

Supplementary Materials

The formation of cavansite and pentagonite in the Wagholi quarries, Pune, India

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In the supplementary materials, the XRD and Raman data are shown of the samples in **Table 1**:

A 1; A 3; D1; Mu 02; Mu 03; Mu 04; Mu 05; Mu 06; Mu 11; Mu 14; Mu 15; Mu 16; Mu 17; and USA 1.

In order to recognize a possible structural difference between the first and second generation of pentagonite crystals, XRD patterns and EDX results for both generations were performed on samples A 1 and A 3.

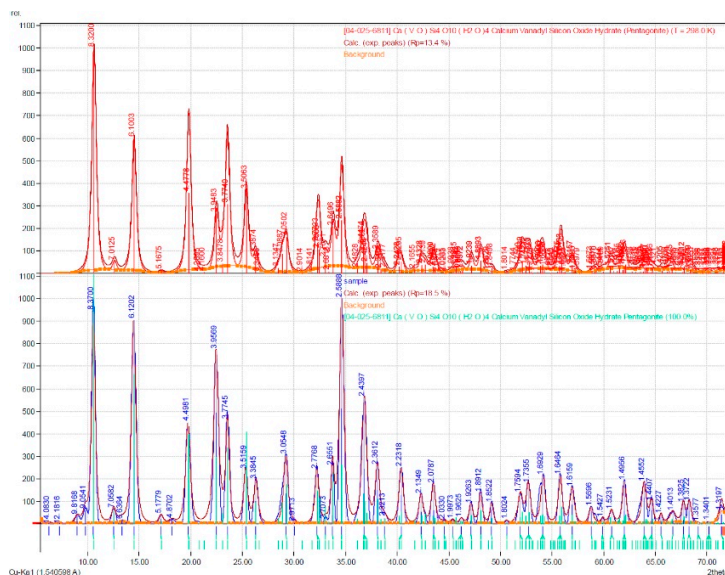


Figure S1. XRD pattern of sample A 1 pentagonite of the first generation. Upper field: red line – calculated data, orange line – background, red bars – XRD peak positions from the data base; lower field: blue line – sample, red line – calculated data (ICDD), orange line – background, and green bars – positions from the data base. The results are in good agreement with the reported data RRUFF ID: R120136.9 pentagonite from Wagholi, India. Additional 2theta subordinate peaks are probably due to contamination of the sample by adhering mordenite fibers.

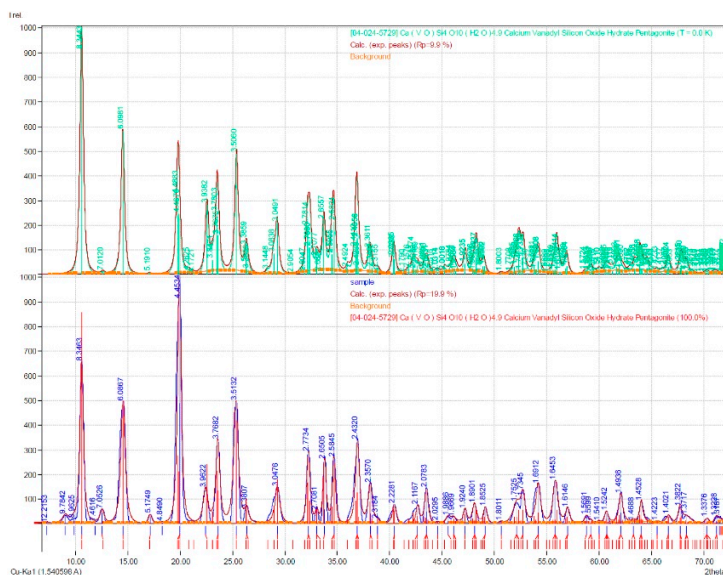


Figure S2. XRD pattern of sample A 1 pentagonite of the second generation. Upper field: red line – calculated data, orange line – background, green bars – XRD peak positions from the data base; lower field: blue line – sample, red line – calculated data (ICDD), orange line – background, and green bars – XRD peak positions from the data base. The results are in good agreement with the reported data RRUFF ID: R120136.9 pentagonite from Wagholi, India. Additional 2theta subordinate peaks are probably due to contamination of the sample by adhering mordenite fibers.

| | | | | | | |
|--|-----------|------------|-------------|--------|--------|--------|
| EDAX PhiZAF Quantification (Standardless) | | | | | | |
| Element Normalized | | | | | | |
| SEC Table : User c:\edax32\eds\genuser.sec | | | | | | |
| Element | Wt % | At % | K-Ratio | Z | A | F |
| SiK | 57.97 | 69.00 | 0.4873 | 1.0395 | 0.8063 | 1.0030 |
| CaK | 19.26 | 16.06 | 0.1712 | 0.9993 | 0.8760 | 1.0156 |
| V K | 22.77 | 14.94 | 0.1845 | 0.8888 | 0.9117 | 1.0000 |
| Total | 100.00 | 100.00 | | | | |
| Element | Net Inte. | Bkqd Inte. | Inte. Error | P/B | | |
| SiK | 1751.62 | 36.81 | 0.42 | 47.59 | | |
| CaK | 384.29 | 21.07 | 0.92 | 18.24 | | |
| V K | 293.05 | 13.55 | 1.04 | 21.63 | | |

| | | | | | | |
|--|-----------|------------|-------------|--------|--------|--------|
| EDAX PhiZAF Quantification (Standardless) | | | | | | |
| Element Normalized | | | | | | |
| SEC Table : User c:\edax32\eds\genuser.sec | | | | | | |
| Element | Wt % | At % | K-Ratio | Z | A | F |
| AlK | 1.07 | 1.32 | 0.0078 | 1.0124 | 0.7018 | 1.0269 |
| SiK | 58.02 | 68.61 | 0.4832 | 1.0381 | 0.7999 | 1.0029 |
| CaK | 19.22 | 15.93 | 0.1703 | 0.9979 | 0.8748 | 1.0148 |
| V K | 21.68 | 14.14 | 0.1754 | 0.8876 | 0.9111 | 1.0000 |
| Total | 100.00 | 100.00 | | | | |
| Element | Net Inte. | Bkqd Inte. | Inte. Error | P/B | | |
| AlK | 30.19 | 36.57 | 5.15 | 0.83 | | |
| SiK | 1738.19 | 38.99 | 0.38 | 44.59 | | |
| CaK | 382.59 | 22.25 | 0.83 | 17.20 | | |
| V K | 278.74 | 15.61 | 0.97 | 17.85 | | |

