SUPPORTING INFORMATION (SI)

Thermodynamics and crystal chemistry of rhomboclase, $(H_5O_2)Fe(SO_4)_2 \cdot 2H_2O$, and the phase $(H_3O)Fe(SO_4)_2$

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Table S1. Initial composition of the charges used to determine solubility of ferric sulfate phases at room temperature. These charges were maintained at room temperature (22±3 °C) for 3 years. Sulfuric acid is 98 % H_2SO_4, ferric sulfate is X-ray amorphous powder with approximate composition $Fe_2(SO_4)_3 \cdot 6.75H_2O$.

sample	water (mL)	sulfuric acid (mL)	ferric sulfate (g)	sample	water (mL)	sulfuric acid (mL)	ferric sulfate (g)
TB-1	2.6729	0.060	4.2278	TB-12	3.3525	0.870	2.0520
TB-2	2.7766	0.200	3.8712	TB-13	3.3998	0.910	1.9338
TB-2-1	2.7860	0.208	3.8384	TB-14	3.4159	0.935	1.8740
TB-2-2	2.7973	0.217	3.8122	TB-15	3.4313	0.951	1.8180
TB-2-3	2.8056	0.226	3.7731	TB-16	3.4404	0.980	1.7487
TB-2-4	2.8170	0.236	3.7523	TB-17	3.4592	1.000	1.7010
TB-2-5	2.8281	0.245	3.7206	TB-18	3.4375	1.010	1.6986
TB-2-6	2.8361	0.253	3.6931	TB-19	3.4522	1.030	1.6350
TB-2-7	2.8456	0.265	3.6587	TB-20	3.4801	1.082	1.5255
TB-2-8	2.8566	0.272	3.6322	TB-21	3.4640	1.092	1.5221
TB-2-9	2.8660	0.281	3.6030	TB-22	3.5059	1.140	1.4069
TB-3	2.8746	0.290	3.5708	TB-23	3.5444	1.150	1.3494
TB-4	3.0183	0.417	3.2198	TB-24	3.5705	1.195	1.2314
TB-5	3.1061	0.520	2.9937	TB-25	3.5996	1.243	1.1079
TB-6	3.1587	0.620	2.6964	TB-26	3.6262	1.299	0.9934
TB-7	3.1931	0.678	2.5221	TB-27	3.6269	1.423	0.7611
TB-8	3.2946	0.711	2.4016	TB-28	3.6587	1.508	0.5893
TB-9	3.3161	0.760	2.2894	TB-29	3.6143	1.660	0.3470
TB-10	3.3307	0.790	2.2273	TB-30	3.5242	1.798	0.1732
TB-11	3.3393	0.843	2.1086				

Table S2. Initial composition of the charges used to determine solubility of ferric sulfate phases at near-freezing temperature. These charges were maintained at 4 °C for 5 years. Sulfuric acid is 98 % H_2SO_4, ferric sulfate is X-ray amorphous powder with approximate composition $Fe_2(SO_4)_3 \cdot 6.75H_2O$.

sample	water (mL)	sulfuric acid (mL)	ferric sulfate (g)
TB1-K	2.6745	0.055	4.2182
TB3-K	2.8795	0.305	3.5739
TB5-K	3.1017	0.525	2.9326
TB7-K	3.2239	0.680	2.5224
TB9-K	3.3184	0.765	2.2872
TB11-K	3.3327	0.840	2.1074
TB13-K	3.4036	0.909	1.9267
TB15-K	3.4286	0.950	1.8195
TB17-K	3.4557	0.999	1.6995
TB19-K	3.4562	1.039	1.6353
TB21-K	3.4664	1.095	1.4232
TB23-K	3.5433	1.149	1.3519
TB25-K	3.6016	1.250	1.1118
TB27-K	3.6243	1.429	0.7626
TB29-K	3.6145	1.650	0.3490

Comparison of the solubility calculation for hydronium jarosite using the Davies equation and the Pitzer model

Figure S1 compares the calculated solubility curves for hydronium jarosite, using the two activity-molality models. It contains the experimental data of Posnjak and Merwin (1922) and solubility of hydronium jarosite calculated by two different approaches. The first one is the application of the Pitzer model of Tosca et al. (2007). The second one is a calculation with the software suite PHREEQC (Parkhurst and Appelo 1999). PHREEQC uses the Davies equation for the calculation of activity coefficients. Admittedly, this equation is not applicable to some of the higher solution molalities plotted in Figure S1 but the goal was a crude test of the performance of the two models, not fine tuning of details. Solubility calculated by full speciation calculations by PHREEQC (using the Davies equation for activity coefficients) fits the experimental data much better than the Pitzer model. Just as for rhomboclase, we observe a distinct shift of the Pitzer-predicted solubility from the experimental data, a shift into the field of the aqueous phase. The Pitzer model predicts the phase diagram qualitatively in terms of its general topology, but the quantitative agreement with the available experimental data remains poor.

