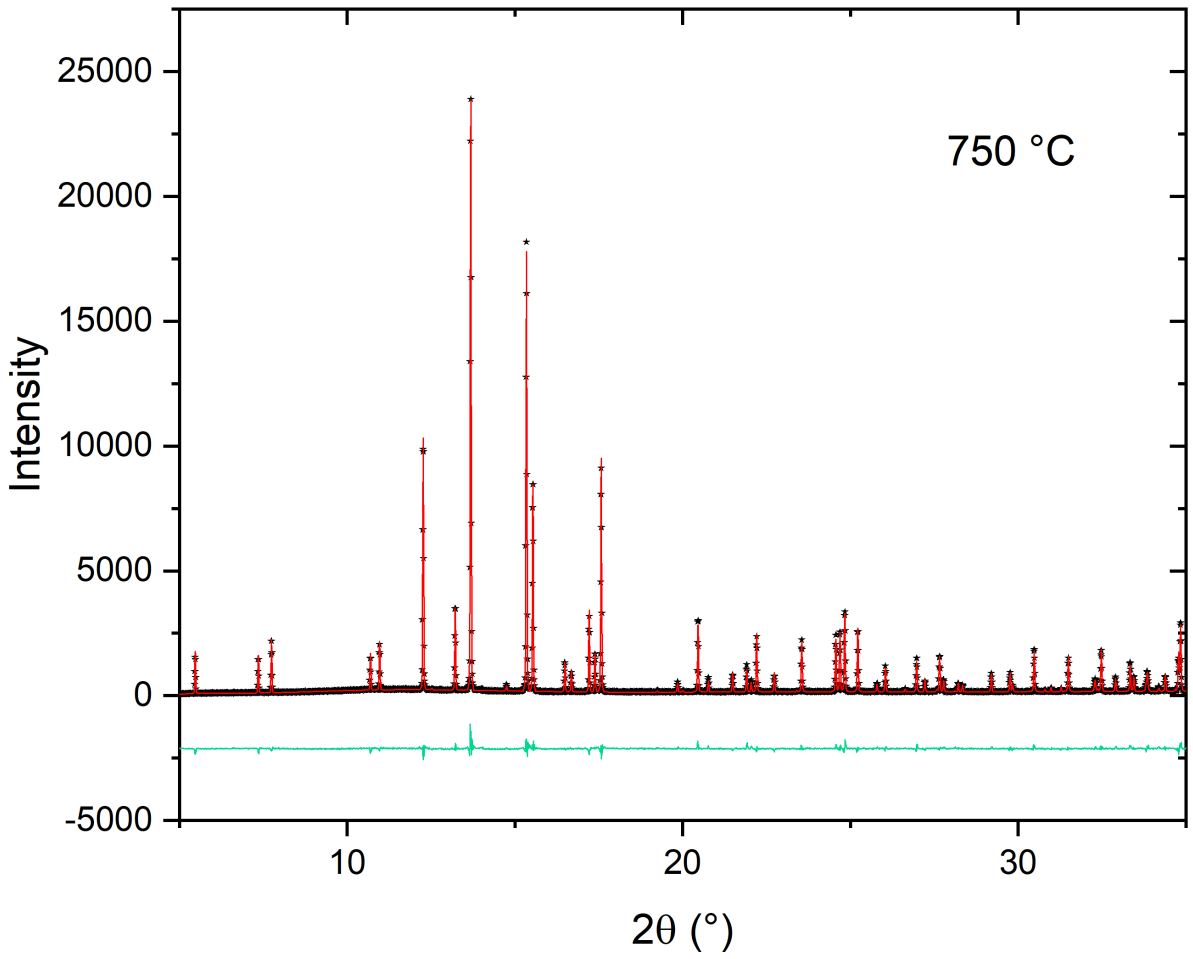
| **Site** | ***s.o.f.*** | ***x*** | ***y*** | ***z*** | $U_{iso/eq}$ |
|---|---|---|---|---|---|
| Ca | 0.465 | 0.3665(4) | 0.2897(3) | 0 | 0.052(4) |
| K | 0.0576 | “ | “ | “ | “ |
| Na | 0.465 | “ | “ | “ | “ |
| T1 | 1 | 0.1587(3) | 0.0984(3) | 0 | 0.023(2) |
| T2 | 1 | 0.1605(2) | 0.4079(2) | 0.2075(8) | 0.029(2) |
| O1 | 1 | 0.0368(8) | 0.154(1) | 0 | 0.067(11) |
| O2 | 1 | 0.186(1) | 0.363(1) | 0 | 0.041(8) |
| O3 | 1 | 0.1541(8) | 0.5487(7) | 0.205(3) | 0.046(7) |
| O4 | 1 | 0.2295(7) | 0.1425(7) | 0.176(3) | 0.055(7) |
| Cl | 0.48 | 0.5 | 0.5 | 0 | 0.056(6) |
| C | 0.12 | 0.543(7) | 0.503(8) | 0 | “ |