Figure S3. EDX results (shown without O) of sample Pen A 1 pentagonite (first generation), two different measurement points 1 and 2. Point 2 – probably contaminated by mordenite.

| Element | Wt % | At % | K-Ratio | Z | A | F |
|---------|--------|--------|---------|--------|--------|--------|
| SiK | 57.03 | 68.29 | 0.4751 | 1.0411 | 0.7978 | 1.0030 |
| CaK | 19.12 | 16.04 | 0.1704 | 1.0008 | 0.8766 | 1.0161 |
| V K | 23.24 | 15.34 | 0.1888 | 0.8903 | 0.9122 | 1.0003 |
| CuK | 0.61 | 0.33 | 0.0052 | 0.8683 | 0.9720 | 1.0000 |
| Total | 100.00 | 100.00 | | | | |

| Element | Net Inte. | Bkqd Inte. | Inte. Error | P/B |
|---------|-----------|------------|-------------|-------|
| SiK | 1791.05 | 33.89 | 0.51 | 52.85 |
| CaK | 401.41 | 22.30 | 1.10 | 18.00 |
| V K | 314.54 | 15.25 | 1.24 | 20.63 |
| CuK | 3.31 | 7.05 | 26.50 | 0.47 |

| Element | Wt % | At % | K-Ratio | Z | A | F |
|---------|--------|--------|---------|--------|--------|--------|
| SiK | 56.87 | 68.58 | 0.4610 | 1.0423 | 0.7757 | 1.0027 |
| CaK | 18.36 | 15.52 | 0.1631 | 1.0021 | 0.8735 | 1.0145 |
| V K | 20.45 | 13.59 | 0.1667 | 0.8914 | 0.9127 | 1.0019 |
| CuK | 4.32 | 2.30 | 0.0366 | 0.8697 | 0.9744 | 1.0000 |
| Total | 100.00 | 100.00 | | | | |

| Element | Net Inte. | Bkqd Inte. | Inte. Error | P/B |
|---------|-----------|------------|-------------|-------|
| SiK | 1514.06 | 45.22 | 0.42 | 33.48 |
| CaK | 334.54 | 20.01 | 0.93 | 16.72 |
| V K | 241.92 | 12.44 | 1.08 | 19.45 |
| CuK | 20.31 | 6.87 | 4.60 | 2.96 |

Figure S4. EDX results (shown without O) of sample Pen A 1 pentagonite (second generation), two different measurement points 1 and 2. Remarkable content of Cu.

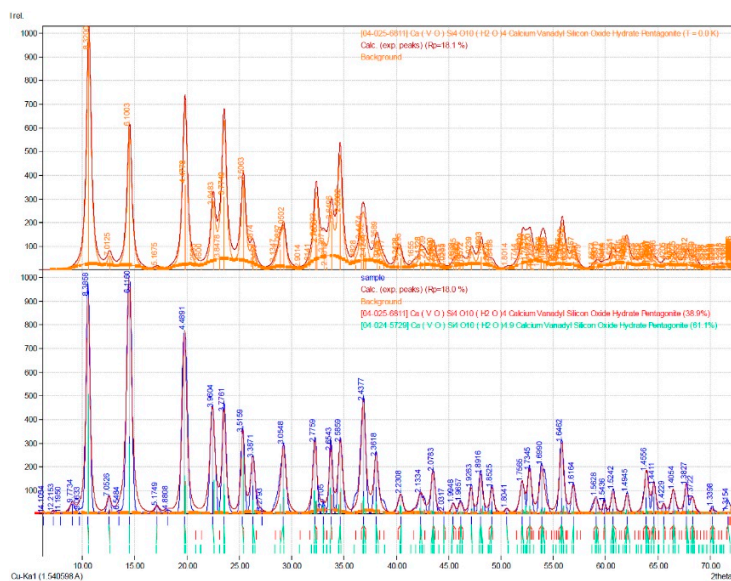


Figure S5. XRD pattern of sample A 3 pentagonite of the first generation. Basic declarations apply analogously to the sample A 1. The 2theta data of the sample correspond to the reference data. No significant differences were found for the peaks of vertical bar lines between the first and second generation of the sample pentagonite A 1 (Figures S1 and S2). Additional 2theta subordinate peaks are probably due to contamination of the sample by adhering mordenite fibers.

