SUPPORTING INFORMATION (SI)

Thermodynamic properties and phase equilibria of the secondary copper minerals libethenite, olivenite, pseudomalachite, kröhnkite, cyanochroite, and devilline

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Details on the determination of the crystal structure of devilline by single-crystal X-ray diffraction

A single-crystal X-ray diffraction of a devilline sample was undertaken to determine if the CO_3 groups can be detected in its structure. The need for this experiment arose from an assumption that the CO_3 groups in the structure can interfere with the calorimetric measurements (see below). Details of the crystallographic experiment are reported in Table S1, and the crystallographic information file (CIF file) can be found in the electronic supplement to this publication. The unit cell was refined from 1851 reflections, which provided a = 20.870(2), b = 6.135(3), c = 22.191(3) Å, β = 102.73(2)° with V = 2771.4(14) Å^3. The diffraction experiment of a selected fragment provided complex frames that revealed additional weak reflections arising from an additional small crystal and a large portion of diffuse scattering. Of the 15708 reflections collected, 3389 were unique and 733 classified as observed [I_{obs}>3σ(I)]. The data were corrected for background, Lorentz effect, and polarization using CrysAlis *RED* (Agilent Technologies, 2014). The combined correction for absorption, utilizing shape of the crystal (employing X-SHAPE program, Stoe & Cie 2005) and empirical absorption, was applied to the data (Jana2006, Petříček *et al*. 2014) leading to the dataset with an R_{int} of 7.4%. The structure was refined using the current dataset and the structural model of Sabelli & Zanazzi (1972), utilizing the full-matrix least-squares option of the Jana2006 program (Petříček *et al.* 2014) based on F^2. The refinement of the structure of devilline fully confirms previous results, including similar statistical factors. The final refinement converged to R_1 = 0.1159 for 733 unique observed reflections and R_1 = 0.2677 for all 3389 reflections. We note that the refinement was difficult owing to multiple twinning (most pronounced rotational twin-domain about ~180° along the [001] axis in direct space) and the diffuse nature of the diffraction peaks. According to our observations, the experimental difficulties affected most negatively the precision of the refinement of the positions of O atoms of the SO_4 groups. The current refinement of the structure is equivalent to the model reported by Sabelli & Zanazzi (1972). Because of the difficulties encountered during the refinement, namely those due to twinning and the diffuse nature of the diffraction maxima, substitution of the S^{6+} by C^{4+} could not be verified.

AGILENT TECHNOLOGIES (2014) CrysAlis CCD and CrysAlis RED. Oxford Diffraction Ltd, Yarnton, Oxfordshire, UK.

PETŘÍČEK, V., DUŠEK, M. & PALATINUS, L. (2014) Crystallographic computing system Jana2006: general features. *Zeitschrift für Kristallographie* **229**, 345–352.

SABELLI, C. & ZANAZZI, P.F. (1972) The crystal structure of devillite. *Acta Crystallographica* **B28**, 1182–1189.

STOE & CIE (2005) *X-SHAPE software*. Stoe & Cie GmbH, Darmstadt,Germany.

Table S1. Data collection and structure refinement details for devilline from Špania Dolina.

Diffractometer	Oxford Diffraction Gemini with Atlas CCD detector
Radiation/power	Mo$K\alpha$ (λ = 0.71075 Å)/50 kV, 30 mA
Temperature	293(2)K
Structural formula	$CaCu_4(SO_4)_2(OH)_6.3H_2O$
Space group	$P2_1/c$
Unit cell parameters	a = 20.870(2) Å
	b = 6.135(3) Å
	c = 22.191(3) Å
	β = 102.73(2)°
V [Å^3]	2771.4(14) Å^3
Z	8
$D_{calc.}$ [g.cm^{-3}]	3.022
F(000)	2432
Crystal dimensions	0.21 x 0.16 x 0.05 mm^3
Limiting θ angles	2.96–29.39°
Limiting Miller indices	$-28 \le h < 27$, $-7 \le k \le 8$, $-29 \le l \le 28$
No. of reflections	15708
No. of unique reflections	3389
No. of observed reflections (criterion)	733 [$I > 3\sigma(I)$]
Absorption correction [mm^{-1}], method	6.82, gaussian
T_{min}/T_{max}	0.541/0.663
Completeness to 28.85°, R_{int}	0.89, 0.074
Refinement by Jana2006 on F^2	
Param. refined, constraints, restraints	236, 4, 3
R_1, wR_2 (obs)	0.1159, 0.2092
R_1, wR_2 (all)	0.2677, 0.2792
GOF (obs, all)	2.95, 1.59
Weighting scheme	$1/(\sigma^2(I) + 0.0004I^2)$
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	–2.11, 3.89
Twin fractions	0.687(4)/0.313(4)
Twin matrix	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ -0.42 & 0 & 1 \end{pmatrix}$

Table S2. Measured heat capacity values for libethenite.