One can only speculate about the reasons for these discrepancies. The most likely cause lies in the speciation of Fe(III) and sulfate. The Pitzer model considers Fe^{3+}, SO_4^{2-}, HSO_4^-, and H^+ as the aqueous species. Speciation is calculated iteratively and the interaction parameters were fitted for these species. The calculations with PHREEQC, however, show that Fe^{3+} and SO_4^{2-} are minor to negligible species at all concentrations except for those at which no Pitzer model is needed. Instead, the entire area shown in Fig. S1 is dominated by $FeSO_4^+$ and $FeHSO_4^{2+}$ as the Fe(III) species. As for sulfate, HSO_4^- predominates essentially everywhere. The consideration of these species in a complicated model (such as the Pitzer model) will modify the actual ionic strength of the solutions for each $Fe_2(SO_4)_3$ and H_2SO_4 molality, and hence also the parametrization of the model. The uneasy task of the modification of the Pitzer model should be undertaken in the future, if a model with better performance should eventually be developed.

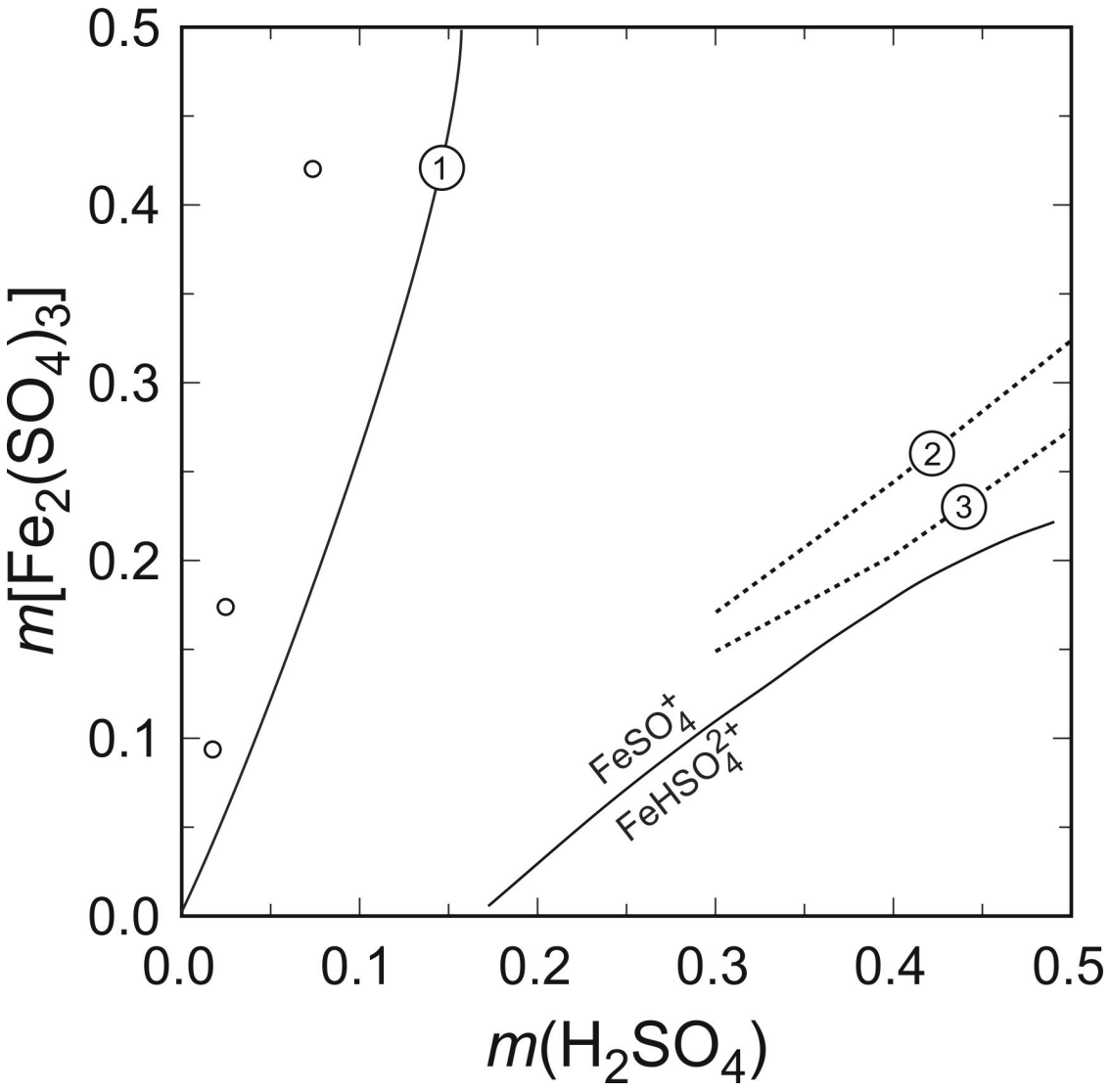

FIGURE S1. Experimental (circles, Posnjak and Merwin 1922, 50 ºC) and calculated solubilities for hydronium jarosite. Curve 1: calculation by the software PHREEQC (Parkhurst and Appelo 1999), curves 2,3: calculation with the Pitzer model (Tosca et al. 2007) with two different parametrizations of the model. The curve with the two Fe(III) species is the predominance boundary of the two species. The predominance fields of Fe^{3+} or other Fe(III) species are too small to be shown in this diagram.

Measurement and fitting of heat capacity data for rhomboclase

Heat capacity of a rhomboclase sample was measured by relaxation calorimetry. The data are summarized in Table S3. As discussed in the paper, there are severe issues with these data which invalidate them to be used for the calculation of entropy. Despite that, upon the request of the reviewer, we will briefly discuss the data and the fitting procedure. We discourage the use of the data for the derivation of thermodynamic quantities; the location of the magnetic transition at low temperature is probably reliable.