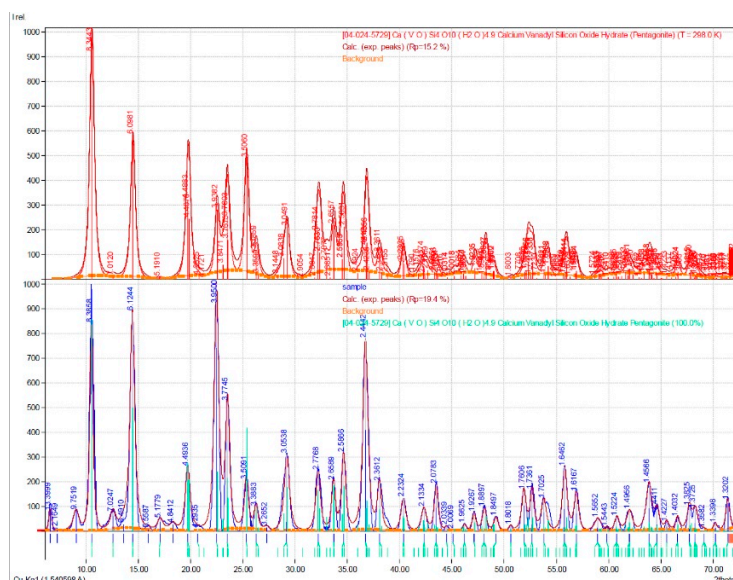


Figure S6. XRD pattern of sample A 3 pentagonite of the second generation. Basic declarations apply analogously to the sample A 1. The 2theta data of the sample correspond to the reference data. No significant differences were found for the peaks of vertical bar lines between the first and second generation of the sample pentagonite A 1 (Figures S1 and S2). Additional 2theta subordinate peaks are probably due to contamination of the sample by adhering mordenite fibers.

| EDAX PhiZAF Quantification (Standardless) | | | | | | | Pen A3 A |
|--|-----------|------------|-------------|--------|--------|--------|----------|
| Element Normalized | | | | | | | |
| SEC Table : User c:\edax32\eds\genuser.sec | | | | | | | |
| Element | Wt % | At % | K-Ratio | Z | A | F | |
| SiK | 54.21 | 66.55 | 0.4280 | 1.0466 | 0.7524 | 1.0027 | |
| CaK | 18.21 | 15.67 | 0.1629 | 1.0063 | 0.8756 | 1.0153 | |
| V K | 21.05 | 14.24 | 0.1727 | 0.8953 | 0.9141 | 1.0028 | |
| CuK | 6.53 | 3.54 | 0.0556 | 0.8738 | 0.9742 | 1.0000 | |
| Total | 100.00 | 100.00 | | | | | |
| Element | Net Inte. | Bkqd Inte. | Inte. Error | | | P/B | |
| SiK | 1042.79 | 30.84 | 0.64 | | | 33.81 | |
| CaK | 248.02 | 17.10 | 1.35 | | | 14.50 | |
| V K | 186.02 | 10.47 | 1.55 | | | 17.77 | |
| CuK | 22.89 | 3.84 | 4.83 | | | 5.97 | |

| EDAX PhiZAF Quantification (Standardless) | | | | | | | Pen A3 B |
|--|-----------|------------|-------------|--------|--------|--------|----------|
| Element Normalized | | | | | | | |
| SEC Table : User c:\edax32\eds\genuser.sec | | | | | | | |
| Element | Wt % | At % | K-Ratio | Z | A | F | |
| SiK | 58.53 | 69.56 | 0.4909 | 1.0392 | 0.8048 | 1.0029 | |
| CaK | 18.76 | 15.62 | 0.1664 | 0.9990 | 0.8745 | 1.0153 | |
| V K | 22.14 | 14.51 | 0.1795 | 0.8886 | 0.9122 | 1.0002 | |
| CuK | 0.57 | 0.30 | 0.0048 | 0.8666 | 0.9729 | 1.0000 | |
| Total | 100.00 | 100.00 | | | | | |
| Element | Net Inte. | Bkqd Inte. | Inte. Error | | | P/B | |
| SiK | 1495.24 | 43.49 | 0.46 | | | 34.38 | |
| CaK | 316.51 | 19.65 | 1.02 | | | 16.11 | |
| V K | 241.65 | 13.26 | 1.16 | | | 18.22 | |
| CuK | 2.48 | 6.41 | 27.09 | | | 0.39 | |

Figure S7. EDX results (shown without O) of sample Pen A 3 pentagonite (A first generation, B second generation). Remarkable content of Cu.

| EDAX PhiZAF Quantification (Standardless) | | | | | | | Pen D1 A |
|--|-----------|------------|-------------|--------|--------|--------|----------|
| Element Normalized | | | | | | | |
| SEC Table : User c:\edax32\eds\genuser.sec | | | | | | | |
| Element | Wt % | At % | K-Ratio | Z | A | F | |
| SiK | 59.10 | 70.04 | 0.4951 | 1.0384 | 0.8044 | 1.0028 | |
| CaK | 18.72 | 15.54 | 0.1652 | 0.9982 | 0.8715 | 1.0148 | |
| V K | 21.58 | 14.10 | 0.1744 | 0.8879 | 0.9103 | 1.0003 | |
| CuK | 0.60 | 0.31 | 0.0051 | 0.8658 | 0.9728 | 1.0000 | |
| Total | 100.00 | 100.00 | | | | | |
| Element | Net Inte. | Bkqd Inte. | Inte. Error | | | P/B | |
| SiK | 1704.14 | 43.18 | 0.57 | | | 39.46 | |
| CaK | 355.93 | 18.95 | 1.27 | | | 18.78 | |
| V K | 265.99 | 12.58 | 1.46 | | | 21.14 | |
| CuK | 2.95 | 4.97 | 27.68 | | | 0.59 | |

Figure S8. EDX results (shown without O) of sample Pen D 1 pentagonite (first generation). Remarkable content of Cu.