T/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}
1.930344	0.012376	5.849079	0.076747	21.22143	4.98866
2.0325	0.013189	5.945481	0.07995	23.54204	6.650293
2.148219	0.014286	6.053031	0.083542	26.11395	8.67747
2.258795	0.015124	6.16019	0.087246	28.97364	11.17745
2.372016	0.016221	6.267931	0.091111	32.14233	14.08252
2.475882	0.017199	6.372981	0.095335	35.59866	17.3363
2.583333	0.018155	6.477884	0.099716	39.39131	22.35532
2.679231	0.019148	6.583977	0.104044	43.89035	25.30619
2.785494	0.020192	6.6886	0.108041	48.66156	29.40804
2.895095	0.021332	6.792877	0.113306	54.00142	34.07299
3.001511	0.023095	6.897286	0.117595	59.90807	38.85735
3.107478	0.023618	7.002845	0.122205	66.4755	44.0985
3.214647	0.025379	7.10626	0.128569	73.77746	49.47118
3.308721	0.026265	7.211116	0.133836	81.89368	55.38309
3.426681	0.027614	7.315924	0.139607	90.91248	61.67151
3.533168	0.029075	7.408841	0.145764	100.9202	67.81933
3.63496	0.030268	7.520952	0.15227	111.0825	73.76943
3.745749	0.032348	7.628069	0.158643	121.0878	79.65084
3.834469	0.033619	7.734335	0.165705	131.131	84.85627
3.959247	0.035074	7.839213	0.172628	141.2508	90.0945
4.049306	0.036269	7.943129	0.179538	151.2928	94.94861
4.175487	0.038428	8.051818	0.187402	161.4192	98.84944
4.27353	0.040313	8.156648	0.195235	171.4673	102.4134
4.365882	0.042089	8.261077	0.203678	181.5477	106.2149
4.489342	0.043912	8.36641	0.212486	191.6657	110.268
4.578995	0.045658	8.47076	0.221849	201.7639	114.4406
4.686025	0.047527	8.574402	0.230819	211.8594	118.4067
4.795293	0.049682	8.677998	0.240361	221.9483	121.7487
4.896967	0.051971	9.24732	0.297533	232.021	125.4642
5.00385	0.054327	10.25459	0.429942	242.054	128.5238
5.108763	0.056393	11.37857	0.625023	252.1636	132.1447
5.216077	0.059125	12.62185	0.908668	262.272	135.1954
5.321375	0.061691	14.00591	1.314667	272.4032	138.0296
5.427178	0.064542	15.52938	1.761443	282.4834	141.1027
5.532764	0.067483	17.27065	2.66507	292.4924	143.6481
5.637325	0.070426	19.10758	3.652037	302.6733	147.0487
5.744263	0.073601				

Table S3. Measured heat capacity values for pseudomalachite.

T/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}
1.898238	0.809114	6.621031	3.597504	33.58452	38.52301
2.039371	0.916905	6.760265	3.570174	37.43652	45.97478
2.461292	1.283382	6.898947	3.545669	41.74022	54.41575
2.599763	1.404365	7.036987	3.512917	46.53982	63.5349
2.736133	1.507676	7.174802	3.48914	51.88361	73.20212
2.87969	1.657205	7.313057	3.462664	57.8418	83.85391
3.01727	1.808613	7.450707	3.440743	64.48481	95.25595
3.158773	1.934888	7.594516	3.40198	71.88933	107.6917
3.28882	2.10263	7.727975	3.396661	80.15205	121.2475
3.432841	2.185233	7.865105	3.391061	89.3672	136.3324
3.57359	2.357883	8.005032	3.37978	99.63853	151.6472
3.713406	2.516872	8.143997	3.3828	111.0876	167.8965
3.852636	2.660801	8.281121	3.383221	121.178	181.9275
3.990012	2.801668	8.418346	3.393756	131.2907	195.3115
4.130704	2.936201	8.5581	3.402162	141.3133	208.425
4.265976	3.056817	8.696501	3.420217	151.348	221.5148
4.411065	3.172927	8.837792	3.443759	161.4585	234.3517
4.553733	3.244993	8.974867	3.478857	171.5585	246.1058
4.684124	3.347867	9.109527	3.500355	181.6326	258.3329
4.820908	3.430604	9.24386	3.543428	191.6525	270.0285
4.958792	3.496011	9.385854	3.575444	201.7483	281.307
5.09382	3.548837	10.15635	3.847395	211.8356	291.0661
5.236139	3.604787	11.31986	4.467419	221.9165	301.5271
5.375522	3.637335	12.65649	5.422547	231.9843	310.211
5.513659	3.66678	14.06484	6.722329	242.1114	318.9983
5.651996	3.676488	15.68024	8.478202	252.226	327.9253
5.790722	3.67062	17.4825	10.78543	262.305	335.905
5.931365	3.686658	19.50018	13.62292	272.2882	343.4573
6.060666	3.669182	21.73395	17.16669	282.4534	350.4072
6.206589	3.658141	24.2291	21.42874	292.5027	356.093
6.345144	3.637005	27.02142	26.17013	302.5162	363.1707
6.483274	3.620782	30.12435	31.90839		

Table S4. Measured heat capacity values for olivenite.

T/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}
1.901814	0.057434	6.559883	0.169516	30.22836	11.64383
2.052585	0.059826	6.699145	0.176056	33.68197	14.91703
2.204596	0.061907	6.838947	0.183462	37.52676	18.69119
2.357455	0.063924	6.977677	0.189869	41.8231	23.08417
2.493606	0.065881	7.117076	0.197518	46.6144	27.91429
2.625169	0.067655	7.255946	0.204778	51.95411	33.12001
2.771075	0.069608	7.394966	0.213457	57.90124	38.87287
2.914898	0.072527	7.51862	0.220901	64.53241	45.01026
3.058173	0.074824	7.669424	0.229927	71.93146	51.57564
3.198504	0.076706	7.813594	0.239121	80.18378	58.79385
3.341147	0.079516	7.953388	0.248503	89.39026	66.55217
3.486317	0.081534	8.097096	0.2597	99.65039	74.18879
3.624093	0.08413	8.232306	0.269668	111.0906	82.00101
3.764897	0.086988	8.372296	0.281033	121.1732	88.74485
3.908048	0.089391	8.512797	0.291732	131.2451	94.93777
4.049597	0.09205	8.650828	0.304518	141.2939	100.68
4.186151	0.094244	8.789993	0.316473	151.4143	106.2986
4.330032	0.097548	8.927762	0.329556	161.4924	111.5748
4.469365	0.100631	9.066163	0.342723	171.5372	116.3664
4.612519	0.104036	9.204961	0.357226	181.6061	121.5399
4.736375	0.106785	9.343492	0.370878	191.7217	126.4295
4.893941	0.110763	9.481051	0.385761	201.8126	131.2646
5.018991	0.114466	10.25604	0.477427	211.8989	135.8072
5.160286	0.118092	11.42573	0.659378	221.978	139.7035
5.300488	0.122135	12.72628	0.889657	232.0461	143.6236
5.4425	0.126562	14.18183	1.295294	242.1281	147.2519
5.58246	0.131351	15.7773	1.828201	252.1569	151.0369
5.723029	0.135765	17.58479	2.5802	262.2224	154.3242
5.862662	0.140946	19.60176	3.595317	272.3619	157.2844
6.006648	0.146046	21.85636	4.976125	282.4225	160.516
6.13525	0.151112	24.34958	6.708841	292.4022	163.5165
6.277927	0.157815	27.12891	8.927394	302.5607	166.6006
6.420353	0.163313				