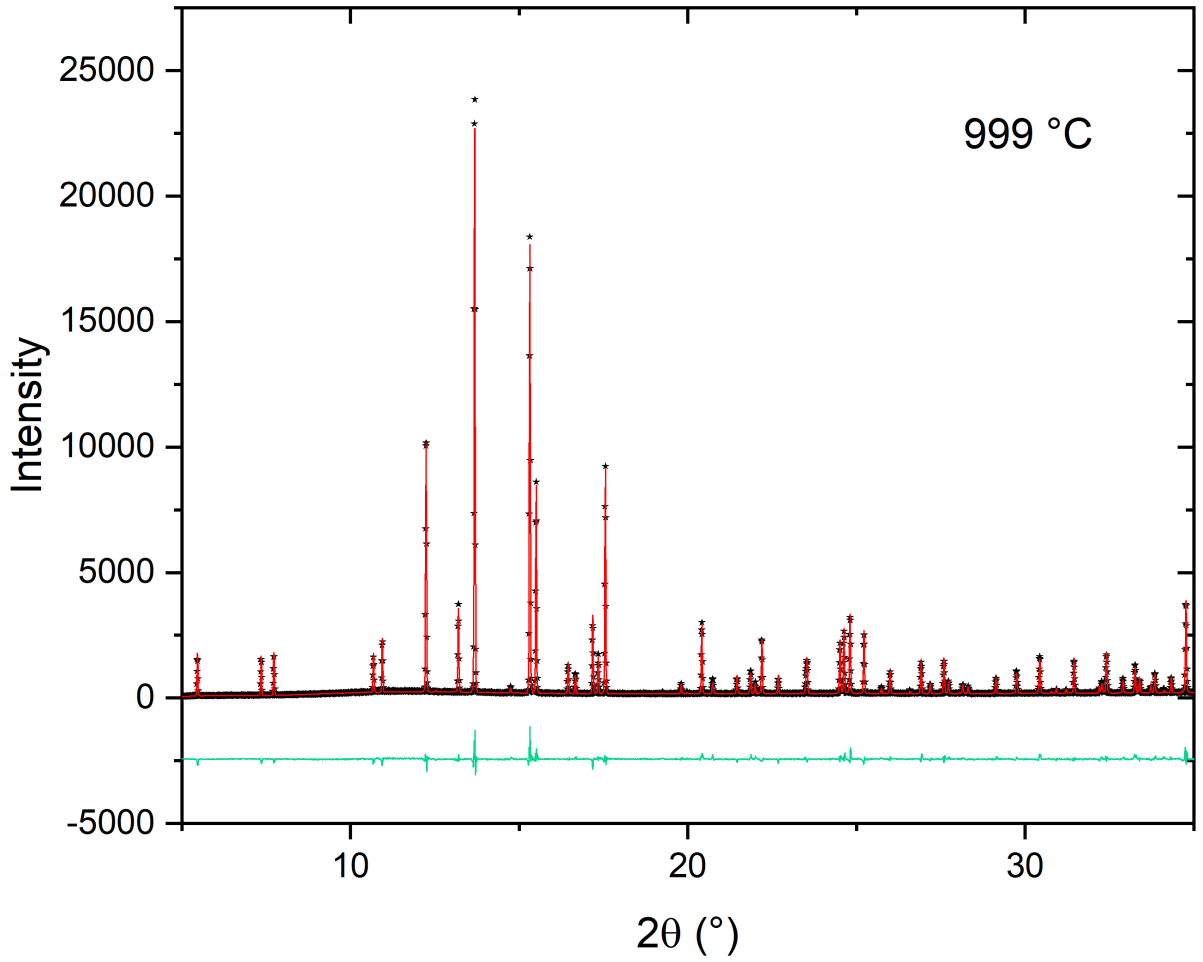
| | | | | | |
|---|---|---|---|---|---|
| Oc1 | 0.12 | 0.471(7) | 0.587(11) | 0 | “ |
| Oc2 | 0.12 | 0.397(10) | 0.492(11) | 0 | “ |
| Oc3 | 0.12 | 0.476(7) | 0.652(7) | 0 | “ |

**Figures S1-S4.** Selected X-ray powder diffraction patterns and calculated peak profiles in the range 5-35° (2θ) from Rietveld refinements from the datasets collected at 25, 450, 750 and 999 °C.




450 °C
Intensity
30000
25000
20000
15000
10000
5000
0
-5000
10
20
30
2θ (°)


750 °C
Intensity
25000
20000
15000
10000
5000
0
-5000
10
20
30
2θ (°)


999 °C
Intensity
25000
20000
15000
10000
5000
0
-5000
10
20
30
2θ (°)