| Mu 02 A | | | | | | | | |
|---------|-------------|-------|-------|--------|--------|--------------------|--------------------|--------------------|
| Element | | Net | Wt % | Norm % | At % | Error (1 sigma) | Error (2 sigma) | Error (3 sigma) |
| O | 8 K-Series | 77852 | 52,26 | 64,52 | 76,57 | 6,00 | 12,00 | 18,0 |
| Si | 14 K-Series | 77225 | 19,67 | 24,29 | 16,42 | 0,85 | 1,69 | 2,5 |
| Al | 13 K-Series | 21621 | 4,66 | 5,75 | 4,04 | 0,25 | 0,49 | 0,7 |
| Ca | 20 K-Series | 5014 | 3,44 | 4,24 | 2,01 | 0,14 | 0,28 | 0,4 |
| Na | 11 K-Series | 2964 | 0,89 | 1,10 | 0,91 | 0,09 | 0,17 | 0,3 |
| K | 19 K-Series | 159 | 0,09 | 0,11 | 0,05 | 0,03 | 0,07 | 0,1 |
| | Sum | 81,00 | | 100,00 | 100,00 | | | |
| Mu 02 B | | | | | | | | |
| Element | | Net | Wt % | Norm % | At % | Error (1 sigma) | Error (2 sigma) | Error (3 sigma) |
| O | 8 K-Series | 78860 | 51,69 | 65,19 | 77,08 | 5,93 | 11,86 | 17,8 |
| Si | 14 K-Series | 75039 | 18,95 | 23,90 | 16,10 | 0,82 | 1,63 | 2,5 |
| Al | 13 K-Series | 21446 | 4,64 | 5,85 | 4,10 | 0,24 | 0,49 | 0,7 |
| Ca | 20 K-Series | 4553 | 3,24 | 4,08 | 1,93 | 0,14 | 0,27 | 0,4 |
| Na | 11 K-Series | 2743 | 0,75 | 0,95 | 0,78 | 0,08 | 0,15 | 0,3 |
| K | 19 K-Series | 49 | 0,03 | 0,03 | 0,02 | 0,00 | 0,01 | 0,0 |
| | Sum | 79,28 | | 100,00 | 100,00 | | | |

Figure S9. EDX results of heulandite, sample Mu 02, two different measurement points A and B. The contents of the cations Ca, Na, and K indicate heulandite-Ca.

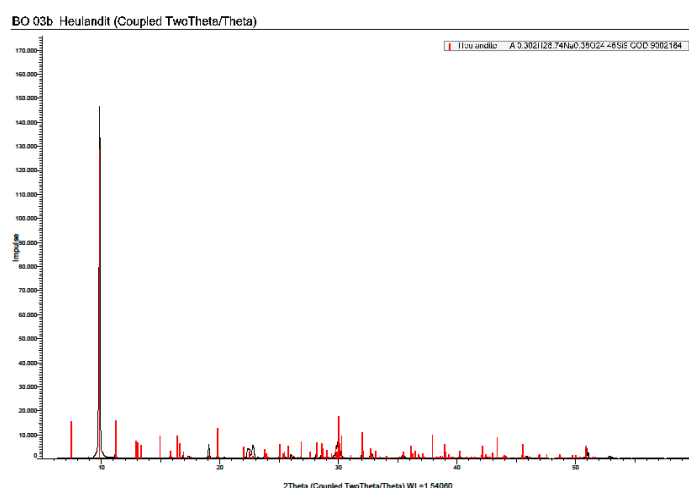


Figure S10. XRD pattern of sample Mu 03 heulandite. The pattern match those of the reference data base for heulandite-Ca and are good agreement with the reported data RRUFF ID: R050017.1 sample from Poona (Pune), India.

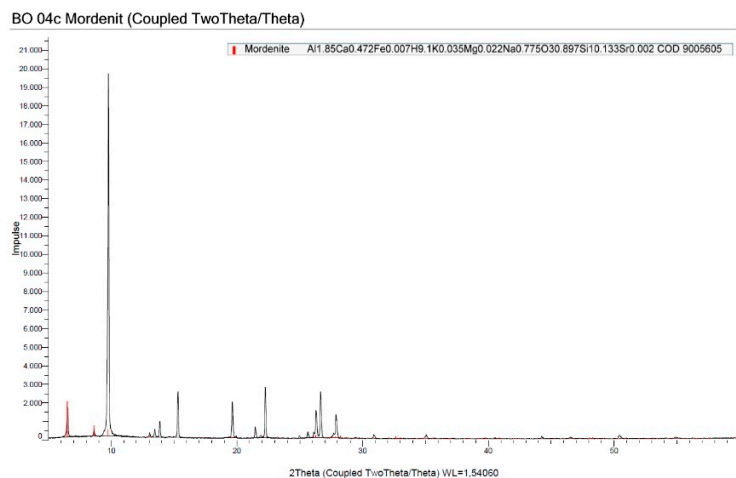


Figure S11. XRD pattern of sample Mu 04 mordenite. The pattern of the sample corresponds with the reference data base for mordenite and are good agreement with the reported data RRUFF ID: R061118.1.

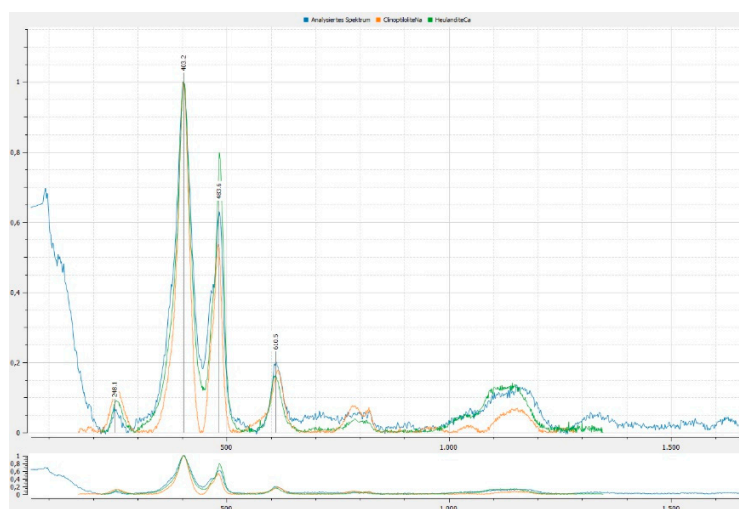


Figure S12. Raman spectrum of sample Mu 04 heulandite. The green lines apply to the reference data for heulandite, the red data for clinoptilolite, and the blue lines for the measured sample. There is a significantly higher agreement between the calculated data for heulandite and the samples. These allow the conclusion to be drawn for heulandite-Ca and they are in good agreement with the reported data RRUFF ID: R050017.3. sample from Poona (Pune). The EDX values also point to heulandite-Ca.