Table S5. Measured heat capacity values for devilline.

T/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}
2.04462	0.907267	7.30942	10.6065	30.648	48.5098
2.04597	0.90786	7.39106	10.5012	30.6716	48.5374
2.04716	0.906002	7.40354	10.4351	33.3565	55.7536
2.22766	1.11829	7.40432	10.4477	33.3584	55.7231
2.22956	1.11729	7.64377	10.1486	33.3879	55.6682
2.23047	1.11862	7.6556	10.0307	36.3079	63.7571
2.42642	1.35971	7.65845	10.1185	36.3107	63.7138
2.42848	1.35713	7.89657	9.93604	36.336	63.7232
2.42953	1.35835	7.90892	9.91149	39.52	72.6678
2.64468	1.64239	7.91131	9.88232	39.5224	72.6428
2.64644	1.64296	7.93192	9.89526	39.5451	72.638
2.64757	1.64117	7.94755	9.85585	43.019	82.3964
2.87792	1.95563	7.94888	9.84647	43.0203	82.3546
2.88058	1.95903	8.1491	9.74637	43.0382	82.4274
2.88172	1.95925	8.16275	9.68541	46.8279	92.8393
3.13637	2.33475	8.16484	9.69036	46.832	92.8442
3.13888	2.33663	8.3994	9.6024	46.8462	92.96
3.13996	2.33814	8.41396	9.58355	50.9749	104.116
3.42032	2.77168	8.41667	9.57569	50.9807	104.125
3.42311	2.77089	8.62788	9.51855	50.9915	104.256
3.42428	2.77388	8.64421	9.49348	55.5131	116.201
3.72085	3.25477	8.64684	9.50965	55.5171	116.261
3.72404	3.26024	8.65689	9.49779	55.5301	116.37
3.7253	3.24845	8.66885	9.48466	60.4337	129.203
4.04996	3.81512	8.67152	9.47557	60.4389	129.098
4.05358	3.81321	8.90766	9.44677	60.4565	129.176
4.05457	3.82297	8.92138	9.42573	65.7983	142.632
4.10376	3.92101	8.92478	9.41388	65.8032	142.599
4.10762	3.92306	9.16152	9.42131	65.8221	142.73
4.1087	3.91873	9.17418	9.39984	71.629	157.114
4.35816	4.41208	9.17745	9.39444	71.6344	156.902
4.36205	4.40188	9.3899	9.41703	71.6551	156.956
4.3633	4.40706	9.40575	9.40535	77.9675	172.161
4.40692	4.49953	9.40753	9.42981	77.9807	172.078
4.4101	4.50113	9.40887	9.41611	78.0012	171.98
4.41138	4.49758	9.42132	9.4208	84.8697	188.335
4.61264	4.9195	9.42651	9.40553	84.8746	188.558
4.61664	4.92763	9.63671	9.48565	84.9114	187.913
4.6177	4.91638	9.6518	9.48511	92.3529	203.757
4.7954	5.32022	9.66011	9.47379	92.359	204.821
4.79878	5.31805	9.86492	9.50501	92.4107	204.63
4.79998	5.32832	9.86892	9.53445	100.535	222.529

Table S5. continued

T/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}
4.86704	5.48259	9.87716	9.53528	100.546	222.547
4.87166	5.48174	10.0298	9.5846	100.604	222.63
4.87304	5.47697	10.0583	9.60557	109.447	240.95
5.12337	6.12282	10.0711	9.62418	109.462	241.328
5.1274	6.11708	10.2208	9.6672	109.478	241.317
5.12834	6.11181	10.235	9.69574	119.161	261.473
5.21793	6.38421	10.2381	9.64899	119.178	261.095
5.22112	6.38685	11.1222	10.1983	119.24	261.411
5.22266	6.37653	11.1361	10.2084	129.738	282.059
5.37727	6.79329	11.1398	10.2105	129.76	281.647
5.38122	6.79995	12.1054	11.0744	129.803	281.922
5.38223	6.79805	12.1168	11.0638	141.258	303.982
5.63588	7.59938	12.1194	11.0521	141.281	303.59
5.63993	7.60554	13.1704	12.2385	141.301	304.661
5.64119	7.60008	13.1817	12.2277	153.802	327.562
5.68437	7.774	13.1837	12.2376	153.824	327.225
5.68513	7.76309	14.3335	13.7221	153.829	328.614
5.68628	7.75771	14.3428	13.7123	167.439	351.715
5.89184	8.57639	14.3441	13.7255	167.453	352.081
5.89485	8.56978	15.5994	15.5787	167.457	351.379
5.89594	8.57842	15.602	15.5772	182.282	378.144
6.14652	9.84456	15.6021	15.5687	182.284	377.73
6.14911	9.83194	16.971	17.884	182.3	377.701
6.14984	9.83168	16.9799	17.8087	198.417	404.553
6.18807	10.054	16.9802	17.8314	198.423	404.81
6.18871	10.0689	18.4586	20.5734	198.457	404.62
6.19354	10.0759	18.4714	20.5226	215.997	432.18
6.39531	11.2512	18.4735	20.4976	216.02	432.408
6.40228	11.2662	20.0887	23.6374	216.054	432.372
6.40337	11.2702	20.1005	23.6445	235.088	460.213
6.65751	11.8339	20.1033	23.7231	235.149	460.53
6.65886	11.8189	21.8511	27.3031	235.184	460.215
6.65909	11.7966	21.8591	27.314	255.855	489.11
6.73439	11.8637	21.8596	27.3903	255.977	489.072
6.75042	11.8305	23.7753	31.6114	256.009	488.508
6.75224	11.834	23.781	31.743	278.444	518.448
6.92216	11.6809	23.7879	31.6161	278.636	519.162
6.93095	11.6702	25.8726	36.7339	278.664	519.966
6.9326	11.6433	25.8797	36.6732	303.069	549.016
7.13846	11.1034	25.8851	36.4146	303.295	548.965
7.15082	11.0364	28.1577	42.1555	303.302	549.099
7.15114	11.0113	28.1583	42.1859		
7.2943	10.6817	28.175	42.1612		
7.30767	10.6132	30.6442	48.5442		

