

Thermodynamics, crystal chemistry and structural complexity of the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases: $\text{Fe}(\text{SO}_4)(\text{OH})$, metahohmannite, butlerite, parabutlerite, amarantite, hohmannite, and fibroferrite

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Abstract: Using combination of acid-solution, high-temperature oxide-melt, relaxation, and differential scanning calorimetry, we have determined the thermodynamic properties of all phases in the system $\text{Fe}(\text{SO}_4)(\text{OH})\text{--H}_2\text{O}$ (estimated values in parentheses):

	x in $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$	$\Delta_f H^\circ$ (kJ·mol ^{−1})	S° (J·K ^{−1} ·mol ^{−1})	$\Delta_f G^\circ$ (kJ·mol ^{−1})	log K_{sp}
$\text{Fe}(\text{SO}_4)(\text{OH})$	0	-1160.2 ± 2.3	145.9 ± 1.2	-1013.7 ± 2.4	−2.862
Metahohmannite	1.5	-1608.2 ± 1.7	(200.3)	-1373.6 ± 1.8	−3.594
Butlerite	2	-1758.0 ± 1.7	(214.0)	-1492.7 ± 1.8	−3.685
Parabutlerite	2	-1758.6 ± 1.7	214.0 ± 1.4	-1493.3 ± 1.8	−3.799
Amarantite	3	-2056.5 ± 1.8	243.8 ± 1.9	-1730.5 ± 1.9	−3.801
Hohmannite	3.5	-2197.8 ± 1.8	(271.4)	-1845.3 ± 1.9	−3.138
Fibroferrite	5	-2641.5 ± 1.8	332.2 ± 2.7	-2202.8 ± 2.0	−3.456

Using these data, phase diagrams for low-temperature (25 °C) systems in contact with aqueous solutions predict that these phases should precipitate from extremely concentrated, low-pH solutions. In a relative humidity–temperature space, only $\text{Fe}(\text{SO}_4)(\text{OH})$, parabutlerite, and amarantite have stability fields; the higher hydrates would require unrealistically high air humidities to form as stable phases. High-temperature high-pressure phase diagrams produce reasonable topologies, although the details of the phase relations between $\text{Fe}(\text{SO}_4)(\text{OH})$, $\text{Fe}_2(\text{SO}_4)_3$, and hydronium jarosite deserve more work. We also present a new structural model for amarantite, including the positions of the H atoms, and an analysis of the hydrogen bonding network in this mineral. Using the concept of information density in minerals, the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases were analyzed. This analysis lends some validity to the premise that more complex structures are also the more stable ones, but other systems should be investigated to test these trends.

Key-words: thermodynamic properties; crystal chemistry; structural complexity; butlerite; parabutlerite; amarantite; hohmannite; fibroferrite; ferric iron sulfate hydroxide; ferric iron sulfate hydroxyhydrate.

1. Introduction

The crystalline phases in the $\text{Fe}(\text{SO}_4)(\text{OH})\text{--H}_2\text{O}$ system are characterized by large structural variations based on simple building blocks. Ferric iron is coordinated octahedrally and sulfur in its hexavalent state tetrahedrally. These coordination polyhedra combine in a number of ways into the structures of the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases whose mineral names and formulae are listed in Table 1. Many of these phases bear some relevance for acid-mine drainage (AMD) systems, as briefly described below. These phases, in

addition, offer a possibility to explore and link thermodynamic and crystal-chemical properties because of their close structural relationship (Scordari, 1981).

The $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases, as most ferric iron sulfates, occur as weathering products of pyrite or pyrrhotite, either in acid-rock drainage or AMD systems. They may be accompanied by other minerals, such as hydronium jarosite or ferricopiapite. Minerals of the jarosite or copiapite groups are much more common at the AMD sites and the reason for this is unknown. It could be of a thermodynamic nature for the pure ferric sulfate

Table 1. Phases used in this study. For some minerals, two formulae with chemically identical content are given. The first one is the formula recognized by the International Mineralogical Association (IMA) for this mineral, the second one is in the format $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ for easier comparisons.

Mineral	Formula	Associated minerals	Locality
Metahohmannite	$\text{Fe}(\text{SO}_4)(\text{OH})$	Botryogen, copiapite	Synthetic
	$\text{Fe}_2\text{O}(\text{SO}_4)_2(\text{H}_2\text{O})_4$		Made by dehydration of natural hohmannite
	$\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_{1.5}$		
Butlerite	$\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_2$	Copiapite	Nuevo Cuyo, Argentina
Parabutlerite	$\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_2$		Mina Santa Elena, La Alcaparrosa, Calingasta, San Juan, Argentina
Amarantite	$\text{Fe}_2\text{O}(\text{SO}_4)_2(\text{H}_2\text{O})_7$	Chalcanthite, copiapite	Mina Quetana, Chuquicamata, Calama, II Region, Atacama desert, Chile
Hohmannite	$\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_3$	Copiapite, amarantite	Copiapó, Atacama desert, Chile
	$\text{Fe}_2\text{O}(\text{SO}_4)_2(\text{H}_2\text{O})_8$		
	$\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_{3.5}$		
Fibroferrite	$\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_5$	Iron oxides	Plaka, Laurion, Greece

compositions, or given by additional elements which are required by and stabilize many jarosite- or copiapite-group minerals.

The $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases play also a major role in the current controversy (Gomez *et al.*, 2013; Mikutta *et al.*, 2013; Paktunc & Manceau, 2013; Wang *et al.*, 2016) related to the local structure of X-ray amorphous hydrous ferric arsenates (HFA). It has been determined that $\text{Fe}(\text{SO}_4)(\text{OH})$ accepts large amount of As^{5+} in its structure on the S^{6+} position (Paktunc *et al.*, 2013). Based on this capability and evaluation of different types of spectra, some authors assume that the X-ray amorphous HFA, a common carrier of arsenic in strongly polluted AMD systems, has a chain structure similar to that in butlerite. Others, however, argue that the local structure of HFA is similar to that of scorodite, partially also because HFA is known to convert to scorodite with time.

In this work, we have determined thermodynamic properties of the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases; the overall uncertainty of the final data reflect the ease or difficulty to obtain phase-pure material. Furthermore, the crystal structure of amarantite is reported here, including the position of the H atoms, not given in the earlier refinements. The structures of butlerite and parabutlerite were also determined but will be described in a separate contribution because they are at variance with previous work. The details of the crystal structure of fibroferrite were recently reported by Ventruti *et al.* (2016b). We attempted to correlate the complexities of the structures with their stability by using the concept of information density of minerals (Krivovichev, 2013, 2014). Phase diagrams presented in the paper display graphically the stability or metastability relations among the studied and related minerals.

2. Materials

The $\text{Fe}(\text{SO}_4)(\text{OH})$ sample was synthesized by mixing 3.0 g of $\text{Fe}_2(\text{SO}_4)_3(\text{H}_2\text{O})_n$ ($n \sim 6$) and 10 mL of H_2O (after Posnjak & Merwin, 1922). The solution was placed in a Teflon-lined Parr bomb and maintained at 200 °C for

2 days. The yellow solid was separated from the remaining liquid by filtration, washed several times with deionized water, and dried at room temperature.

Samples of all other $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases (*i.e.*, for $x > 0$) used in this study were natural. They were all purchased from mineral collectors or acquired from collections, disintegrated and separated from other minerals under binocular microscope. Every batch used for calorimetry or chemical analyses was checked separately by powder X-ray diffraction (pXRD). Associated minerals were also separated and identified by pXRD. The localities of origin of the samples used in this work are listed in Table 1.

No natural metahohmannite sample could be located. We have therefore converted a small amount of hohmannite to metahohmannite by heating the sample at 120 °C for 2 h in a Pt crucible.

3. Methods

pXRD analyses were conducted with a Bruker D8 Advance diffractometer (Institute of Geoscience of the University of Jena, Germany) in the angular range of 5°–90° 2 θ at room temperature. The step size was set to 0.01° 2 θ and dwell to 1 s per step. In order to reduce the noise of the Fe fluorescence excited by the Cu emission radiation from the iron-rich samples, the energy window of the Lynxeye detector was set to 0.18–0.25 V.

Variable-temperature pXRD data were collected with the same instrument equipped with a temperature stage CHC+ Plus Cryo & Humidity Chamber (Anton-Paar GmbH, Graz, Austria) fitted with a platinum heater. A Pt 100 temperature sensor was integrated in the sample holder for accurate measurement and control of the temperature. The *in situ* high-temperature (high-*T*) diffraction data were collected either in air from 20 to 300 °C or in vacuum from 20 to 400 °C, in both cases with a temperature step of 20 °C. The high-*T* XRD patterns were measured from 5° to 60° 2 θ , with a step of 0.02° 2 θ and counting time of 2.5 s per step. All data sets were processed with a full-profile refinement, using the program GSAS (Larson & von Dreele, 1994).

Table 2. Crystal data, collection and refinement parameters for amarantite.

Structural formula	$\text{Fe}_4\text{H}_{28}\text{O}_{32}\text{S}_4$
Unit-cell parameters	$a = 6.6599(5) \text{ \AA}$ $b = 8.9161(8) \text{ \AA}$ $c = 11.6069(8) \text{ \AA}$ $\alpha = 97.221(6)^\circ$ $\beta = 95.655(6)^\circ$ $\gamma = 90.412(6)^\circ$
$V (\text{\AA}^3)$	$679.89(9) \text{ \AA}^3$
Z	1
Space group	$P\bar{1}$
$D_{\text{calc.}} (\text{g}\cdot\text{cm}^{-3})$	2.178
Temperature	296 K
Wavelength	$\text{MoK}\alpha$, 0.71075 $\text{\AA}$
Crystal dimensions	$0.082 \times 0.031 \times 0.012 \text{ mm}^3$
Limiting θ angles	$3.98\text{--}27.85^\circ$
Limiting Miller indices	$-8 \leq h < 8$, $-11 \leq k \leq 11$, $-15 \leq l \leq 15$
No. of reflections	10 531
No. of unique reflections	2986
No. of observed reflections (criterion)	2034 [$I > 3\sigma(I)$]
Absorption correction (mm^{-1}), method	2.52, multi-scan
$T_{\text{min}}/T_{\text{max}}$	0.67326/1
Completeness to θ_{max} , R_{int}	0.98, 0.065
F_{000}	458
<i>Refinement by Jana2006 on F^2</i>	
Param. refined, constraints, restraints	223, 14, 14
R , wR (obs.)	0.0394, 0.0814
R , wR (all)	0.0728, 0.0949
GOF (obs., all)	1.25, 1.18
Weighting scheme	$1/(\sigma^2(I) + 0.0005827396I^2)$
$\Delta\rho_{\text{min}}$, $\Delta\rho_{\text{max}} (\text{e \AA}^{-3})$	−0.82, 0.84

