

SUPPORTING INFORMATION

Evolution of fumarolic anhydrous copper sulfate minerals during successive hydration/dehydration

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Table S1. Crystallographic parameters, molar masses and structural complexity values of the fumarolic minerals used in hydration/dehydration experiments.

| Mineral | Formula | Sp. group | a (Å), α (°) | b (Å), β (°) | c (Å), γ (°) | V (Å ³), R_1 | Mol. mass | I_G | $I_{G,total}$ | Ref |
|--------------------|---|--------------------|-----------------------|----------------------|-----------------------|------------------------------|-----------|-------|---------------|-------|
| Chalcocyanite | Cu(SO ₄) | <i>Pnma</i> | 8.412 | 6.704 | 4.830 | 272.41 0.021 | 159.602 | 2.252 | 54.039 | [1] |
| Dolerophanite | Cu ₂ O(SO ₄) | <i>C2/m</i> | 9.370 | 6.319 122.34 | 7.639 | 382.10 0.035 | 239.147 | 2.750 | 44.000 | [2] |
| Alumoklyuchevskite | K ₃ Cu ₃ AlO ₂ (SO ₄) ₄ | <i>P</i> $\bar{1}$ | 4.952 87.12 | 11.978 80.25 | 14.626 78.07 | 836.30 0.049 | 767.135 | 4.892 | 283.763 | [3,4] |
| Itelmenite | Na ₂ CuMg ₂ (SO ₄) ₄ | <i>Pbca</i> | 9.568 | 8.790 | 28.715 | 2415.0 0.034 | 542.36 | 4.644 | 928.771 | [5] |
| Euchlorine | KNaCu ₃ O(SO ₄) ₃ | <i>C2/c</i> | 18.131 | 9.386 113.22 | 14.353 | 2245.0 0.046 | 556.893 | 4.440 | 372.955 | [6] |

Table S2. Crystallographic parameters, molar masses and structural complexity values of the hydrated offsprings observed during the hydration experiments and anhydrous products obtained during successive dehydration experiments.