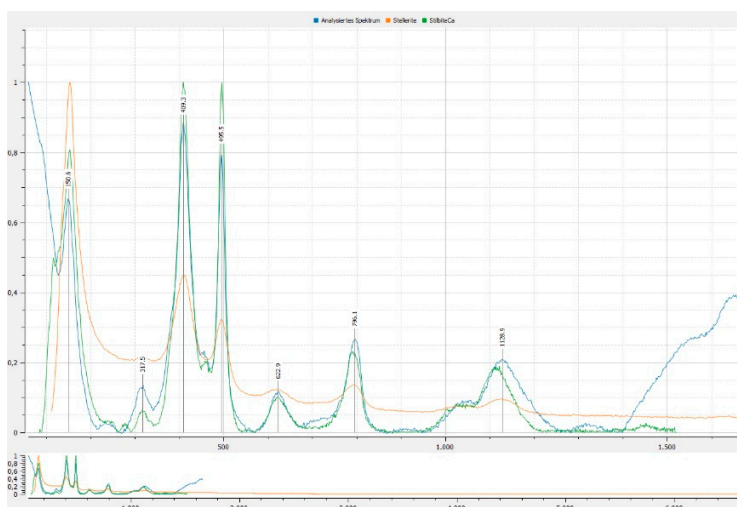


Figure S13. Raman spectrum of sample Mu 04 stilbite. Green lines are for the reference data of stilbite-Ca, red for stellerite, and the blue for the measured sample. There is a significantly higher agreement between the calculated data for stilbite-Ca and the samples. From this, the conclusion for stilbite-Ca can be drawn, which is in agreement with the result of the EDX analysis.

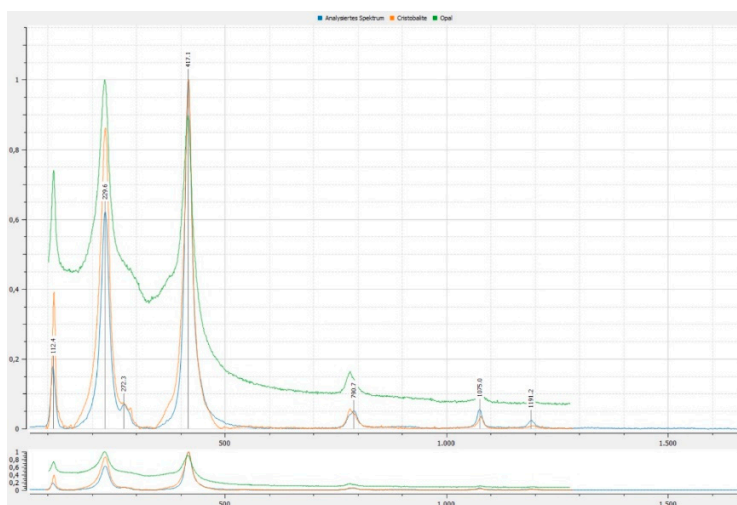


Figure S14. Raman spectrum of sample Mu 05 cristobalite. The red line shows the reference data for cristobalite, and green those for opal. The blue line corresponds to the data of the sample and shows an agreement with cristobalite. Raman spectrum for cristobalite sample Mu 05 shows also an agreement with the cristobalite spectrum from the Ellora caves, India (Ruff ID: R061064).

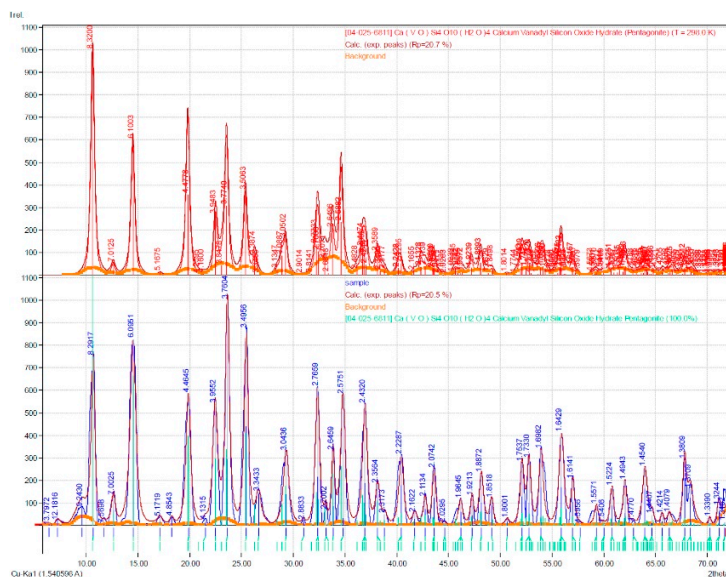


Figure S15. XRD pattern of sample Mu 05 pentagonite. XRD data show a basic agreement with the data from samples A1 and A1. This is all the more remarkable as the pentagonite examined was largely overgrown by mordenite and was not changed structurally.