In order to elucidate positions of the H-atoms in the structure of amarantite, a single-crystal X-ray study was done on a $0.082 \times 0.031 \times 0.012 \text{ mm}^3$ fragment of prismatic crystal using an Rigaku/Oxford Diffraction SuperNova single-crystal diffractometer equipped with Atlas S2 detector and employing the mirror-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) from a micro-focus X-ray tube, providing a high-flux brilliant beam. Correction for background, Lorentz effect and polarization was applied to the data during reduction in the CrysAlis package (Rigaku). The correction for absorption was done using spherical harmonics in CrysAlis program, giving the R_{int} of the dataset equal to 0.065. The structure was refined by Jana2006 software (Petříček *et al.*, 2014) starting from the atomic coordinates taken from Süsse (1968). The positions of hydrogen atoms were localized from the difference-Fourier maps and refined keeping soft constraints of 0.94 (4) $\text{\AA}$ on the O–H distances and with the U_{iso} of each H set to 1.2 times that of the donor O atom. The final refinement including 223 parameters, 14 restraints and 14 constraints smoothly converged to $R = 0.0394$, $wR = 0.0814$ for 2034

unique observed reflections, having $I > 3\sigma(I)$, with GOF = 1.25. Crystallographic details, data collection and refinement parameters are given in Table 2. Atom coordinates and displacement parameters are listed in Table 3. The bond-valence analysis (after Brown, 1981, 2002; Brown & Altermatt, 1985), based on refined interatomic distances (Table 4) is provided in Table 5. The crystallographic information file (CIF) and the structure factors list were deposited and are freely available as Supplementary Material linked to this article on the GSW website of the journal: <http://eurjmin.geoscienceworld.org/>.

The information content of the studied phases was calculated with the program TOPOS (Blatov *et al.*, 2014). The information content is a measure of complexity of a given structure related to the concept of Shannon entropy. Further details and examples of the calculation of information content for crystal structures were given by Krivovichev (2014), who argued that this variable performs better than other, similar measures of structural complexity proposed earlier.

Polished thin sections were prepared from selected samples. In all steps of preparation, water as a solvent was excluded because many of the iron sulfates and the associated minerals are water-soluble. The sections were inspected in transmitted polarized light and the minerals were chemically analyzed by an electron microprobe (see below). Some of the sections, however, were impossible to analyze. Despite repeated coating with carbon, they would charge so much in the electron microprobe that it was impossible to image or analyze them. The reason for this behavior is not clear; for some of the natural sulfates, we had to analyze them by wet-chemical methods.

The chemical composition of butlerite, parabutlerite, and hohmannite in thin sections was determined by electron microprobe analysis using a JEOL JXA-8230 at the University of Jena. The operating conditions were set to an accelerating voltage of 15 kV and a beam current of 15 nA. The wavelength dispersive X-ray spectrometers were used to measure the elements and X-ray lines of Mg ($K\alpha$), Al ($K\alpha$), S ($K\alpha$), Ca ($K\alpha$), Fe ($K\alpha$), Zn ($K\alpha$), Mn ($K\alpha$) and As ($L\alpha$). To improve the count-rate statistics the counting times were 30 s on each peak and 15 s on the background. The standard specimens used for calibration were MgO for Mg, Al_2O_3 for Al, apatite for Ca, barite for S, Fe_2O_3 for Fe, ZnS for Zn, rhodonite for Mn and InAs for As. Peak overlap correction was used to avoid peak interference between the lines of Mg and As. The detection limits, calculated from the peak and background counts, the measurement time, the current and the standard material concentration, are (all in wt%) 0.03 for Mg, 0.04 for Ca, 0.02 for Al, 0.01 for Fe, 0.04 for S, 0.04 for Mn, 0.02 for As and 0.02 for Zn.

For the chemical analyses of natural amarantite and fibroferite and the powdery synthetic $\text{Fe}(\text{SO}_4)(\text{OH})$ sample, a small amount of each of them was dissolved in ultrapure HNO_3 and analyzed by inductively-coupled plasma optical emission spectrometry (ICP-OES), using the Variant 725 ICP-OES instrument with a charge-couple device detector.

Table 3. Atom fractional coordinates, equivalent and anisotropic displacement parameters for amaranthite.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U_{iso}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.14403(9)	0.91270(8)	0.93600(5)	0.0132(2)	0.0117(3)	0.0165(4)	0.0115(3)	0.0008(3)	0.0015(2)	0.0016(3)
Fe2	0.22511(9)	0.92593(8)	0.23675(5)	0.0144(2)	0.0130(3)	0.0194(4)	0.0113(3)	0.0009(3)	0.0011(2)	0.0038(3)
S1	0.07893(16)	0.83257(14)	0.65069(9)	0.0158(4)	0.0144(6)	0.0217(7)	0.0112(5)	0.0011(5)	0.0013(4)	0.0012(5)
S2	0.44595(16)	0.21124(13)	0.93214(9)	0.0137(3)	0.0115(5)	0.0163(6)	0.0141(5)	0.0009(4)	0.0017(4)	0.0043(5)
O1	0.0350(5)	0.0253(4)	0.3418(3)	0.0211(11)	0.0214(17)	0.024(2)	0.0198(16)	0.0063(14)	0.0067(13)	0.0075(15)
O2	0.0485(5)	0.2928(4)	0.4062(3)	0.0281(12)	0.034(2)	0.026(2)	0.0210(18)	−0.0068(16)	−0.0075(15)	−0.0025(16)
O3	0.1462(4)	0.8023(4)	0.7722(2)	0.0166(10)	0.0206(17)	0.0181(19)	0.0108(15)	0.0017(14)	0.0016(12)	0.0001(14)
O4	0.2589(5)	0.8528(4)	0.5923(3)	0.0261(12)	0.0170(17)	0.048(3)	0.0163(16)	0.0074(16)	0.0073(13)	0.0090(17)
O5	0.4328(4)	0.8314(4)	0.9619(2)	0.0166(10)	0.0138(16)	0.0222(19)	0.0145(15)	0.0037(13)	0.0010(12)	0.0056(14)
O6	0.4175(4)	0.7816(4)	0.1604(2)	0.0157(10)	0.0154(16)	0.0193(19)	0.0142(15)	0.0004(13)	0.0049(12)	0.0061(14)
O7	0.3528(5)	0.3552(4)	0.9589(3)	0.0210(11)	0.0238(18)	0.0182(19)	0.0228(17)	0.0079(14)	0.0081(14)	0.0052(15)
O8	0.2915(4)	0.0919(4)	0.8899(3)	0.0194(10)	0.0167(16)	0.0196(19)	0.0227(17)	−0.0063(14)	−0.0013(13)	0.0083(15)
O9	0.1115(4)	0.9863(3)	0.0956(2)	0.0146(10)	0.0128(16)	0.0188(19)	0.0125(15)	−0.0016(13)	0.0021(12)	0.0025(14)
O10	0.3981(5)	0.5349(4)	0.7773(3)	0.0306(13)	0.039(2)	0.026(2)	0.027(2)	0.0032(17)	0.0012(17)	0.0049(18)
O11	0.3928(5)	0.8836(4)	0.3862(3)	0.0264(12)	0.0200(18)	0.046(2)	0.0152(17)	0.0095(16)	0.0030(14)	0.0093(17)
O12	0.0478(5)	0.7379(4)	0.2323(3)	0.0246(12)	0.0170(18)	0.024(2)	0.036(2)	0.0009(15)	0.0090(15)	0.0087(17)
O13	0.2625(5)	0.2812(4)	0.6259(3)	0.0295(13)	0.028(2)	0.034(2)	0.0242(19)	0.0016(18)	−0.0042(15)	0.0025(17)
O14	0.0283(5)	0.7042(4)	0.9598(3)	0.0222(11)	0.0239(19)	0.024(2)	0.0200(18)	−0.0040(15)	0.0076(14)	0.0029(16)
O15	0.1860(5)	0.4559(4)	0.2330(3)	0.0324(13)	0.025(2)	0.030(2)	0.044(2)	0.0002(17)	0.0046(18)	0.0111(19)
O16	0.4073(5)	0.1145(4)	0.2519(3)	0.0198(11)	0.0148(17)	0.026(2)	0.0184(17)	−0.0043(14)	−0.0006(13)	0.0058(15)
H1	0.349(7)	0.895(6)	0.460(2)	0.0317 ^a						
H2	0.513(5)	0.833(5)	0.387(4)	0.0317 ^a						
H3	0.111(7)	0.650(4)	0.248(4)	0.0295 ^a						
H4	−0.051(5)	0.746(6)	0.283(3)	0.0295 ^a						
H5	0.319(7)	0.619(4)	0.782(4)	0.0367 ^a						
H6	0.388(8)	0.500(6)	0.848(3)	0.0367 ^a						
H7	0.193(7)	0.306(6)	0.559(3)	0.0354 ^a						
H8	0.300(8)	0.375(3)	0.667(4)	0.0354 ^a						
H9	−0.060(6)	0.659(5)	0.899(3)	0.0266 ^a						
H10	−0.043(6)	0.691(6)	1.021(3)	0.0266 ^a						
H11	0.326(3)	0.464(6)	0.234(4)	0.0388 ^a						
H12	0.151(7)	0.402(6)	0.291(4)	0.0388 ^a						
H13	0.447(6)	0.143(5)	0.186(3)	0.0237 ^a						
H14	0.524(4)	0.109(6)	0.300(3)	0.0237 ^a						

^a Atoms refined with isotropic displacement parameter are set to $1.2 \cdot U_{eq}$ of the parent O atoms.

For the solution calorimetric experiments at $T = 25^\circ\text{C}$, we used a commercial IMC-4400 isothermal microcalorimeter (Calorimetry Sciences Corporation) which we modified for the purposes of acid-solution calorimetry. The liquid bath of the calorimeter was held at a constant temperature of 298.15 K with fluctuations smaller than 0.0005 K. The calorimetric solvent was 25 g of deionized water or 25 g of 5 N HCl contained in a polyetheretherketone (PEEK) cup with a total volume of 60 mL. The cup was then closed with a PEEK screw lid and inserted into the calorimeter well. The calorimeter stabilized after ~8 h. During the stabilization and the experiment, the solvent was stirred by a SiO₂ glass stirrer by a motor positioned about 40 cm from the active zone of the instrument. The samples were pressed into a pellet and weighed on a micro-balance with a precision of 0.002 mg (as stated by the manufacturer). The pellets were then dropped through an SiO₂ glass tube into the solvent and the heat produced or consumed during the dissolution was measured. The heat flow between the reaction cup and the constant-temperature reservoir was then integrated to calculate the caloric effect. A typical experiment lasted 50–60 min and

the end of the experiment was judged from the return of the baseline to the pre-experiment position. The pellet mass of each measured phase was calculated according to the stoichiometry of the thermochemical cycle. The calorimeter was calibrated by dissolving ~20 mg pellets of KCl in 25 g of deionized water. Prior to each calibration measurement the potassium chloride was heated overnight in the furnace at 800 K to remove adsorbed water. The expected heat effect for the calibration runs was calculated from [Parker \(1965\)](#).