| Mineral phase | Formula | Sp. group | a (Å) α (°) | b (Å) β (°) | c (Å) γ (°) | V (Å ³) R_1 | Mol. mass | I_G | $I_{G.total}$ | Ref |
|-----------------------------------|--|--------------|-------------------------|-------------------------------|-------------------------|--------------------------------|---------------------|-------|---------------|---------|
| Hydrated species | | | | | | | | | | |
| «poitevinite» | Cu(SO ₄)·H ₂ O | $P\bar{1}$ | 5.040 108.39 | 5.157 108.99 | 7.569 90.40 | 175.19 0.034 | 177.617 | 3.281 | 59.059 | [7] |
| «bonattite» | Cu(SO ₄)·3H ₂ O | Cc | 5.592 | 13.029 97.05 | 7.341 | 530.81 0.069 | 213.647 | 3.907 | 117.207 | [8] |
| «chalcanthite» | Cu(SO ₄)·5H ₂ O | $P\bar{1}$ | 6.14 82.27 | 10.7360 107.43 | 5.986 102.67 | 366.36 0.037 | 249.677 | 4.440 | 186.477 | [9] |
| «kobayashevite» | Cu ₅ (SO ₄) ₂ (OH) ₆ ·4H ₂ O | $P\bar{1}$ | 6.073 102.88 | 11.060 92.35 | 5.509 92.60 | 359.87 0.040 | 683.944 | 4.362 | 170.13 | [10] |
| «antlerite» | Cu ₃ (SO ₄)(OH) ₄ | $Pnma$ | 8.244 | 6.043 | 11.987 | 597.17 0.031 | 354.722 | 3.500 | 224.00 | [11] |
| «cyanochroite» | K ₂ Cu(SO ₄) ₂ ·6H ₂ O | $P2_1/a$ | 9.085 | 12.130 104.45 | 6.167 | 658.17 0.030 | 441.944 | 3.986 | 247.160 | [12] |
| «kröhnkite» | Na ₂ Cu(SO ₄) ₂ ·2H ₂ O | $P2_1/c$ | 5.807 | 12.656 108.32 | 5.517 | 384.91 0.031 | 337.668 | 3.301 | 125.421 | [13] |
| «kaliochalcite- natrochalcite» | (K,Na)Cu ₂ (SO ₄) ₂ (OH)·H ₂ O | $C2/m$ | 8.935/8.809 | 6.252/6.187 117.318/118.74 | 7.602/7.509 | 377.30/358.83 0.100/0.038 | 377.216/ 393.324 | 3.059 | 55.059 | [14,15] |
| «brochantite» | Cu ₄ (SO ₄)(OH) ₆ | $P2_1/n$ | 12.776 90.15 | 9.869 | 6.026 | 759.79 0.049 | 452.282 | 4.392 | 368.955 | [16] |
| «pentahydrate» | Mg(SO ₄)·5H ₂ O | $P\bar{1}$ | 6.314 81.12 | 10.565 109.82 | 6.030 105.08 | 364.42 0.057 | 210.436 | 4.440 | 186.477 | [17] |
| «starkeyite» | Mg(SO ₄)·4H ₂ O | $P2_1/n$ | 5.922 | 13.604 90.85 | 7.905 | 636.78 0.078 | 192.421 | 4.170 | 300.235 | [18] |
| «sanderite» | Mg(SO ₄)·2H ₂ O | $P2_12_12_1$ | 8.893 | 8.488 | 12.440 | 939.06 0.019 | 156.391 | 4.000 | 256.000 | [19] |
| «brucite» | Mg(OH) ₂ | $P-3m$ | 3.042 | | 4.283 | 34.32 | 58.319 | 1.522 | 7.610 | [20] |
| «hexahydrate» | Mg(SO ₄)·6H ₂ O | $C2/c$ | 10.110 | 7.212 98.30 | 24.410 | 1761.17 0.115 | 228.451 | 4.627 | 444.156 | [21] |
| «alpersite» | (Mg,Cu)(SO ₄)·7H ₂ O | $P2_1/c$ | 14.166 | 6.534 105.922 | 10.838 | 964.69 | 266.087 | 3.777 | 196.423 | [22] |
| «epsomite» | Mg(SO ₄)·7H ₂ O | $P2_12_12_1$ | 11.887 | 12.013 | 6.861 | 979.74 0.030 | 246.466 | 4.755 | 513.528 | [23] |
| «konyaite» | Na ₂ Mg(SO ₄) ₂ ·5H ₂ O | $P2_1/c$ | 5.769 | 23.951 95.43 | 8.046 | 1106.76 0.033 | 352.472 | 4.807 | 538.424 | [22] |
| «Cu-pentahydrate» | (Mg _{0.4} ,Cu _{0.6})(SO ₄)·5H ₂ O | $P\bar{1}$ | 6.2470 82.530 | 10.5995 109.408 | 6.0395 104.794 | 364.23 | 233.981 | 4.440 | 186.477 | [22] |

| Mineral phase | Formula | Sp. group | a (Å) α (°) | b (Å) β (°) | c (Å) γ (°) | V (Å ³) R_1 | Mol. mass | I_G | $I_{G, total}$ | Ref |
|-------------------|---|---------------------------|-------------------------|------------------------|-------------------------|--------------------------------|-----------|-------|----------------|------|
| Anhydrous species | | | | | | | | | | |
| «tenorite» | CuO | <i>C2/c</i> | 4.683 | 3.421 99.57 | 5.129 | 81.03 0.070 | 79.545 | 1.000 | 4.000 | [24] |
| | K ₂ Cu(SO ₄) ₂ | | | | | | 333.854 | | | [25] |
| «wulfite» | K ₃ NaCu ₄ O ₂ (SO ₄) ₄ | <i>Pn2₁a</i> | 14.281 | 4.948 | 24.113 | 1703.79 0.075 | 810.69 | 4.907 | 588.827 | [26] |
| | Mg(SO ₄) | <i>Cmcm</i> | 5.182 | 7.893 | 6.506 | 266.11 | 120.361 | 1.918 | 23.020 | [27] |
| | MgO | <i>P6₃mc</i> | 3.279 | | 4.874 | 45.37 | 40.304 | 1.000 | 4.000 | [28] |
| «metathenardite» | Na ₂ (SO ₄) | <i>P6₃/mmc</i> | 5.394 | | 7.247 | 182.56 0.045 | 142.036 | 2.156 | 34.490 | [29] |
| «vanthoffite» | Na ₆ Mg(SO ₄) ₄ | <i>P2₁/c</i> | 9.797 | 9.217 113.50 | 8.199 | 678.96 0.064 | 546.469 | 3.792 | 204.764 | [30] |

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