Table S6. Measured heat capacity values for cyanochroite.

T/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}
2.0207	0.0181585	10.887	2.77084	61.2497	129.566
2.02131	0.0182004	11.3456	3.18052	61.256	129.544
2.02206	0.018198	11.3503	3.17676	63.8812	135.714
2.10561	0.0197611	11.3549	3.1809	63.8862	135.708
2.10636	0.0199058	11.838	3.65739	63.8914	135.746
2.10735	0.0198362	11.8434	3.65628	66.6297	142.269
2.19536	0.0218679	11.8486	3.66144	66.6335	142.238
2.19601	0.0219251	12.3475	4.19279	66.6423	142.254
2.19716	0.0218763	12.3518	4.19391	69.4976	148.767
2.28947	0.0243744	12.3581	4.19483	69.5015	148.745
2.29	0.0243522	12.8781	4.79821	69.5107	148.729
2.29095	0.0244665	12.8835	4.79735	72.4938	155.378
2.38699	0.0266475	12.8886	4.80289	72.5017	155.164
2.38741	0.0269383	13.4303	5.48581	72.5075	155.355
2.38882	0.026736	13.4367	5.48364	75.6135	161.457
2.48945	0.0293258	13.4426	5.48567	75.6156	161.477
2.49032	0.0293386	14.0064	6.23306	75.6269	161.326
2.49132	0.0294031	14.0128	6.23145	78.8627	168.247
2.59648	0.0325371	14.0188	6.23231	78.8674	168.127
2.59725	0.0324673	14.6085	7.08989	78.8803	167.872
2.59827	0.0325252	14.6153	7.08474	82.2539	174.764
2.70786	0.0360399	14.6213	7.09199	82.2606	174.645
2.70875	0.036093	15.2357	8.04532	82.2707	174.669
2.7099	0.0363304	15.2433	8.04372	85.7894	181.078
2.82265	0.0397455	15.2496	8.03872	85.7927	181.261
2.82311	0.0401544	15.8914	9.10103	85.8062	180.983
2.82475	0.0397347	15.899	9.08818	89.4955	187.959
2.94465	0.0445298	15.9052	9.09183	89.4993	188.063
2.94532	0.044656	16.574	10.2651	89.5076	187.761
2.94674	0.0446214	16.5841	10.2662	93.339	194.308
3.07133	0.0503182	16.589	10.26	93.3464	194.289
3.07224	0.0503324	17.2908	11.5558	93.3495	194.454
3.07376	0.0504393	17.3001	11.5407	97.3523	201.787
3.20514	0.0564526	17.3048	11.538	97.3556	201.714
3.20603	0.0566484	18.0355	12.9847	97.364	201.661
3.2075	0.0567978	18.0465	12.9706	101.538	208.928
3.34792	0.064092	18.0495	12.9592	101.542	208.946
3.34887	0.0640075	18.814	14.5283	101.549	208.848
3.35042	0.0641581	18.8238	14.5171	105.911	216.284
3.48996	0.0717834	18.8277	14.4966	105.917	216.19
3.49073	0.0723699	19.6245	16.2582	105.925	216.088
3.49262	0.0720423	19.6354	16.2117	110.469	223.801
3.6391	0.0811577	19.6357	16.2165	110.474	223.74