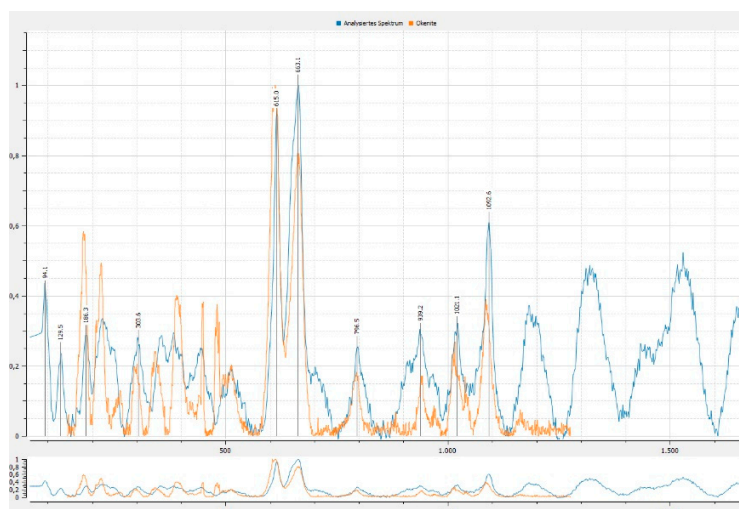


Figure S16. Raman spectrum of sample Mu 05 okenite. Further white fibrous objects were visible on the surface of a spherical mordenite formation, indicating a possibly different mineral. The orange line represents the reference data for okenite, and the blue line for the measured data of the sample. The Raman spectrum for okenite sample Mu 05 shows an agreement with the okenite spectrum from the Poona (Pune), India (Ruff ID: R070602). The suggested result “okenite” for the sample is reasonable, as okenite and mordenite below it are chemically and mineralogically closely related.

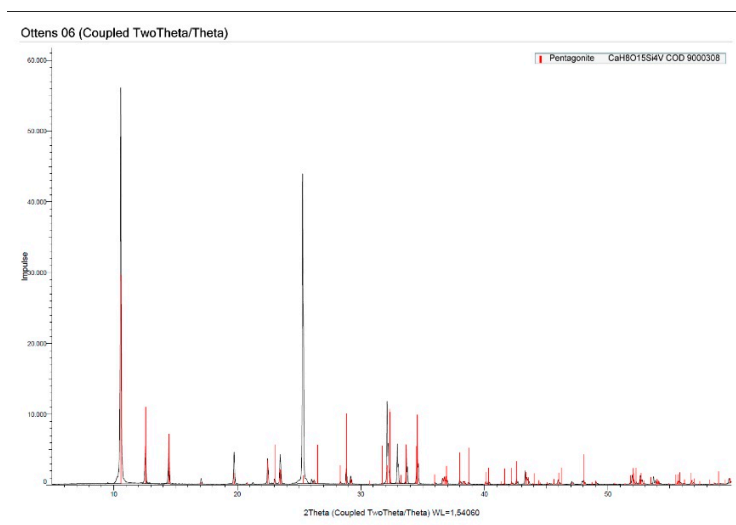


Figure S17. XRD pattern of sample Mu 06 pentagonite. The pattern match those of the reference data base for pentagonite and are good agreement with the reported data RRUFF ID: R120136.9 sample from Wagholi, India.

| Mu 11 A | | | | | | Error | Error | Error |
|---------|-------------|--------|-------|--------|--------|-----------|-----------|-----------|
| Element | | Net | Wt % | Norm % | At % | (1 sigma) | (2 sigma) | (3 sigma) |
| O | 8 K-Series | 27489 | 35,11 | 42,78 | 56,73 | 4,38 | 8,77 | 13,15 |
| Si | 14 K-Series | 98782 | 35,77 | 43,59 | 32,93 | 1,52 | 3,03 | 4,54 |
| Al | 13 K-Series | 18949 | 6,25 | 7,61 | 5,98 | 0,32 | 0,64 | 0,96 |
| Na | 11 K-Series | 3975 | 2,41 | 2,94 | 2,71 | 0,19 | 0,37 | 0,56 |
| Ca | 20 K-Series | 5331 | 2,47 | 3,00 | 1,59 | 0,11 | 0,22 | 0,33 |
| K | 19 K-Series | 177 | 0,07 | 0,08 | 0,05 | 0,03 | 0,06 | 0,09 |
| | Sum | 82,08 | | 100,00 | 100,00 | | | |
| Mu 11 B | | | | | | Error | Error | Error |
| Element | | Net | Wt % | Norm % | At % | (1 sigma) | (2 sigma) | (3 sigma) |
| O | 8 K-Series | 34753 | 36,80 | 44,63 | 58,60 | 4,49 | 8,99 | 13,48 |
| Si | 14 K-Series | 112414 | 34,71 | 42,10 | 31,49 | 1,47 | 2,94 | 4,41 |
| Al | 13 K-Series | 21751 | 5,96 | 7,23 | 5,63 | 0,31 | 0,61 | 0,91 |
| Na | 11 K-Series | 4380 | 2,37 | 2,88 | 2,63 | 0,18 | 0,37 | 0,55 |
| Ca | 20 K-Series | 5878 | 2,52 | 3,06 | 1,60 | 0,11 | 0,22 | 0,33 |
| K | 19 K-Series | 231 | 0,08 | 0,10 | 0,05 | 0,03 | 0,06 | 0,09 |
| | Sum | 82,45 | | 100,00 | 100,00 | | | |

Figure S18. EDX results of mordenite, sample Mu 11, two different measurement points A and B. The K content appears to be relatively low.