For fitting of the C_p data below (Table S3), a polynomial $A_2T^2 + A_4T^4 + A_5T^5$ was found to be the best. The usual Debye polynomial (A_3T^3) or extended Debye polynomials ($A_3T^3 + A_5T^5 + \ldots$) did not perform well at all. Other polynomials, such as $A_1T + A_2T^2 + A_3T^3$, fitted the data well but plunged below zero (i.e., having negative heat capacity) between the data point with the lowest temperature and T = 0 K. The adjustable fit constants were A_2 = 0.0642737088683, A_4 = 0.02652140004, and A_5 = –0.00474192604081.

For the rest of the data, entropy was calculated by numerical integration, that is, simple addition of trapezoids below the measured data points.

Table S3. Heat capacity data, measured for rhomboclase by relaxation calorimetry in Salzburg (molecular mass 321.03 g·mol^{-1}). Temperature (T) in K, heat capacity (C_p) in J·K^{-1}·mol^{-1}.

T	C_p	T	C_p	T	C_p
2.02936	0.478404	9.35509	12.4174	43.4844	54.1665
2.20993	0.619116	9.38423	12.6337	47.3118	61.6923
2.40796	0.794798	9.63708	15.1374	51.4744	69.7081
2.62108	1.00412	9.88229	14.5362	56.0194	78.0803
2.85357	1.24993	10.137	11.4927	60.9518	87.7601
3.10623	1.54468	10.1775	11.369	66.3257	96.9532
3.38643	1.8912	10.3902	10.9026	72.1684	107.496
3.6846	2.2638	10.6428	10.5602	78.493	118.287
4.00939	2.67478	10.8956	10.3329	85.4014	129.288
4.36405	3.12648	11.0778	10.2123	92.9166	141.948
4.74998	3.60269	11.1482	10.1722	101.078	155.308
5.1699	4.11007	11.2561	10.1554	109.992	168.972
5.627	4.68991	12.2502	9.66278	119.68	184.9
6.13012	5.32562	13.3283	9.48185	130.228	201.719
6.67389	6.03284	14.5022	9.59019	141.718	219.511
7.10413	6.63156	15.7814	10.114	154.278	240.96
7.25699	6.85195	17.1714	11.0322	167.83	260.642
7.35752	7.02592	18.6841	12.3673	182.682	277.423
7.61062	7.42826	20.329	14.0904	198.75	290.055
7.86347	7.87388	22.119	16.4224	216.218	304.325
7.89874	7.92861	24.0674	19.2722	235.233	318.568
8.11664	8.36093	26.1899	22.6617	255.879	334.717
8.36967	8.90483	28.4972	26.1836	278.172	357.458
8.59826	9.44914	31.0118	30.5314	301.822	395.891
8.62288	9.53177	33.7455	35.5319		
8.87629	10.2817	36.7235	41.0953		
9.12994	11.2571	39.9639	47.4717		