Table S6. continued

T/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}
3.64028	0.0813787	20.4754	18.0319	110.478	223.564
3.64198	0.081313	20.4809	18.1096	115.229	231.265
3.79506	0.0917071	20.4827	18.0438	115.235	231.025
3.79592	0.0917784	21.3554	20.0489	115.236	231.508
3.79764	0.0920774	21.3585	20.1473	120.187	238.74
3.95913	0.103652	21.3635	20.0768	120.193	238.788
3.95993	0.10364	22.2745	22.3246	120.196	238.429
3.96191	0.104028	22.2778	22.2278	125.357	245.808
4.12979	0.117952	22.2837	22.2775	125.366	245.581
4.13059	0.117965	23.2303	24.7271	125.367	245.624
4.13251	0.117755	23.2333	24.6065	130.755	253.54
4.3068	0.134836	23.2414	24.6327	130.759	253.17
4.3077	0.13418	24.2297	27.1535	130.76	253.493
4.30952	0.134512	24.2321	27.2561	136.381	261.36
4.49035	0.152769	24.2372	27.1957	136.386	261.37
4.49129	0.152139	25.2627	30.0087	136.386	260.961
4.49366	0.153148	25.2736	30.004	142.255	269.498
4.68434	0.173396	25.2857	29.805	142.259	269.54
4.68556	0.173872	26.3524	32.9477	142.261	268.926
4.68772	0.174429	26.3604	33.142	148.379	277.742
4.88418	0.19662	26.37	32.7056	148.384	277.298
4.88561	0.195889	27.4837	36.3489	148.387	277.509
4.88777	0.196456	27.4841	35.8805	154.758	285.663
5.09398	0.222599	27.5088	35.452	154.767	286.111
5.09513	0.223504	28.6724	39.2246	154.777	285.777
5.09768	0.223291	28.6764	39.2316	161.454	293.484
5.31297	0.25467	28.6817	39.3261	161.46	294.311
5.31416	0.254092	29.9079	42.7271	161.472	294.455
5.31686	0.255148	29.911	42.7488	168.389	302.844
5.53986	0.291751	29.9188	42.7544	168.399	303.362
5.54157	0.290121	31.1929	46.4889	168.412	303.418
5.5444	0.290468	31.1953	46.4706	175.648	311.783
5.78451	0.333808	31.2068	46.4527	175.658	311.435
5.78631	0.33471	32.5347	50.4333	175.665	311.968
5.78761	0.334027	32.5374	50.4186	183.232	320.367
6.03124	0.382182	32.5492	50.4057	183.236	320.707
6.04056	0.384904	33.9332	54.5277	183.244	321.106
6.06462	0.391884	33.9353	54.5321	191.12	329.343
6.29305	0.440823	33.9464	54.5073	191.136	330.179
6.29487	0.438298	35.3935	58.7828	191.142	330.601
6.29612	0.440812	35.3952	58.7894	199.359	339.564
6.55996	0.504863	35.4054	58.781	199.362	340.045
6.56202	0.503455	36.9218	63.2922	199.378	339.986
6.56526	0.50518	36.9231	63.2721	207.925	349.726

Table 6. continued

T/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}
6.86192	0.58546	36.9339	63.2302	207.94	349.587
6.86236	0.584939	38.5131	67.9482	207.955	349.38
6.86332	0.583581	38.5162	67.9466	216.88	360.807
7.1391	0.666509	38.5241	67.949	216.896	361.369
7.14115	0.666491	40.1742	72.8911	216.909	361.125
7.14432	0.667229	40.1756	72.8903	226.205	371.84
7.44756	0.766816	40.1838	72.8956	226.228	372.015
7.44954	0.765626	41.9023	77.893	226.24	371.823
7.45312	0.768006	41.9058	77.9233	235.933	381.225
7.76536	0.883205	41.9113	77.895	235.962	381.566
7.76756	0.883831	43.7061	83.0107	235.97	381.324
7.77185	0.884659	43.7083	83.0196	246.098	392.854
8.09961	1.02034	43.7149	83.0456	246.134	393.464
8.10163	1.01905	45.59	88.3119	246.136	393.333
8.10615	1.02053	45.5923	88.2776	256.665	403.36
8.44739	1.17602	45.5986	88.3349	256.709	403.329
8.4499	1.17584	47.5514	93.8411	256.712	403.857
8.45417	1.17825	47.5553	93.861	267.68	414.821
8.81059	1.35915	47.5574	93.895	267.74	415.325
8.81308	1.35805	49.6003	99.4636	267.745	415.254
8.81746	1.35988	49.6044	99.5512	279.182	428.201
9.18879	1.56683	49.6045	99.4682	279.246	427.863
9.19165	1.56606	51.7367	105.236	279.252	428.095
9.19651	1.56833	51.7405	105.366	291.139	442.582
9.58464	1.80809	51.7411	105.262	291.264	442.23
9.58779	1.80879	53.9662	111.224	291.272	442.506
9.59254	1.80999	53.969	111.222	303.555	451.07
9.9962	2.08483	53.9699	111.224	303.752	451.296
10.0001	2.08368	56.292	117.217	303.753	451.381
10.0049	2.08692	56.2954	117.241		
10.4282	2.40349	56.3	117.317		
10.4327	2.40269	58.718	123.402		
10.4375	2.40485	58.7217	123.396		
10.8778	2.76941	58.7284	123.387		
10.8816	2.76721	61.2464	129.539		

Table S7. Measured heat capacity values for the mixture of kröhnkite and thénardite.