Heat capacity was measured by relaxation calorimetry using a commercial Physical Properties Measurement System (from Quantum Design, San Diego, California) at the University of Salzburg, Austria. With due care, accuracy can be within 1% for 5–300 K, and 5% for 0.7–5 K ([Kennedy *et al.*, 2007](#)). Powdered samples were wrapped in a thin Al foil and compressed to produce a ~0.5 mm thick pellet, which was then placed onto the sample platform of the calorimeter for measurement. The heat capacity between 280 and 300 K was measured by differential scanning calorimetry (DSC) using a Perkin Elmer Diamond DSC. Details of the method are described in [Benisek *et al.* \(2012\)](#).

Table 4. Selected interatomic distance (all in Å) and angles (in °) in the structure of amaranthite.

Fe1–O3	2.030(3)	Fe2–O1 ⁱⁱ	1.980(3)
Fe1–O5	2.067(3)	Fe2–O6	2.010(3)
Fe1–O8 ⁱⁱ	2.024(3)	Fe2–O9	1.878(3)
Fe1–O9 ⁱⁱ	1.920(3)	Fe2–O11	2.046(3)
Fe1–O9 ^{iv}	1.955(3)	Fe2–O12	2.036(4)
Fe1–O14	2.068(4)	Fe2–O16 ⁱⁱ	2.045(3)
⟨Fe1–O⟩	2.011	⟨Fe2–O⟩	1.999
S1–O1 ^v	1.479(3)	S2–O5 ^{vii}	1.494(3)
S1–O2 ^v	1.448(3)	S2–O6 ^{vi}	1.481(3)
S1–O3	1.495(3)	S2–O7	1.441(3)
S1–O4	1.454(3)	S2–O8	1.477(3)
⟨S1–O⟩	1.469	⟨S2–O⟩	1.473
H-bonds			
	<i>D–H</i>	<i>H...A</i>	⟨ <i>D–H...A</i> ⟩
O11–H1...O4	0.93(3)	1.78(4)	162(5)
O11–H2...O13 ^{vi}	0.93(4)	1.82(4)	174(4)
O12–H3...O15	0.92(4)	1.80(3)	161(4)
O12–H4...O13 ^v	0.92(4)	1.88(4)	168(5)
O10–H5...O3	0.92(4)	2.01(4)	174(5)
O10–H6...O7	0.92(4)	1.97(5)	159(4)
O13–H7...O2	0.91(4)	1.93(3)	162(5)
O13–H8...O10	0.93(3)	1.86(4)	166(4)
O14–H9...O15 ^v	0.92(3)	1.86(4)	167(4)
O14–H10...O7 ^{viii}	0.91(4)	2.14(4)	135(3)
O15–H11...O10 ^{vi}	0.93(2)	1.85(2)	174(5)
O15–H12...O2	0.93(5)	1.92(5)	174(4)
O16–H13...O5 ^{vi}	0.90(4)	2.00(4)	169(4)
O16–H14...O4 ^{vi}	0.92(3)	1.82(3)	165(4)

Symmetry codes: (i) $-x, -y+2, -z+2$; (ii) $x, y+1, z$; (iii) $x, y, z+1$; (iv) $-x, -y+2, -z+1$; (v) $-x, -y+1, -z+1$; (vi) $-x+1, -y+1, -z+1$; (vii) $-x+1, -y+1, -z+2$; (viii) $-x, -y+1, -z+2$; (ix) $x, y-1, z$; (x) $-x+1, -y, -z+1$; (xi) $-x, -y+2, -z$; (xii) $x, y, z-1$; and (xiii) $-x+1, -y+2, -z+1$.

Table 5. Bond-valence analysis of the amaranthite crystal structure.

	Fe1	Fe2	S1	S2	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10	H11	H12	H13	H14	ΣBV
O1		0.55	1.48																2.03
O2			1.61								0.24					0.24			2.09
O3	0.48		1.42						0.22										2.12
O4			1.58		0.28													0.26	2.12
O5	0.43			1.42													0.22		2.07
O6		0.51		1.47															1.98
O7				1.64						0.23				0.19					2.06
O8	0.49			1.49								0.25			0.26				1.98
O9	0.65, 0.59	0.72																	1.96
O10									0.69	0.69						0.26			1.89
O11		0.46			0.68	0.68													1.82
O12		0.47					0.69	0.69											1.85
O13						0.26		0.25			0.70	0.68							1.89
O14	0.43												0.69	0.70					1.92
O15							0.27						0.25		0.68	0.68			1.88
O16		0.46															0.70	0.69	1.95
ΣBV	3.07	3.18	6.09	6.02	0.96	0.94	0.96	0.94	0.91	0.92	0.94	0.93	0.94	0.89	0.94	0.92	0.92	0.95	

All values are given in valence units (vu). Bond-valence parameters taken from [Brown & Altermatt \(1985\)](#) (for $\text{Fe}^{3+}\text{--O}$, $\text{S}^{6+}\text{--O}$) and from [Brown \(2002\)](#) ($\text{H}^+\text{--O}$).

High-temperature oxide melt calorimetry has been described in detail by [Navrotsky \(1997\)](#). The evaluation of experimental data requires empirical calibration, using

~15 mg pellets of $\alpha\text{-Al}_2\text{O}_3$ (Alfa Aesar, 99.997 wt% metals basis). The samples, in the form of ~15 mg pellets, were dissolved in the calorimetric solvent ($3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$) at

Table 6. Chemical composition, lattice parameters, and calculated information content (Blatov *et al.*, 2014) of $\text{Fe}(\text{SO}_4)(\text{OH})$ and the natural $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases used in this work (minerals are labeled by the first three letters of their name). n = number of averaged EMP analyses.

	$\text{Fe}(\text{SO}_4)(\text{OH})$	Ama	Fib	But	Par	Hoh	Met
n				7	12	3	
MgO	0.0	0.0	0.0	0.0	0.0	0.0	
As ₂ O ₅	0.0	0.0	0.0	0.0	0.0	0.0	
Al ₂ O ₃	0.0	0.1	0.1	0.1	0.0	0.0	
SO ₃	48.7	35.2	30.8	42.4	39.3	30.4	
CaO	0.1	0.1	0.1	0.0	0.0	0.0	
MnO	0.0	0.0	0.0	0.0	0.0	0.0	
Fe ₂ O ₃	48.1	35.9	31.4	39.5	35.9	37.4	
ZnO	0.0	0.0	0.0	0.0	0.0	0.0	
Total	96.9	71.3	62.4	82.0	75.2	67.9	
Space group	<i>Pnma</i>	$P\bar{1}$	$R\bar{3}$	$P2_1/m$	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.3312(4)	8.935(3)	24.153(6)	6.5246(9)	36.980(5)	9.140(3)	7.297(7)
b (Å)	6.4185(4)	11.610(4)		7.3698(7)	20.0629(34)	10.932(3)	9.741(9)
c (Å)	7.1345(4)	6.742(2)	7.637(2)	5.8545(8)	7.2261(14)	7.2056(15)	7.108(5)
α (°)		95.84(3)				90.503(19)	91.62(5)
β (°)		90.43(2)		108.59(1)		90.524(19)	98.46(5)
γ (°)		97.22(4)				107.42(1)	86.22(6)
V (Å ³)	335.72(3)	690.1(4)	3858.3(4)	266.8(3)	5361.3(15)	686.84(31)	498.6(8)
Starting model	Johansson	Süsse	Scordari	Fanfani <i>et al.</i>	Borene	Scordari	Scordari <i>et al.</i>
	1962	1968	1981	1971	1970	1978	2004
<i>Information content without H atoms</i>							
ν (atoms)	32	41	73	20	76	43	34
I_G (bits/atom)	2.75	4.382	3.64	2.922	3.722	4.45	4.087
$I_{G,\text{total}}$ (bits/unit-cell)	88.00	179.66	265.74	58.439	282.842	191.329	138.974
<i>Information content with H atoms</i>							
ν (atoms)		68	108	24	96		
I_G (bits/atom)		5.087	4.170	3.252	4.002		
$I_{G,\text{total}}$ (bits/unit-cell)		345.95	450.35	78.04	384.16		

975 K. The measured heat effect is the heat of drop solution (ΔH_{dsol}), that is, the sum of heat content ($H_{975} - H_{298}$) and heat of solution (ΔH_{sol}) at 975 K. To expel the water vapor evolved from the sample during dissolution in the calorimetric solvent, the calorimetric assembly was flushed with argon (65 mL/min).

4. Results and discussion

All samples used for calorimetric experiments in this study were crystalline, with sharp pXRD peaks. No X-ray amorphous impurity was discernible from the pXRD patterns or visible optically under a binocular microscope (as rusty coatings or grains in the natural samples). Only phase-pure portions of the samples, hand-picked under a binocular microscope, were used for the calorimetric experiments. The refined lattice parameters of all phases are listed in Table 6.

The natural $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases turned out to be surprisingly chemically pure. They contained only trace amounts of oxide components other than Fe_2O_3 and SO_3 , as determined either by electron microprobe or ICP-OES analyses (Table 6).

4.1. Variable-temperature pXRD

The thermal behavior of hohmannite and fibroferrite were recently investigated in detail by Ventrucci *et al.* (2015a, 2016a), respectively, and there is no reason to repeat these experiments. We did, however, explore the thermal behavior of butlerite, parabutlerite, and amarantite. The reason for these experiments was the hypothesis that, if one of the polymorphs (butlerite and parabutlerite) is metastable with respect to the other, it could transform to the stable polymorph before other structural changes or dehydration could take place. Another question was to which one of these polymorphs would amarantite transform upon partial dehydration. This qualitative information could support the quantitative calorimetric data.