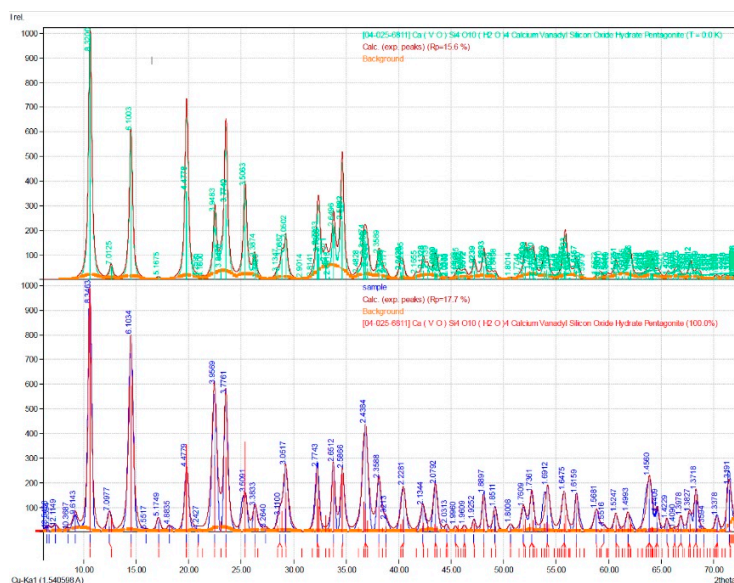


Figure S19. XRD pattern of sample Mu 14 pentagonite. Crystals of this sample consist of a single generation. XRD data of the sample show a basic agreement with the data from samples A1, A1, and Mu 05.

EDAX PhiZAF Quantification (Standardless) Pen Mu 14
Element Normalized
SEC Table : User c:\edax32\eds\genuser.sec

| Element | Wt % | At % | K-Ratio | Z | A | F |
|---------|--------|--------|---------|--------|--------|--------|
| SiK | 57.25 | 68.45 | 0.4777 | 1.0407 | 0.7994 | 1.0030 |
| CaK | 19.15 | 16.05 | 0.1706 | 1.0005 | 0.8762 | 1.0160 |
| V K | 23.14 | 15.25 | 0.1878 | 0.8899 | 0.9118 | 1.0002 |
| CuK | 0.46 | 0.24 | 0.0039 | 0.8680 | 0.9719 | 1.0000 |
| Total | 100.00 | 100.00 | | | | |

| Element | Net Inte. | Bkqd Inte. | Inte. Error | P/B |
|---------|-----------|------------|-------------|-------|
| SiK | 1610.37 | 32.82 | 0.45 | 49.07 |
| CaK | 359.36 | 18.83 | 0.98 | 19.09 |
| V K | 279.93 | 14.43 | 1.11 | 19.40 |
| CuK | 2.20 | 6.54 | 31.49 | 0.34 |

Figure S20. EDX results (shown without O) of sample Pen Mu 14 pentagonite (first generation). Low content of Cu.

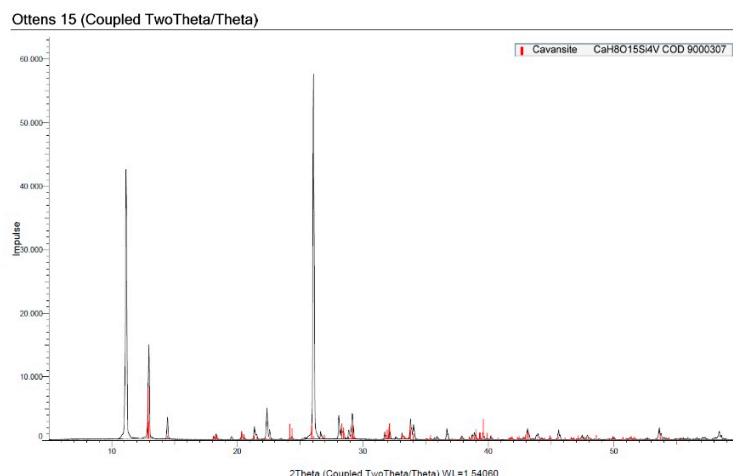


Figure S21. XRD pattern of sample Mu 15 cavansite. The pattern matches those of the reference data base for cavansite and are in good agreement with the reported data RRUFF ID: R050400.1 sample from Poona (Wagholi), India.

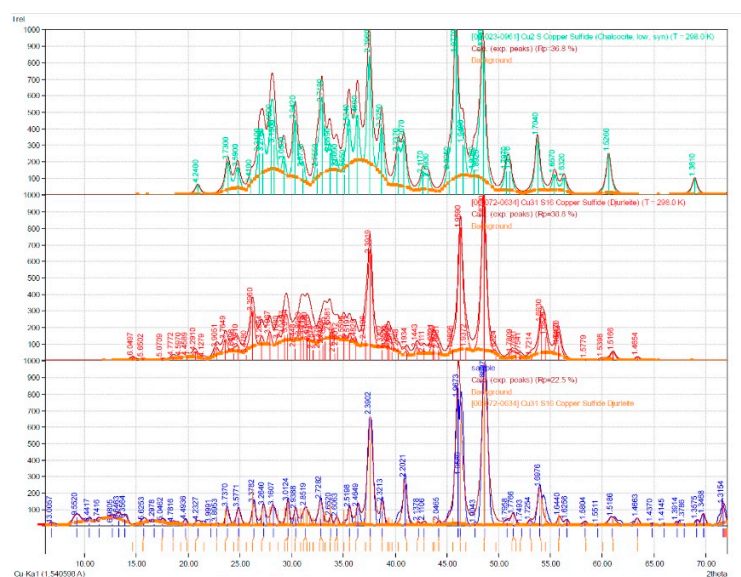


Figure S22. XRD pattern of sample Mu 16 djurleite. In the upper field all lines are for chalcocite and in the middle field lines for djurleite. In the bottom field, the lower blue line shows the observed data of the djurleite sample that largely corresponds to the reference data of djurleite and are in good agreement with the reported data RRUFF ID: R050400.1.