T/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}
Run 1					
5.10236	0.163209	20.3079	5.86121	86.9679	116.099
5.10494	0.162507	21.7434	7.25817	87.0184	116.012
5.10741	0.163547	21.745	7.27733	93.1988	124.199
5.48104	0.166423	21.7473	7.25192	93.2055	124.16
5.48397	0.165911	23.2937	9.01266	93.2499	124.252
5.48533	0.168758	23.2974	8.98308	99.8948	132.983
5.87867	0.174792	23.3028	8.97976	99.9029	133.021
5.87988	0.177244	24.9647	11.0586	99.9486	133.126
5.88293	0.175709	24.9672	11.0126	107.081	141.625
6.29375	0.191381	24.9929	10.8849	107.092	141.61
6.29687	0.190198	26.7558	13.4932	107.136	141.854
6.29933	0.191074	26.7664	13.5275	114.782	150.538
6.75714	0.21063	26.7671	13.3936	114.794	150.548
6.75716	0.211369	28.6702	16.2239	114.832	150.637
6.75903	0.211861	28.677	16.1982	123.031	159.232
7.19634	0.23703	28.6912	16.4622	123.045	159.107
7.19714	0.237253	30.7216	19.4091	123.086	159.336
7.20103	0.237396	30.735	19.4154	131.893	168.267
7.70691	0.274683	30.7392	19.7004	131.911	168.267
7.70864	0.274979	32.9263	23.1056	131.935	168.497
7.7136	0.274945	32.9305	23.1014	141.391	177.554
8.25344	0.324502	32.9563	23.1368	141.407	177.696
8.25527	0.32394	35.2886	27.2546	141.424	177.801
8.25982	0.324445	35.291	27.2303	151.55	187.431
8.84179	0.389188	35.319	27.2362	151.567	187.735
8.84288	0.389614	37.8211	31.8639	151.573	187.197
8.84711	0.390873	37.8239	31.8346	162.447	197.275
9.46693	0.472616	37.8491	31.8794	162.449	197.49
9.46899	0.470805	40.5366	36.9868	162.469	197.044
9.4754	0.473571	40.5384	36.9827	174.131	207.494
10.1453	0.583275	40.5608	37.0479	174.136	207.322
10.1485	0.583123	43.4464	42.5031	174.151	207.532
10.1559	0.584886	43.4495	42.5163	186.695	217.833
10.8797	0.728457	43.4667	42.5823	186.715	217.586
10.8819	0.72577	46.5643	48.4578	186.719	217.86
10.8886	0.727197	46.5688	48.4879	200.09	228.615
11.6539	0.915083	46.5814	48.5751	200.114	228.386
11.6569	0.912708	49.9084	54.8614	200.138	228.255
11.6649	0.91391	49.9121	54.8367	214.465	239.614
12.4871	1.15126	49.9268	54.9563	214.493	239.502
12.4905	1.14825	53.4951	61.6072	214.522	239.308
12.4984	1.14996	53.4994	61.6061	229.836	249.922
13.3797	1.46132	53.512	61.672	229.894	250.135

Table S7. continued

T/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}
13.3839	1.45813	57.3456	68.7731	229.921	249.963
13.3934	1.45638	57.3483	68.7283	246.316	261.419
14.3499	1.84182	57.3681	68.7552	246.425	261.632
14.352	1.83744	61.4796	76.1096	246.443	261.817
14.3591	1.83929	61.4851	76.1571	263.945	273.062
15.3805	2.33283	61.4983	76.2273	264.103	272.608
15.3842	2.32814	65.9035	83.7043	264.121	273.167
15.3921	2.33062	65.912	83.6794	282.836	285.852
16.4821	2.95332	65.929	83.7469	283.061	285.349
16.4873	2.9344	70.6419	91.6117	283.08	285.673
16.4957	2.94327	70.6476	91.6488	303.075	296.372
17.6673	3.72857	70.6669	91.59	303.417	297.309
17.6696	3.71817	75.7188	99.322	303.424	297.114
17.6773	3.71981	75.7253	99.5125		
18.93	4.676	75.7398	99.4397		
18.9343	4.66634	81.1475	107.518		
18.9441	4.66764	81.1612	107.686		
20.3021	5.84843	81.1769	107.719		
20.3037	5.84172	86.9678	116.012		

T/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}
Run 2					
2.01923	0.399014	13.0692	1.34498	84.8713	112.687
2.02401	0.396798	13.0713	1.34908	84.8782	112.559
2.02476	0.396486	13.0736	1.34442	84.8953	112.551
2.19449	0.356122	14.2265	1.79084	92.4067	122.579
2.19989	0.35514	14.2276	1.79961	92.413	122.394
2.20122	0.353687	14.2326	1.79155	92.4301	122.346
2.38515	0.316904	15.4893	2.39111	100.604	133.402
2.39074	0.315555	15.4914	2.4024	100.605	133.36
2.3924	0.314716	15.496	2.39224	100.622	133.144
2.59469	0.281886	16.8642	3.18284	109.523	144.157
2.60039	0.279795	16.8653	3.1982	109.527	144.053
2.60226	0.27976	16.8706	3.18315	109.539	143.658
2.82311	0.253868	18.3585	4.21849	119.241	155.337
2.82873	0.253232	18.36	4.2414	119.248	155.369
2.83073	0.25282	18.3645	4.22143	119.258	154.859
3.07514	0.235025	20.0057	5.58479	129.814	166.141
3.08036	0.234568	20.0092	5.57837	129.82	166.003
3.08251	0.234612	20.0117	5.61398	129.825	165.611
3.35287	0.223623	21.7732	7.29315	141.34	177.272
3.35803	0.223503	21.7769	7.32913	141.341	177.416
3.35962	0.223315	21.7793	7.29449	141.344	177.692
3.64657	0.21302	23.7039	9.45484	153.87	188.917