Butlerite and parabutlerite were heated to 400 °C in vacuum by steps of 20 °C and the results are graphically shown in Figs. 1 and 2. In either case, no transformation between butlerite and parabutlerite was observed. Instead, both phases persist to 160–200 °C, with a gradual loss of crystallinity. Some of the smaller XRD peaks disappear completely, the stronger ones broaden and the uncertainties related to the refined lattice parameters increase. The samples amorphize at temperatures above 200 °C, para-

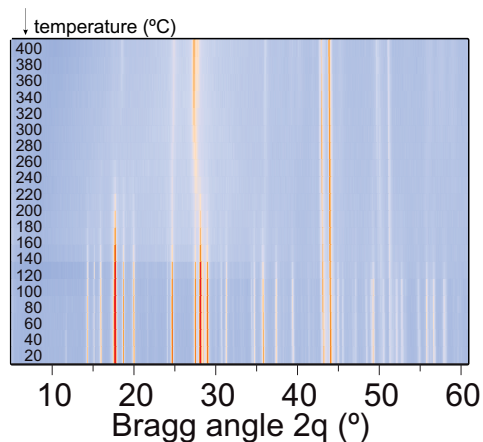


Fig. 1. Evolution of the powder XRD pattern during heating of butlerite from 20 to 400 °C in vacuum, with the intensities at each Bragg angle encoded by colors (blue = low intensities, red = high intensities). Note that the sample amorphizes at temperatures between 200 and 260 °C. At higher temperature, the phase $\text{Fe}(\text{SO}_4)(\text{OH})$ crystallizes. Two strong peaks between 43° and 45° 2θ and several weaker peaks at higher Bragg angles originate from diffraction from the holder material.

butlerite persists to somewhat higher temperatures than butlerite, indicating perhaps that parabutlerite may be the more stable polymorph. At temperatures near 300 °C, broad peaks of the phase $\text{Fe}(\text{SO}_4)(\text{OH})$ appear and sharpen slightly up to 400 °C. No other phase transformations were observed. Further phase transformations, up to 800 °C, are documented in [Ventruti *et al.* \(2015a\)](#), their Fig. 12 and associated text).

The thermal behavior of amaranite (Fig. 3) was also studied. Amaranite dehydrates neither to butlerite nor to parabutlerite but to metahohmannite instead. Given the close structural relationship between amaranite and hohmannite (*cf.* [Hawthorne *et al.*, 2000](#)), this dehydration path could have been expected. This transformation takes place between 60 and 80 °C and seems to be accompanied by partial amorphization of the sample. At ~160 °C, the XRD peaks of metahohmannite disappear and are gradually replaced by the peaks of $\text{Fe}(\text{SO}_4)(\text{OH})$.

The transformation sequences of the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases are summarized in Fig. 4. The highest hydrate, fibroferrite, dehydrates through a series of phases unknown from Nature to butlerite and $\text{Fe}(\text{SO}_4)(\text{OH})$. Amaranite and hohmannite initially transform to metahohmannite and then eventually to $\text{Fe}(\text{SO}_4)(\text{OH})$.

4.2. Solution calorimetry and enthalpies of formation

Two types of solution calorimetry were used because the phase $\text{Fe}(\text{SO}_4)(\text{OH})$ dissolved so sluggishly in the acid that the data were unusable. Dissolution of $\text{Fe}(\text{SO}_4)(\text{OH})$ in 5 N HCl dragged on for several hours and the calorimetric baseline did not return to its original position for a long time. Even after 8 h, remnants of the pellets could be found to float in the acid in the calorimetric crucible. The dissolution of $\text{Fe}(\text{SO}_4)(\text{OH})$ in the high-temperature solvent (near-eutectic mixture of Na_2MoO_4 and MoO_3 , [Navrotsky & Kleppa, 1967](#)), however, was rapid and reproducible.

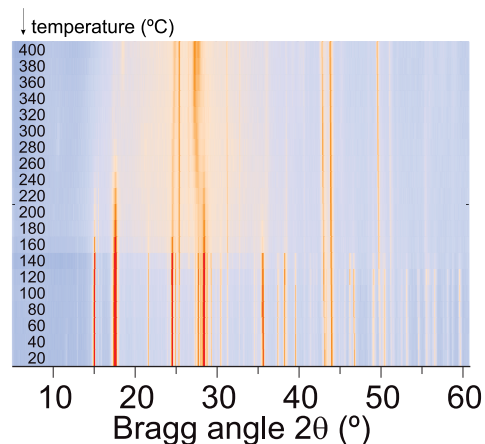


Fig. 2. Evolution of the powder XRD pattern during heating of parabutlerite from 20 to 400 °C in vacuum, with the intensities at each Bragg angle encoded by colors (blue = low intensities, red = high intensities). Note that the sample amorphizes at temperatures around 260 °C. At higher temperature, the phase $\text{Fe}(\text{SO}_4)(\text{OH})$ crystallizes. Two strong peaks between 43° and 45° 2θ and several weaker peaks at higher Bragg angles originate from diffraction from the holder material.

All samples and reference compounds dissolved rapidly and completely in the respective solvents. The dissolution experiments were repeated in order to obtain satisfactory statistics for each measured datum. The exception were the dissolution experiments for hohmannite and metahohmannite where only one experiment was performed for each phase. This limitation is due to the exceedingly difficult separation of hohmannite from the associated copiapite. With large effort, we were able to obtain 2 mg of material; 1 mg was used for the dissolution experiment on hohmannite, the other 1 mg was converted to metahohmannite and dissolved in the calorimeter as well. Therefore, the solution calorimetric data for these two phases (Table 7) have no uncertainties and they have to be enjoyed with caution, although our experience in this and other studies showed that the calorimetric results are highly reproducible.

Enthalpies of formation were calculated from the measured data *via* thermochemical cycles. The thermochemical cycle for the acid-solution calorimetry is shown in Table 7, the one for the high-temperature oxide-melt calorimetry in Table 8. The thermochemical cycle and the reference phases for the acid-solution calorimetry followed the protocol established for ferric sulfates in our group, with enthalpy values in [Majzlan *et al.* \(2015\)](#). High-temperature oxide-melt experiments followed the protocol established by [Majzlan *et al.* \(2002\)](#). The resulting enthalpies of formation from elements in their standard state at standard conditions are listed in Table 9.

4.3. Relaxation calorimetry, heat capacities and entropies

Low-temperature heat capacity was measured for $\text{Fe}(\text{SO}_4)(\text{OH})$, parabutlerite, amaranite, and fibroferrite (Fig. 5a, Tables S1–S8 in Supplementary Material). For butlerite,

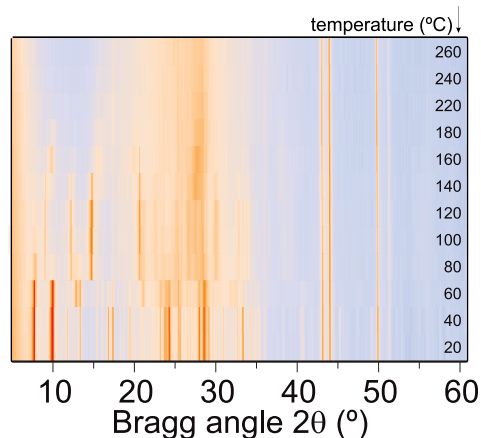


Fig. 3. Evolution of the powder XRD pattern during heating of amarantite from 20 to 300 °C in air, with the intensities at each Bragg angle encoded by colors (blue=low intensities, red=high intensities). The sample persists to 80 °C and then transforms to metahohmannite that amorphizes and slowly transforms to poorly crystalline $\text{Fe}(\text{SO}_4)(\text{OH})$. Two strong peaks between 43° and 45° 2θ and several weaker peaks at higher Bragg angles originate from diffraction from the holder material.

we assume that its thermophysical properties (heat capacity, entropy) are very similar to its polymorph parabutlerite. The measurements for hohmannite and metahohmannite were impossible because of the small amount of material available.

No problems were encountered during the low-temperature C_p measurements on $\text{Fe}(\text{SO}_4)(\text{OH})$, parabutlerite, amarantite. The fibroferrite sample lost 5.8 wt% of mass during the handling or measurement but regained the mass at room temperature afterwards. The reason for this behavior is not clear.

All four phases show anomalous low-temperature behavior in their heat capacity that can be ascribed to the magnetic properties of the Fe^{3+} ions (Fig. 5b). Fibroferrite shows a weak C_p anomaly at 8.5 K, parabutlerite at 14.5 K, and $\text{Fe}(\text{SO}_4)(\text{OH})$ at 3.5 K. There is no visible anomaly in the data for amarantite but they show an upturn as the temperature gets down to 2 K. Therefore, there must be a magnetic transition below this temperature. It is somewhat puzzling that the phase with the densest arrangement of the Fe^{3+} ions, that is $\text{Fe}(\text{SO}_4)(\text{OH})$, has the magnetic transition at very low temperature. Fibroferrite with its relatively open structure, on the other hand, has a much higher temperature of magnetic transition.

The accuracy of the C_p data measured by relaxation calorimetry was tested by independent measurements by DSC at 280–320 K. The agreement was $\pm 0.5\%$ for parabutlerite, amarantite, and $\text{Fe}(\text{SO}_4)(\text{OH})$. For fibroferrite, the DSC data were 1.0% lower than the relaxation calorimetry data. The worse agreement for fibroferrite could be perhaps related to the mass loss during the measurement (relaxation calorimetry) of this phase.

The C_p/T function was integrated by numerical integration to calculate entropy at given temperatures. The results of this procedure are summarized in Table 9. Raw C_p data are deposited as an appendix, available in Supplementary Material.

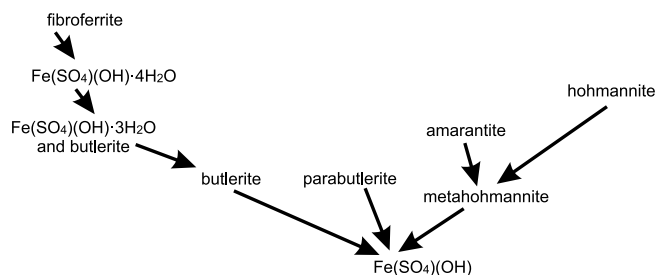


Fig. 4. Transformation sequence of the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases, based on the work of Venturini *et al.* (2015a) and this work. The height of a phase or a mineral in this scheme corresponds to its hydration state (*i.e.*, number of H_2O molecules per formula unit).

The entropy of hohmannite and metahohmannite was estimated from the linear dependence of the measured entropy on the water content (x) of the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases (Fig. 6). The entropy of butlerite, as mentioned above, was assumed to be numerically identical to the entropy of parabutlerite.