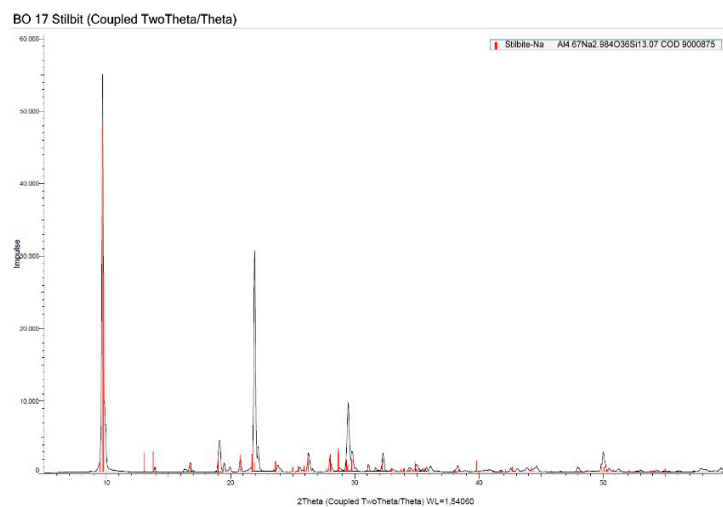


Figure S23. XRD pattern of sample Mu 17 stilbite. The pattern of the sample are identical to those of stilbite-Ca and match that of RRUFF ID: R050106.1. The EDX results also indicate stilbite-Ca.

| Element | Mu 17 A | Net | Wt % | Norm % | At % | Error (1 sigma) | Error (2 sigma) | Error (3 sigma) |
|---------|-------------------|-------|------|--------|--------|-----------------|-----------------|-----------------|
| O | 8 K-Series 46550 | 44,85 | | 52,01 | 66,40 | 5,34 | 10,68 | 16,0 |
| Si | 14 K-Series 92857 | 26,46 | | 30,67 | 22,31 | 1,13 | 2,26 | 3,4 |
| Al | 13 K-Series 28513 | 7,07 | | 8,19 | 6,20 | 0,36 | 0,72 | 1,1 |
| Ca | 20 K-Series 11955 | 6,87 | | 7,97 | 4,06 | 0,24 | 0,49 | 0,7 |
| Na | 11 K-Series 2525 | 1,00 | | 1,16 | 1,03 | 0,09 | 0,19 | 0,3 |
| | Sum | 86,25 | | 100,00 | 100,00 | | | |
| Element | Mu 17 B | Net | Wt % | Norm % | At % | Error (1 sigma) | Error (2 sigma) | Error (3 sigma) |
| O | 8 K-Series 45921 | 43,68 | | 51,38 | 65,74 | 5,21 | 10,42 | 15,6 |
| Si | 14 K-Series 93613 | 26,43 | | 31,08 | 22,65 | 1,13 | 2,25 | 3,4 |
| Al | 13 K-Series 28900 | 7,17 | | 8,44 | 6,40 | 0,36 | 0,73 | 1,1 |
| Ca | 20 K-Series 11615 | 6,48 | | 7,62 | 3,89 | 0,23 | 0,46 | 0,7 |
| Na | 11 K-Series 3225 | 1,26 | | 1,48 | 1,32 | 0,11 | 0,22 | 0,3 |
| | Sum | 85,02 | | 100,00 | 100,00 | | | |

Figure S24. EDX results of sample Mu 17 stilbite, two different measurement points A and B. The contents of the cations Ca and Na indicate stilbite-Ca.

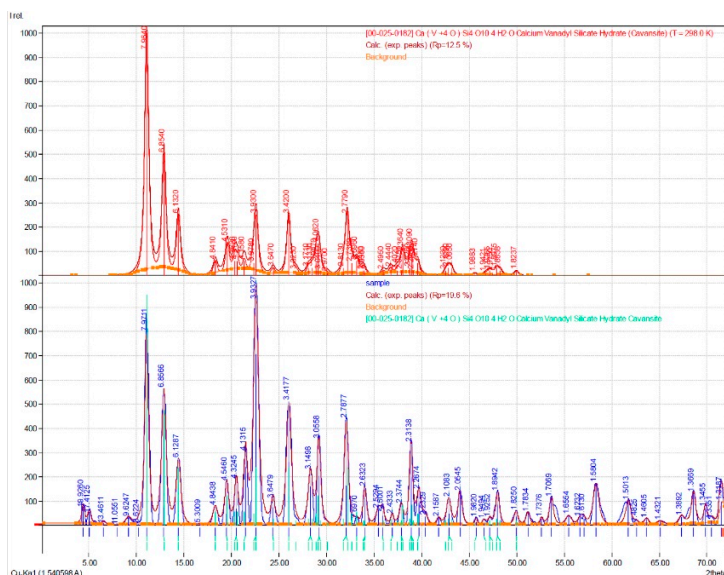


Figure S25. XRD pattern of sample USA 1 cavansite. The upper field: red line shows the reference data, in the lower field: blue line of the sample, red line reference data, and green bars – XRD peak positions from the data base. The 2theta data show a high conformity between them and match that of RRUFF ID: R050400, sample from Poona (Wagholi).

EDAX PhiZAF Quantification (Standardless) Cav USA01
 Element Normalized
 SEC Table : User c:\edax32\eds\genuser.sec

| Element | Wt % | At % | K-Ratio | Z | A | F |
|---------|--------|--------|---------|--------|--------|--------|
| SiK | 58.85 | 69.70 | 0.4965 | 1.0381 | 0.8103 | 1.0029 |
| CaK | 19.35 | 16.06 | 0.1714 | 0.9979 | 0.8745 | 1.0149 |
| V K | 21.80 | 14.23 | 0.1762 | 0.8876 | 0.9106 | 1.0000 |
| Total | 100.00 | 100.00 | | | | |

| Element | Net Inte. | Bkgd Inte. | Inte. Error | P/B |
|---------|-----------|------------|-------------|-------|
| SiK | 1704.79 | 38.60 | 0.44 | 44.16 |
| CaK | 367.68 | 21.13 | 0.98 | 17.40 |
| V K | 267.41 | 14.53 | 1.14 | 18.40 |

Figure S26. EDX results sample Cav USA 1 cavansite.