Table S7. continued

T/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}
3.65291	0.212963	23.7095	9.44976	153.883	189.244
3.65483	0.211823	23.7125	9.49285	153.888	189.027
3.97063	0.180066	25.8029	12.1187	167.511	201.379
3.97561	0.179989	25.8059	12.1755	167.538	201.743
3.97776	0.180461	25.8201	12.086	167.539	201.624
4.32204	0.167971	28.0939	15.4377	182.476	213.814
4.32706	0.167797	28.1037	15.3119	182.5	214.145
4.32817	0.167298	28.107	15.2069	182.503	214.282
4.71845	0.162258	30.5936	19.1596	198.658	226.673
4.72072	0.161784	30.6009	19.1683	198.685	227.496
4.72121	0.162208	30.6141	19.3494	198.696	227.039
5.12174	0.16137	33.308	23.7422	216.289	240.63
5.12423	0.162646	33.3126	23.7458	216.297	240.901
5.12774	0.161743	33.3381	23.8366	216.323	241.038
5.57975	0.16838	36.2642	28.9674	235.446	253.719
5.58261	0.167953	36.2676	28.9624	235.471	254.104
5.58561	0.167726	36.2966	29.0328	235.493	253.835
6.07253	0.182946	39.4876	34.9556	256.3	268.021
6.07526	0.182056	39.49	34.9754	256.355	268.215
6.07892	0.181693	39.5149	35.0449	256.382	268.097
6.6242	0.205462	42.9918	41.5769	278.954	283.489
6.62533	0.205484	42.9957	41.5768	279.074	283.566
6.62705	0.204147	43.0197	41.7216	279.086	283.726
7.20955	0.240124	46.8079	48.8656	303.605	297.459
7.20973	0.239701	46.8126	48.8778	303.812	297.662
7.2119	0.239674	46.834	49.0336	303.821	297.571
7.84507	0.287943	50.9629	56.7582		
7.84636	0.289008	50.9681	56.7689		
7.84846	0.289093	50.9899	56.9532		
8.54373	0.357489	55.4893	65.2666		
8.54419	0.358465	55.4957	65.2673		
8.54697	0.358391	55.513	65.4812		
9.30005	0.453163	60.4166	74.185		
9.30016	0.452782	60.4233	74.1953		
9.30395	0.452087	60.4504	74.3527		
10.1257	0.58371	65.773	83.5489		
10.1265	0.585877	65.7796	83.5185		
10.1299	0.583523	65.8085	83.6312		
11.0237	0.762765	71.6191	93.0726		
11.0259	0.765105	71.6248	93.1517		
11.0278	0.764003	71.6558	93.172		
12.0051	1.01056	77.9666	102.767		
12.0056	1.01377	77.9699	102.949		
12.0096	1.0095	78.0006	103.027		

Table S8. Heat capacity values for the kröhnkite after correction for the thénardite impurity.

T/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}
2.01923	0.407038827	15.3842	2.326401125	70.6669	91.21647532
2.02401	0.404777025	15.3921	2.328849514	71.6191	92.69058904
2.02476	0.404458565	15.4893	2.389552504	71.6248	92.77106923
2.19449	0.36324607	15.4914	2.401050148	71.6558	92.79053216
2.19989	0.362243154	15.496	2.390634747	75.7188	98.90646944
2.20122	0.360760349	16.4821	2.951894964	75.7253	99.10059972
2.38515	0.323194187	16.4873	2.932526051	75.7398	99.02576589
2.39074	0.321816593	16.4957	2.941473465	77.9666	102.3373896
2.3924	0.320960177	16.8642	3.181267963	77.9699	102.5229727
2.59469	0.287417096	16.8653	3.19692636	78.0006	102.6014293
2.60039	0.285282162	16.8706	3.181501247	81.1475	107.0705082
2.60226	0.285245999	17.6673	3.727068985	81.1612	107.2414456
2.82311	0.258768991	17.6696	3.716423836	81.1769	107.2745647
2.82873	0.258118444	17.6773	3.717985147	84.8713	112.2169511
2.83073	0.257697486	18.3585	4.216410775	84.8782	112.0861148
3.07514	0.239464143	18.36	4.239763112	84.8953	112.0773801
3.08036	0.238996074	18.3645	4.219314558	86.9678	115.540468
3.08251	0.239040241	18.93	4.673187645	86.9679	115.6292357
3.35287	0.227727414	18.9343	4.663253781	87.0184	115.5388217
3.35803	0.227602893	18.9441	4.664404089	92.4067	122.0697966
3.35962	0.227410424	20.0057	5.579938122	92.413	121.8808384
3.64657	0.21677965	20.0092	5.573316679	92.4301	121.8313392
3.65291	0.216718461	20.0117	5.609600984	93.1988	123.69868
3.65483	0.215554337	20.3021	5.842863759	93.2055	123.6586832
3.97063	0.182985984	20.3037	5.835983862	93.2499	123.7512114
3.97561	0.182904591	20.3079	5.855783129	99.8948	132.4649407
3.97776	0.183384977	21.7434	7.249238007	99.9029	132.5034833
4.32204	0.170427163	21.745	7.268750191	99.9486	132.6093182
4.32706	0.170246237	21.7473	7.242768566	100.604	132.8723097
4.32817	0.16973633	21.7732	7.284224648	100.605	132.8294264
4.71845	0.164305152	21.7769	7.320849342	100.622	132.6085478
4.72072	0.163819674	21.7793	7.285447324	107.081	141.0835349
4.72121	0.16425191	23.2937	9.000560186	107.092	141.0679327
5.10236	0.164939793	23.2974	8.970280066	107.136	141.3157121
5.10494	0.164221062	23.3028	8.966749413	109.523	143.6017833
5.10741	0.165279894	23.7039	9.44072976	109.527	143.4955604
5.12174	0.163044965	23.7095	9.435393998	109.539	143.0922023
5.12423	0.164344565	23.7125	9.479279476	114.782	149.9794386
5.12774	0.163419834	24.9647	11.04148883	114.794	149.9893524
5.48104	0.167833198	24.9672	10.99447917	114.832	150.0792467
5.48397	0.167307565	24.9929	10.86342552	119.241	154.770948
5.48533	0.170211026	25.8029	12.09802412	119.248	154.803438
5.57975	0.169719899	25.8059	12.15588832	119.258	154.2828263
5.58261	0.169280955	25.8201	12.06413087	123.031	158.6595758