4.4. Stability of the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases

Each type of solution calorimetry has its own set of advantages and pitfalls. There is a need to check that the two types of calorimetry (acid-solution and high-temperature oxide-melt) yield consistent results. A positive outcome of such check is a good indicator, but not a proof, that the data are accurate. For this check, we used the fact that in a series of hydrates, such as $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$, the enthalpies of dissolution in the 5 N HCl (the calorimetric solvent for acid-solution calorimetry) correlate with x and vary nearly linearly for the hydrated phases but the datum for the anhydrous phase deviates much from this linear trend. Such trends can be well seen in the data for $\text{MgSO}_4(\text{H}_2\text{O})_x$, $\text{Fe}_2(\text{SO}_4)_3(\text{H}_2\text{O})_x$, and $\text{FeAsO}_4(\text{H}_2\text{O})_x$ (Fig. 7). This is also the case for the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases and the anhydrous phase $\text{Fe}(\text{SO}_4)(\text{OH})$, anhydrous in a sense that there is no H_2O molecule in its structure. From the calculated enthalpy of formation of $\text{Fe}(\text{OH})\text{SO}_4$ ($-1160.2 \pm 2.3 \text{ kJ} \cdot \text{mol}^{-1}$), we have back-calculated a theoretical datum for its enthalpy of dissolution in 5 N HCl. This value is $-28.15 \text{ kJ} \cdot \text{mol}^{-1}$. All data are reported in Fig. 7. The datum for $\text{Fe}(\text{SO}_4)(\text{OH})$ deviates in the exothermic direction from the line that fits the other $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases, just like the other hydrated systems. The magnitude of the deviation for $\text{Fe}(\text{SO}_4)(\text{OH})$ is smaller than in the other systems. Having worked with all these phases, the magnitude of the deviation can be qualitatively related to the tendency of the anhydrous phase to pick up moisture from the air. $\text{Fe}(\text{SO}_4)(\text{OH})$ picks up water sluggishly. It increases its water content slowly but does not transform to butlerite or parabutlerite even after years of exposure to air, which is consistent with the behavior of the dissolution enthalpies for the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases shown in Fig. 7.

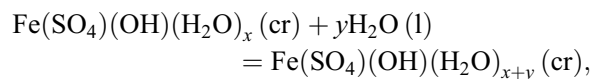
The measured enthalpies of formation and measured or estimated entropies were combined into Gibbs free energies of formation and solubility products. These data

Table 7. Thermochemical cycle for the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases for acid-solution calorimetry. Calculated enthalpies of formation are listed in Table 9. Abbreviations: cr = crystalline solid; l = liquid; aq = aqueous species; g = gas. All values in $\text{kJ}\cdot\text{mol}^{-1}$. All reactants and products at 298 K.

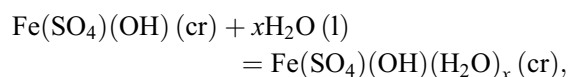
Reaction number	Reaction	
1	$\text{MgO (cr)} + 2\text{H}^+ (\text{aq}) = \text{Mg}^{2+} (\text{aq}) + \text{H}_2\text{O (aq)}$	
2	$\gamma\text{-FeOOH}\cdot 0.162\text{H}_2\text{O (cr)} + 3\text{H}^+ (\text{aq}) = \text{Fe}^{3+} (\text{aq}) + 2.162\text{H}_2\text{O (aq)}$	
3	$\alpha\text{-MgSO}_4 (\text{cr}) = \text{Mg}^{2+} (\text{aq}) + \text{SO}_4^{2-} (\text{aq})$	
4	$\text{H}_2\text{O (l)} = \text{H}_2\text{O (aq)}$	
5	$\gamma\text{-FeOOH}\cdot 0.162\text{H}_2\text{O (cr)} = \gamma\text{-FeOOH (cr)} + 0.162\text{H}_2\text{O (l)}$	
6	$\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x + \text{H}^+ = \text{Fe}^{3+} (\text{aq}) + \text{SO}_4^{2-} (\text{aq}) + (x+1)\text{H}_2\text{O (aq)}$	
7	$\text{Mg (cr)} + 1/2\text{O}_2 (\text{g}) = \text{MgO (cr)}$	
8	$\text{Fe (cr)} + \text{O}_2 (\text{g}) + 1/2\text{H}_2 (\text{g}) = \gamma\text{-FeOOH (cr)}$	
9	$\text{Mg (cr)} + \text{S (cr)} + 2\text{O}_2 (\text{g}) = \alpha\text{-MgSO}_4 (\text{cr})$	
10	$\text{H}_2 (\text{g}) + 1/2\text{O}_2 (\text{g}) = \text{H}_2\text{O (l)}$	
11	$\text{Fe (cr)} + \text{S (cr)} + (2.5 + x/2)\text{O}_2 (\text{g}) + (0.5 + x)\text{H}_2 (\text{g}) = \text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x (\text{cr})$	
$\Delta H_1 = \Delta_{\text{dissolution}} H(\text{MgO in } 5\text{ N HCl}) = -149.68 \pm 0.60(9)$		Majzlan <i>et al.</i> (2015)
$\Delta H_2 = \Delta_{\text{dissolution}} H(\gamma\text{-FeOOH}\cdot 0.162\text{H}_2\text{O in } 5\text{ N HCl}) = -46.62 \pm 0.13(12)$		Majzlan <i>et al.</i> (2015)
$\Delta H_3 = \Delta_{\text{dissolution}} H(\alpha\text{-MgSO}_4 \text{ in } 5\text{ N HCl}) = -53.50 \pm 0.48(7)$		Majzlan <i>et al.</i> (2015)
$\Delta H_4 = \Delta_{\text{dilution}} H(5\text{ N HCl}) = -0.54$		Calculated from Parker (1965)
$\Delta H_5 = \text{enthalpy of water desorption from lepidocrocite} = +1.41 \pm 0.17$		Majzlan <i>et al.</i> (2015)
$\Delta H_6 = \Delta_{\text{dissolution}} H(\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x \text{ in } 5\text{ N HCl})$		
	$\Delta H_6(\text{metahohmannite})$	$-9.66(1)$
	$\Delta H_6(\text{butlerite})$	$-3.06 \pm 0.08(5)$
	$\Delta H_6(\text{parabutlerite})$	$-2.41 \pm 0.17(4)$
	$\Delta H_6(\text{amarantite})$	$+9.07 \pm 0.37(5)$
	$\Delta H_6(\text{hohmannite})$	$+7.23(1)$
	$\Delta H_6(\text{fibroferrite})$	$+21.43 \pm 0.17(5)$
$\Delta H_7 = \Delta_f H^\circ(\text{MgO}) = -601.6 \pm 0.3$		Robie & Hemingway (1995)
$\Delta H_8 = \Delta_f H^\circ(\gamma\text{-FeOOH}) = -549.4 \pm 1.4$		Majzlan <i>et al.</i> (2003)
$\Delta H_9 = \Delta_f H^\circ(\alpha\text{-MgSO}_4) = -1288.8 \pm 0.5$		DeKock (1986)
$\Delta H_{10} = \Delta_f H^\circ(\text{H}_2\text{O}) = -285.8 \pm 0.1$		Robie & Hemingway (1995)
$\Delta H_{11} = \Delta_f H^\circ = -\Delta H_1 + \Delta H_2 + \Delta H_3 + (x - 0.162)\Delta H_4 - \Delta H_5 - \Delta H_6 - \Delta H_7 + \Delta H_8 + \Delta H_9 + x\Delta H_{10}$		

are summarized in Table 9 and can be inserted in commonly used geochemical codes. Enthalpies of the dissolution reactions are also given for codes that use the van't Hoff approximation for the calculations of equilibrium constants at temperatures other than 298.15 K.

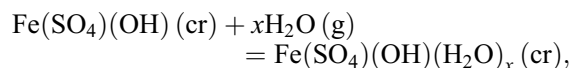
The Gibbs free energies for hydration–dehydration reactions



between the neighboring hydrates are balanced, within a few $\text{kJ}\cdot\text{mol}^{-1}$. The reaction energy with the large magnitude is that between $\text{Fe}(\text{SO}_4)(\text{OH})$ and metahohmannite ($-4.2\text{ kJ}\cdot\text{mol}^{-1}$). The Gibbs free energies of the reaction



are all negative, varying between -1.6 and $-5.4\text{ kJ}\cdot\text{mol}^{-1}$. The Gibbs free energies for the reaction



are large and negative at standard conditions (-17.0 to $-46.1\text{ kJ}\cdot\text{mol}^{-1}$), meaning that under these conditions, the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ hydrates are all stable with respect to $\text{Fe}(\text{SO}_4)(\text{OH})$. Such hypothetical conditions (ideal steam at $P=1$ bar) cannot be realized but even similar conditions (real steam at $P=1$ bar) are unlikely at $T=298.15\text{ K}$ in natural environments. Equilibrium thermodynamic calculations (Fig. 8) show that $\text{Fe}(\text{SO}_4)(\text{OH})$ has a stability field and is predicted to transform to parabutlerite at a relative humidity of $\sim 33\%$ at $T=298.15\text{ K}$. Amarantite has a small stability field at high relative humidities but the higher $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ hydrates could be only stabilized by water vapor pressures above the saturation pressure of water. Hence, the most conducive environment for the metastable formation of these hydrates is close moist spaces because the thermodynamic differences between the hydrates are small.

Table 8. Thermochemical cycle for the high-temperature oxide-melt calorimetry on $\text{Fe}(\text{SO}_4)(\text{OH})$. Temperatures of reactants and products in K. The calculated enthalpy of formation is given in Table 9.

Reaction number	Reaction
12	$\text{Fe}_2\text{O}_3 (\text{cr}, 298) = \text{Fe}_2\text{O}_3 (\text{sol}, 975)$
13	$\text{H}_2\text{O} (1, 298) = \text{H}_2\text{O} (\text{g}, 975)$
14	$\text{CaSO}_4 (\text{cr}, 298) = \text{CaO} (\text{sol}, 975) + \text{SO}_3 (\text{sol}, 975)$
15	$\text{CaO} (\text{cr}, 298) = \text{CaO} (\text{sol}, 975)$
16	$\text{Fe}(\text{SO}_4)(\text{OH}) (\text{cr}, 298) = 0.5\text{Fe}_2\text{O}_3 (\text{sol}, 975) + \text{SO}_3 (\text{sol}, 975) + 0.5\text{H}_2\text{O} (\text{g}, 975)$
17	$0.5\text{O}_2 (\text{g}, 298) + \text{H}_2 (\text{g}, 298) = \text{H}_2\text{O} (1, 298)$
18	$\text{Ca} (\text{cr}, 298) + 0.5\text{O}_2 (\text{g}, 298) = \text{CaO} (\text{cr}, 298)$
19	$\text{Ca} (\text{cr}, 298) + \text{S} (\text{cr}, 298) + 2\text{O}_2 (\text{g}, 298) = \text{CaSO}_4 (\text{cr}, 298)$
20	$2\text{Fe} (\text{cr}, 298) + 1.5\text{O}_2 (\text{g}, 298) = \text{Fe}_2\text{O}_3 (\text{hematite}, 298)$
21	$\text{Fe} (\text{cr}, 298) + \text{S} (\text{cr}, 298) + 0.5\text{H}_2 (\text{g}, 298) + 2.5\text{O}_2 (\text{g}, 298) = \text{Fe}(\text{SO}_4)(\text{OH}) (\text{cr}, 298)$