Table S8. continued

T/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}
5.58561	0.16904592	26.7558	13.47058537	123.045	158.531721
5.87867	0.175903618	26.7664	13.50524303	123.086	158.7644737
5.87988	0.178403998	26.7671	13.36859492	129.814	165.5636374
5.88293	0.176833888	28.0939	15.41038541	129.82	165.4227036
6.07253	0.183969781	28.1037	15.28169098	129.825	165.0226203
6.07526	0.183057968	28.107	15.17444124	131.893	167.6900937
6.07892	0.182682617	28.6702	16.19274109	131.911	167.6897264
6.29375	0.1922656	28.677	16.16628106	131.935	167.9239185
6.29687	0.191053969	28.6912	16.43516006	141.34	176.6929684
6.29933	0.191944209	30.5936	19.11880401	141.341	176.8398807
6.6242	0.206124693	30.6009	19.12740892	141.344	177.1214421
6.62533	0.206145308	30.6141	19.31170298	141.391	176.9797446
6.62705	0.204778302	30.7216	19.36860092	141.407	177.1243326
6.75714	0.211177765	30.735	19.37452743	141.424	177.2311487
6.75716	0.211931774	30.7392	19.66517147	151.55	186.8724596
6.75903	0.212430627	32.9263	23.05504263	151.567	187.1823479
7.19634	0.237321099	32.9305	23.05058959	151.573	186.6332908
7.19714	0.237547095	32.9563	23.08568056	153.87	188.3480887
7.20103	0.237685498	33.308	23.68930022	153.883	188.681519
7.20955	0.240452554	33.3126	23.6927882	153.888	188.4600149
7.20973	0.240020595	33.3381	23.7844089	162.447	196.7308367
7.2119	0.239988843	35.2886	27.19153121	162.449	196.95018
7.70691	0.27468045	35.291	27.16663543	162.469	196.4947707
7.70864	0.274978619	35.319	27.17147519	167.511	200.8357936
7.7136	0.274932863	36.2642	28.89767983	167.538	201.2067688
7.84507	0.287896647	36.2676	28.89243199	167.539	201.0853304
7.84636	0.288980341	36.2966	28.96301882	174.131	206.9706713
7.84846	0.28906221	37.8211	31.78532455	174.136	206.7950926
8.25344	0.324201876	37.8239	31.75530456	174.151	207.0091344
8.25527	0.32362372	37.8491	31.79990412	182.476	213.2926034
8.25982	0.324127263	39.4876	34.86549006	182.5	213.6299847
8.54373	0.35708393	39.49	34.8855846	182.503	213.7697288
8.54419	0.358078521	39.5149	34.95537336	186.695	217.3314409
8.54697	0.3579953	40.5366	36.89029684	186.715	217.0791225
8.84179	0.388570093	40.5384	36.88603095	186.719	217.3586419
8.84288	0.38900151	40.5608	36.95153211	198.658	226.1829197
8.84711	0.390273499	42.9918	41.45995062	198.685	227.0223037
9.30005	0.452401436	42.9957	41.45966565	198.696	226.5558511
9.30016	0.452012315	43.0197	41.60628719	200.09	228.1449719
9.30395	0.451290546	43.4464	42.38364161	200.114	227.9109852
9.46693	0.471684061	43.4495	42.39696438	200.138	227.7769934
9.46899	0.469829069	43.4667	42.46349811	214.465	239.1797017
9.4754	0.472629172	46.5643	48.31136788	214.493	239.0650675
10.1257	0.582583461	46.5688	48.34186504	214.522	238.8667516

Table S8. continued

T/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}	*T*/K	*Cp,m* / J·mol^{-1}·K^{-1}
10.1265	0.584791368	46.5814	48.43023662	216.289	240.1933893
10.1299	0.582375826	46.8079	48.71579793	216.297	240.4698052
10.1453	0.582060941	46.8126	48.72802097	216.323	240.6092675
10.1485	0.581892972	46.834	48.88596661	229.836	249.5090002
10.1559	0.583662052	49.9084	54.68452016	229.894	249.7256454
10.8797	0.72700267	49.9121	54.6591391	229.921	249.5498227
10.8819	0.724250652	49.9268	54.78046536	235.446	253.3171373
10.8886	0.725675234	50.9629	56.56913009	235.471	253.7096823
11.0237	0.761323559	50.9681	56.57979746	235.493	253.4349497
11.0259	0.763700563	50.9899	56.76679914	246.316	261.0492689
11.0278	0.762566949	53.4951	61.39515858	246.425	261.2653791
11.6539	0.913500026	53.4994	61.39383023	246.443	261.4539426
11.6569	0.911060275	53.512	61.46046816	256.3	267.6755814
11.6649	0.912242943	55.4893	65.03390073	256.355	267.8729372
12.0051	1.008934509	55.4957	65.03431096	256.382	267.7522441
12.0056	1.012206927	55.513	65.25174334	263.945	272.7383868
12.0096	1.007826618	57.3456	68.52404909	264.103	272.2735132
12.4871	1.149551188	57.3483	68.47821027	264.121	272.8437061
12.4905	1.146458185	57.3681	68.50472735	278.954	283.2311852
12.4984	1.148152446	60.4166	73.90336171	279.074	283.308661
13.0692	1.343293242	60.4233	73.91356371	279.086	283.4718088
13.0713	1.347461807	60.4504	74.07292343	282.836	285.6076899
13.0736	1.342690631	61.4796	75.81855305	283.061	285.0924918
13.3797	1.459738964	61.4851	75.86676979	283.08	285.4229218
13.3839	1.456452583	61.4983	75.93779843	303.075	296.1838631
13.3934	1.454595749	65.773	83.21817843	303.417	297.1374803
14.2265	1.789150641	65.7796	83.18687268	303.424	296.9384607
14.2276	1.798089664	65.8085	83.30061056	303.605	297.2891838
14.2326	1.789822414	65.9035	83.37107214	303.812	297.4948297
14.3499	1.840092345	65.912	83.34529633	303.821	297.4019128
14.352	1.835604687	65.929	83.41343247		
14.3591	1.837429748	70.6419	91.23963893		
15.3805	2.331225007	70.6476	91.27726108		