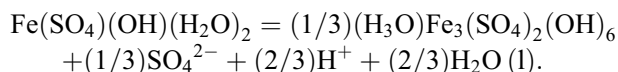
$\Delta H_{12} = \Delta_{\text{dsol}} H(\text{hematite}) = 95.63 \pm 0.50$ Majzlan *et al.* (2002)
 $\Delta H_{13} = H_{975 \text{ K}} - H_{298 \text{ K}} (\text{H}_2\text{O}) = 69.0$ Calculated from Robie & Hemingway (1995)
 $\Delta H_{14} = \Delta_{\text{dsol}} H(\text{anhydrite}) = 108.44 \pm 0.66$ Majzlan *et al.* (2002)
 $\Delta H_{15} = \Delta_{\text{dsol}} H(\text{CaO}) = -91.50 \pm 0.85$ Majzlan *et al.* (2002)
 $\Delta H_{16} = \Delta_{\text{dsol}} H(\text{Fe}(\text{SO}_4)(\text{OH})) = 87.08 \pm 1.13(7)$ This work
 $\Delta H_{17} = \Delta_f H^\circ (\text{H}_2\text{O}) = -285.8 \pm 0.1$ Robie & Hemingway (1995)
 $\Delta H_{18} = \Delta_f H^\circ (\text{CaO}) = -635.1 \pm 0.9$ Robie & Hemingway (1995)
 $\Delta H_{19} = \Delta_f H^\circ (\text{anhydrite}) = -1434.5 \pm 1.3$ Nordstrom & Munoz (1994)
 $\Delta H_{20} = \Delta_f H^\circ (\text{hematite}) = -826.2 \pm 1.3$ Robie & Hemingway (1995)
 $\Delta H_{21} = \Delta_f H^\circ = 0.5\Delta H_{12} + 0.5\Delta H_{13} + \Delta H_{14} - \Delta H_{15} - \Delta H_{16} + 0.5\Delta H_{17} - \Delta H_{18} + \Delta H_{19} + 0.5\Delta H_{20}$

Table 9. Summary of the thermodynamic data for the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases. Enthalpies and Gibbs free energies in $\text{kJ}\cdot\text{mol}^{-1}$, entropies in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Estimated entropies in parentheses. The values with the subscript sp are related to the dissolution reaction $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x + \text{H}^+ = \text{Fe}^{3+} + \text{SO}_4^{2-} + (x+1)\text{H}_2\text{O}$ with all participating phases and aqueous species in their standard state.

	$\Delta_f H^\circ$	S°	$\Delta_f S^\circ$	$\Delta_f G^\circ$	$\Delta_{\text{sp}} G^\circ$	$\log K_{\text{sp}}$	$\Delta_{\text{sp}} H^\circ$
$\text{Fe}(\text{SO}_4)(\text{OH})$	-1160.2 ± 2.3	145.9 ± 1.2	-491.4 ± 1.2	-1013.7 ± 2.4	16.3 ± 2.4	-2.862	-85.0
Metahohmannite	-1608.2 ± 1.7	(200.3)	-786.9	-1373.6 ± 1.8	20.5 ± 2.0	-3.594	-65.8
Butlerite	-1758.0 ± 1.7	(214.0)	-889.8	-1492.7 ± 1.8	21.0 ± 2.0	-3.685	-58.9
Parabutlerite	-1758.6 ± 1.7	214.0 ± 1.4	-889.8 ± 1.4	-1493.3 ± 1.8	21.7 ± 2.0	-3.799	-58.2
Amarantite	-2056.5 ± 1.8	243.8 ± 1.9	-1093.3 ± 1.9	-1730.5 ± 1.9	21.7 ± 2.0	-3.801	-46.3
Hohmannite	-2197.8 ± 1.8	(271.4)	-1182.4	-1845.3 ± 1.9	17.9 ± 2.0	-3.138	-47.8
Fibroferrite	-2641.5 ± 1.8	332.2 ± 2.7	-1471.4 ± 2.7	-2202.8 ± 2.0	19.7 ± 2.1	-3.456	-32.9

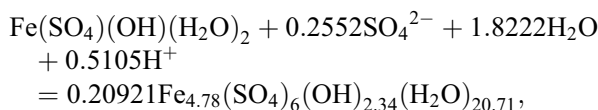
4.5. Stability of the studied phases in the system $\text{Fe}_2\text{O}_3\text{--SO}_3\text{--H}_2\text{O}$

The transformation of parabutlerite to hydronium jarosite is described by this reaction



Note that the reaction is normalized to 1 Fe atom for an easier comparison of the $\Delta_r G^\circ$ values with reactions below. The standard-state Gibbs free energy change of the reaction is $+11.8 \text{ kJ}\cdot\text{mol}^{-1}$, with $\Delta_r G^\circ$ datum for hydronium jarosite taken from Majzlan *et al.* (2004). Under these conditions, parabutlerite and the other $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases are stable with respect to hydronium jarosite. Lowering the activities of sulfate or protons (*i.e.*, diluting the solution and increasing pH) stabilizes hydronium jarosite. For example, at $a(\text{SO}_4^{2-}) = 0.01$ and pH of 2.5, the Gibbs free energy change of this reaction is $-1.5 \text{ kJ}\cdot\text{mol}^{-1}$.

The relation of parabutlerite to ferricopiapite is described by



where the composition and $\Delta_r G^\circ$ of ferricopiapite were taken from Majzlan *et al.* (2005). The composition of ferricopiapite, which deviates from the nominal one, was determined in that study by a combination of different chemical analyses on the material used in calorimetric experiments. The $\Delta_r G^\circ$ value for this reaction is $4.5 \text{ kJ}\cdot\text{mol}^{-1}$. Increasing sulfate activity or decreasing pH will stabilize ferricopiapite.

These calculations predict that the stability field of parabutlerite (and the other $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases) is flanked on the side of dilute, relatively high-pH solutions by that of hydronium jarosite and on the side of concentrated, low-pH solutions by that of ferricopiapite. They conform very well with the experimental observations of Posnjak &

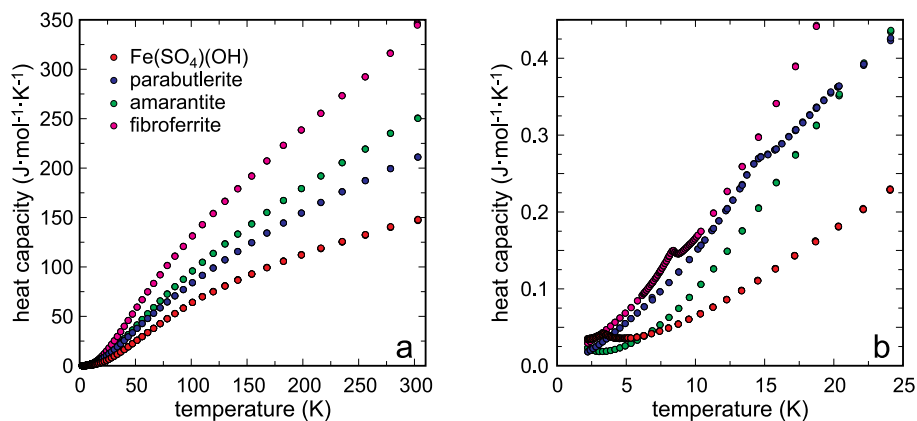


Fig. 5. Heat capacity of the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases: (a) the entire measurement range from 2 up to 300 K and (b) low-temperature portion of the data, showing the magnetic anomalies in the C_p data.

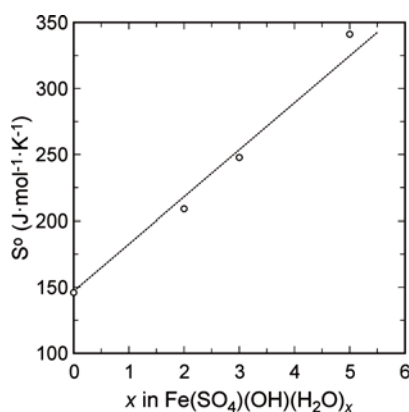


Fig. 6. Linear correlation of the entropies for the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases. From this correlation, the entropies of hohmannite and metahohmannite were estimated.

Merwin (1922) who synthesized hydronium jarosite from relatively dilute ferric sulfate solutions and butlerite from more concentrated ones. Solutions with yet higher ferric sulfate concentrations precipitated ferricopiapite. The solutions that yielded hydronium jarosite, butlerite, or ferricopiapite were pure ferric sulfates solutions, without addition of sulfuric acid. Addition of sulfuric acid stabilizes phases like paracoquimbite, kornelite, or rhomboclase.

The relationship between parabutlerite as a representative of the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases to other phases in the system $\text{Fe}_2\text{O}_3\text{--SO}_3\text{--H}_2\text{O}$ is graphically shown in an activity–activity diagram in Fig. 9. The diagram conforms well to the sequence of precipitates from circumneutral to strongly acidic waters, namely ferrihydrite in near-neutral solutions, schwertmannite in mildly acidic solutions and jarosite (*sensu stricto*, meaning K-jarosite) in very acidic solutions. This sequence was observed in many field systems. The field of parabutlerite is restricted to even more extreme conditions than those required for the formation of jarosite. It is also interesting to note that if K-jarosite is suppressed in these calculations, a stability field of hydronium jarosite will be missing, taken over by the field

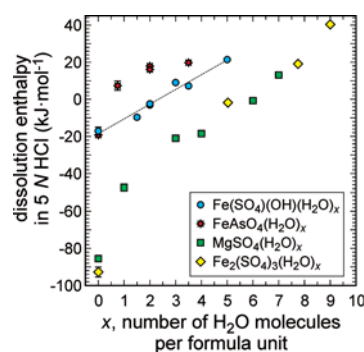


Fig. 7. Dissolution enthalpies of a number of phases in 5 N HCl, measured in our laboratory. These phases belong to several systems of hydrates with progressively more H_2O molecules per formula unit. The data show a linear relationship between the number of H_2O molecules and the dissolution enthalpies, with the exception of the anhydrous phases. Error bars shown only if the measurement uncertainty is larger than the symbol. The dashed line shows the linear correlation between the two variables and serves only as a guide to the eye.

of parabutlerite. Hydronium jarosite is less stable than K-jarosite but it is interesting that if many $\text{Fe}_2\text{O}_3\text{--SO}_3\text{--H}_2\text{O}$ phases are considered (Fig. 9), hydronium jarosite does not appear, in agreement with its rarity in nature.

4.6. High-temperature high-pressure equilibria among the ferric sulfates

Natural assemblages document, not surprisingly, that the hydrated $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases are restricted to near-surface environments with their low temperatures and atmospheric pressure. The phase $\text{Fe}(\text{SO}_4)(\text{OH})$, however, could participate in assemblages typical for metamorphic conditions, although such a phase was not yet described from nature. Stoffregen (1993) also used this phase to generate phase diagrams for Fe(III) sulfates at elevated temperatures and pressures.

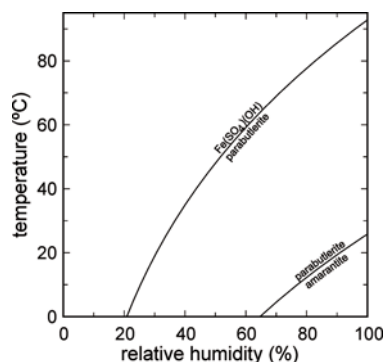
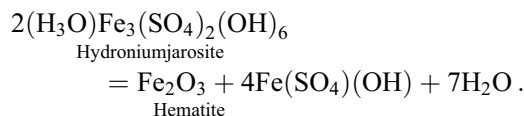


Fig. 8. Relative humidity vs. temperature diagram for the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases.

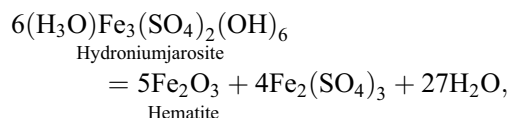
For calculation of phase diagrams at elevated temperatures and pressures, we used the software winTWQ (version 2.34, Berman, 1991) with its embedded equation of state for water (Haar *et al.*, 1984). The phases considered in these calculations were $\text{Fe}_2(\text{SO}_4)_3$, hydronium jarosite $((\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6)$, and $\text{Fe}(\text{SO}_4)(\text{OH})$. The necessary thermodynamic data (enthalpies of formation, entropies) were taken from earlier work (Majzlan *et al.*, 2004, 2005) but there are no high-temperature C_p polynomials available for any of these phases. Therefore, we used the adiabatic or relaxation calorimetry data (Majzlan *et al.*, 2004, 2005, this work, measurements up to 300 or 400 K), combined with the Dulong-Petit limit for each phase at 1000 K, to fit the polynomials $C_p = K_0 + K_1 \cdot T^{-0.5} + K_2 \cdot T^{-2} + K_3 \cdot T^{-3}$. This polynomial, with negative powers of T , is suitable for fitting data sets with gaps (such as these C_p data sets) and extrapolation to higher temperatures, if needed. The results of the fitting procedure, together with other thermodynamic data used, are summarized in Table 10. The coefficients for volume expansion at elevated temperature or volume contraction at higher pressure were set to zero for all these phases in absence of reliable data. The thermodynamic data for hematite (Fe_2O_3) were taken from the winTWQ database.

Results of the calculations are shown in Fig. 10a. The curve separating the stability field of $\text{Fe}(\text{SO}_4)(\text{OH})$ from that of $\text{Fe}_2(\text{SO}_4)_3 + \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$ approaches the low-pressure limit of the diagram with a very flat slope, making this calculation a relatively insensitive test for the validity of the data. Yet, the calculated transformation temperature at atmospheric pressure of $\sim 400^\circ\text{C}$ agrees well with the observations of Ventrucci *et al.* (2015a) that $\text{Fe}(\text{SO}_4)(\text{OH})$ decomposes between 330 and 550°C . A direct comparison between the two data sets is difficult because the experiments of Ventrucci *et al.* (2015a) were dynamic, where equilibrium may or may not have been achieved at any time of the experiment. Ventrucci *et al.* (2015a) identified additional intervening phases such as $\text{Fe}_2\text{O}(\text{SO}_4)_2$ and FeSO_4 and it is not clear if these are metastable transient phases or phases with their stability field in the P - T space.

Another conclusion from these calculations (Fig. 10a) is that hydronium jarosite is predicted to be metastable with respect to $\text{Fe}(\text{SO}_4)(\text{OH})$ via the reaction



For the measured thermodynamic data of $\text{Fe}(\text{SO}_4)(\text{OH})$, the position of this univariant reaction curve is displaced to subambient temperatures and does not appear in Fig. 10a. Making the phase $\text{Fe}(\text{SO}_4)(\text{OH})$ less stable by adjusting its enthalpy of formation to $-1151 \text{ kJ} \cdot \text{mol}^{-1}$ makes these relationships more understandable (Fig. 10b). The univariant curve for the reaction above appears on the diagram. The metastable univariant curve for the reaction



is also shown and this reaction is predicted to occur between 100 and 200°C . Thermogravimetric measurements on hydronium jarosite (Majzlan *et al.*, 2004), however, show that the first significant mass loss occurs at $\sim 300^\circ\text{C}$. Just like in the case of Ventrucci *et al.* (2015a), these were also dynamic experiments and it is difficult to judge how close they come to the equilibrium transformation temperature for the phases involved.

4.7. Crystal structure and hydrogen-bonding network in amaranite

The crystal structure of amaranite investigated in the current work corresponds to the structural model proposed by Süssse (1968). Here, we present additionally the positions of the H atoms, which were not localized in the original structure determination.

The structure of amaranite consists of infinite chains running parallel to c , composed of Fe-based octahedra and SO_4 tetrahedra. Between the chains, there are three symmetrically independent *free* H_2O molecules that are not linked directly to any Fe cation (O10, O13, O15). The Fe1 atom is octahedrally coordinated by two O atoms (symmetrically related O9) linking Fe1 octahedra to Fe2 octahedra, three O atoms (O3, O5, O8) linking the Fe1 to SO_4 tetrahedra ($\text{O3} \rightarrow \text{S1}$, $\text{O5} \rightarrow \text{S2}$, $\text{O8} \rightarrow \text{S2}$) and one O atom (O14), which belongs actually to an H_2O group. The Fe2 atom is coordinated octahedrally but stereochemically in a distinct manner, by one O (O9) atom that is linked to two Fe1 atoms, two O (O1 and O6) atoms linked to S1 and S2 atoms, respectively, and three O atoms (O11, O12, O16) that belong to H_2O groups. While pairs of Fe2 octahedra share the common edge, the Fe1 octahedron shares a corner with the dimers of Fe2 octahedra.

In hydrated oxysalts, there are generally several types of H_2O moieties in the crystal structure, each of them playing a slightly distinct structural role, as reviewed by Hawthorne (1992, 2012), Hawthorne & Schindler (2008), Schindler &

Table 10. Thermodynamic data used for high-temperature high-pressure modeling with the winTWQ program. Heat capacity is expressed as a polynomial $C_p = K_0 + K_1 \cdot T^{-0.5} + K_2 \cdot T^{-2} + K_3 \cdot T^{-3}$. These polynomials were constrained by the original data (Majzlan *et al.*, 2004, 2005, this work) and the Dulong-Petit limit for each phase at 1000 K. hjaro = hydronium jarosite with composition $(\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$. Enthalpies in $\text{kJ} \cdot \text{mol}^{-1}$, entropies in $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, volumes in $\text{J} \cdot \text{bar}^{-1}$.

Phase	$\Delta_f H^\circ$	S°	V°	K_0	K_1	K_2	K_3
$\text{Fe}_2(\text{SO}_4)_3$	−2585.2	305.6	11.875	575.875	−4608.824	−7 356 385	1 235 146 047
$\text{Fe}(\text{SO}_4)(\text{OH})$	−1160.2	145.9	5.060	198.241	333.804	−10 498 728	1 237 392 590
Hjaro	−3770.2	448.2	15.776	1014.260	−8695.17	−19 979 805	4 026 137 202

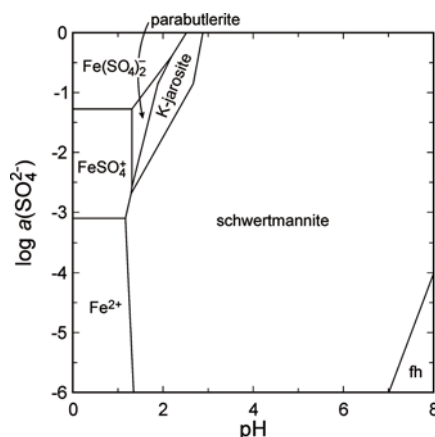


Fig. 9. Low-temperature (25 °C) phase diagram showing the stability fields of parabutlerite, jarosite, schwertmannite, and ferrihydrite (fh). The diagram was calculated with $\log a(\text{Fe}^{3+}) = -1$, $p\epsilon = 12$, $\log a(\text{K}^+) = -4$, hematite and goethite suppressed from the calculations.

Hawthorne (2008) or Hawthorne & Sokolova (2012). Particular types of H_2O can be distinguished based on the coordination number of O atoms in these H_2O groups. In the structures of oxysalts, there are transformer, non-transformer, and inverse transformer H_2O groups with 3, 4, and 5-fold coordinated O atoms, respectively. Their role is generally to transfer the bond-valence from cations (Lewis acids) to anions (Lewis bases), keeping the structure together, as the strengths of these components are equal or similarly matching, following the valence-matching principle of the bond-valence theory (Brown, 2002, 2009; Hawthorne, 2012).

The geometry of hydrogen bonds in the crystal structure of amaranite is given in Table 4 and can be seen in Fig. 11. The information on coordination number of each particular O atom within the H_2O group can be easily read out from the results of the bond-valence analysis (Table 5). The O atoms (O11, O12, O14, O16) of the (H_2O) groups that are ligands of both Fe1 and Fe2 octahedra are [3]-coordinated, *i.e.*, transformer (H_2O) groups. The rest of (H_2O) groups in the structure are non-transformer (H_2O) groups that have [4]-coordinated O atom (providing two stronger $\text{O} \rightarrow \text{H}$ bonds and accepting two weaker $\text{H} \rightarrow \text{O}$ bonds). The structural formula of amaranite is therefore $\text{Fe}^{3+}(\text{H}_2^{[3]}\text{O})\text{Fe}^{3+}(\text{H}_2^{[3]}\text{O})_3[(\text{SO}_4)_2\text{O}](\text{H}_2^{[4]}\text{O})_3$, $Z = 1$.

Amarantite, $\text{Fe}_2[(\text{SO}_4)_2\text{O}](\text{H}_2\text{O})_7$, and hohmannite, $\text{Fe}_2[(\text{SO}_4)_2\text{O}](\text{H}_2\text{O})_8$, are structurally closely related and differ, in a chemical sense, only by one H_2O molecule. The structure of hohmannite has been revisited by Ventruti *et al.* (2015b), whose structure model includes also positions of the H atoms and allows for a comparison between the two phases. The unit cell of hohmannite is slightly larger, by about $\sim 10 \text{ \AA}^3$, due to presence of the additional H_2O molecule. The bond-valence analysis (Ventruti *et al.*, 2015b) shows that the additional H_2O molecule in hohmannite belongs to a non-transformer (H_2O) group with the O atom being [4]-coordinated, accepting H-bonds from other H_2O molecule. The close structural and chemical relationship could prompt the hypothesis that amaranite may form as an intermediate step of the hohmannite to metahohmannite transition. Such hypothesis would have to be tested by additional experiments, however.

4.8. Structural complexity and thermodynamic stability

It is of great interest to link the crystal structures of solids and their thermodynamic stability. Such methods were developed for clay minerals (Tardy and Garrels, 1974; Vieillard, 2002), zeolites (La Iglesia and Aznar, 1986; Matigod and McGrail, 1999), hydrotalcites (Allada *et al.*, 2002), secondary copper minerals (Yoder *et al.*, 2010), or secondary uranyl minerals (Chen *et al.*, 1999). Many of these methods are based on a virtual decomposition of the known crystal structures into building blocks which are assigned Gibbs free energies and enthalpies. This assignment must be done using known, preferably complex structures similar to the unknown phases, and the thermodynamic properties of these known complex structures. Although these estimates usually appear relatively precise, especially when considering the large enthalpies of formation from the elements, they can rarely truly capture the phase equilibria in nature. For a series of related phases, such as the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases, the relationship between the structural complexity and stability can be explored.

Krivovichev (2013) asserted that metastable phases tend to be less complex than their stable counterparts. This statement is based on the observed complexity and stability of polymorphs. In our case, parabutlerite is marginally (by $0.65 \pm 0.19 \text{ kJ} \cdot \text{mol}^{-1}$) more stable than butlerite. The minute

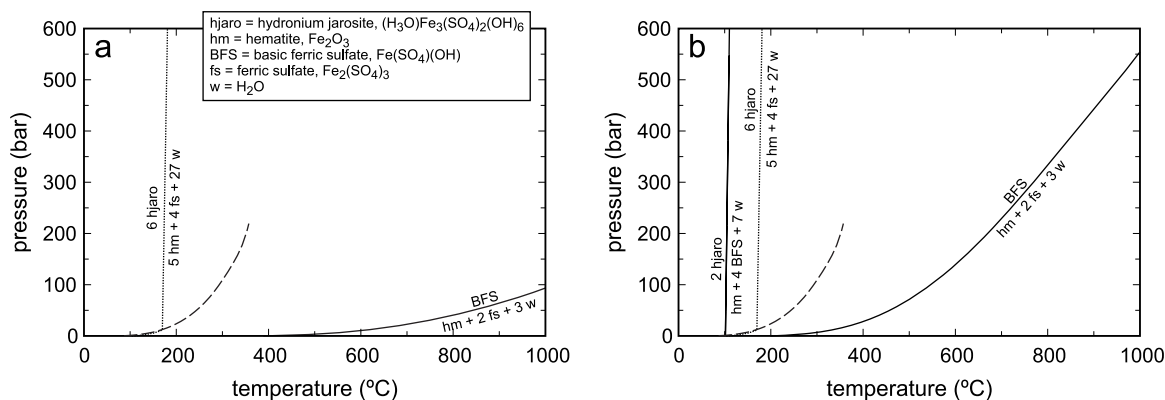


Fig. 10. Phase relations in the Fe_2O_3 – SO_3 – H_2O system in the P – T space. The univariant curves were calculated with the software winTWQ, using its database and (a) additional data listed in Table 10 or (b) the same data with the exception of $\Delta_f H^\circ(\text{Fe}(\text{SO}_4)(\text{OH}))$, set to $-1151 \text{ kJ}\cdot\text{mol}^{-1}$. Stable equilibria shown by solid lines, metastable ones by stippled lines. The dashed line is the saturation curve for H_2O .

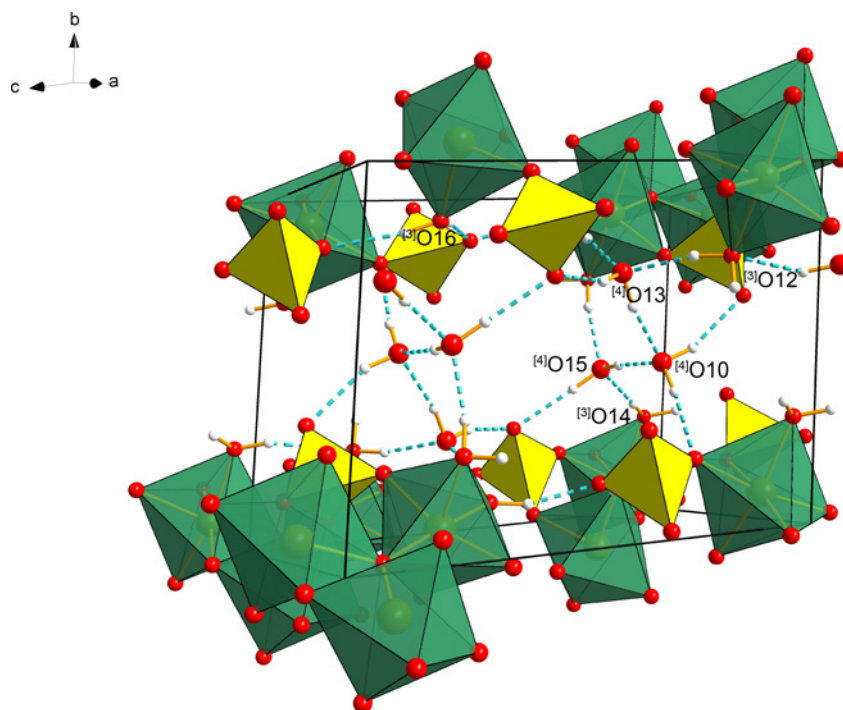


Fig. 11. Fragment of the crystal structure of amaranthite. Fe^{3+} is housed in the green octahedra, S^{6+} in the yellow tetrahedra. Oxygen and hydrogen atoms shown by red and white balls, respectively. Blue dashed lines represent the hydrogen bonds.

margin of thermodynamic stability, however, is associated with a large difference in the complexity of the two phases (Table 6). Hence, qualitatively, the statement about the complexity and stability of polymorphs holds also in this case, but a quantitative connection is difficult to establish. We note that such large differences in the complexity for the polymorphs may not be unusual. Although there is not much data available, Krivovichev (2017) showed that the difference in complexity is also large for the polymorphs clinoclase and gilmartite ($\text{Cu}_3(\text{AsO}_4)(\text{OH})_3$) with $I_{G,\text{total}} = 213.212$ and 53.303 bits/cell, respectively. More work is needed to determine the magnitude of complexity differences among polymorphs.

If a relationship between stability and complexity holds between polymorphs, then one may consider the possibility of a similar relation among a series of chemically and structurally related phases, such as the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases. We note, however, that the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases constitute two groups in a structural sense. One of them contains amaranthite, hohmannite, and metahohmannite, all three of them having a complex chain (Fig. 20o in Hawthorne *et al.*, 2000). The other group with butlerite, parabutlerite, fibroferrite, and $\text{Fe}(\text{SO}_4)(\text{OH})$ possesses a simpler chain (Fig. 20c in Hawthorne *et al.*, 2000) with variations of the packing of this chain in the structure. Nevertheless, the two

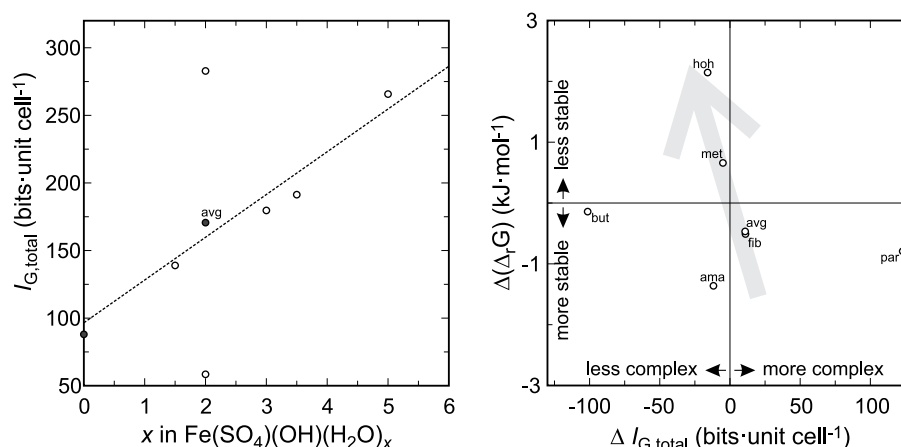


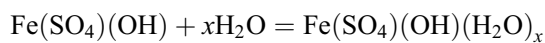
Fig. 12. (a) Information content of the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases as a function of x , the number of H_2O molecules per formula unit. The dashed line is a linear fit through the open symbols (the grey symbols were not considered for the fit). The symbol “avg” represents the average of the values for butlerite and parabutlerite. The calculated information content is listed for each phase in Table 6. (b) Deviation of the Gibbs free energies of reaction and information content for the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases from their respective linear fits as a function of x . Such fit is shown in the panel (a) for the information content. The deviation was calculated as the vertical distance of a datum from the linear fit.

groups are considered together because all these phases are examples of an arrangement of a similar chemical content in a three-dimensional periodic structure.

Here, we explore the relationship between stability and complexity by examination of the deviations of the properties of the $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases from a linear trend, where the properties (stability, complexity) are plotted as a function of x . The phase $\text{Fe}(\text{SO}_4)(\text{OH})$ is excluded because, as shown above, its thermodynamic properties deviate from a linear trend common for the other phases and this could lead to a bias in the resulting data.

A plot of x versus calculated complexity (as $I_{G,\text{total}}$) is shown in Fig. 12a. The linear dependence of complexity on x is easily seen. The deviations, labeled as $\Delta I_{G,\text{total}}$ in Fig. 12b, were calculated as the vertical distance of each data point from the fit line. The value of $\Delta I_{G,\text{total}} = 0$ corresponds to the complexity along the fit line. Lower values indicate lower complexity than that indicated from the linear trend and *vice versa*. The fields above and below $\Delta I_{G,\text{total}} = 0$ in Fig. 12b are labeled accordingly.

Similarly, the Gibbs free energies of reaction ($\Delta_r G^\circ$)



were calculated for each $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phase and fit with a line. The deviation were calculated in the same manner and plotted in Fig. 12b as $\Delta(\Delta_r G^\circ)$. The deviations from the linear trend mark more and less stable phases and there are also two fields marked in Fig. 12b.

If the premise of more stable structures being more complex would hold generally, then the points in Fig. 12b should cluster either in the lower right quadrant (more stable and more complex) or in the upper left quadrant (less stable and less complex). Apart from the data points for butlerite and parabutlerite whose complexity differs much (discussed above), there is some indication that the more complex structures may be also more stable. The

trend defined by the data points for fibroferrite, hohmannite, and metahohmannite conforms to this assumption. Even the average point for butlerite and parabutlerite lies on this trend, although this position may be only coincidental. Amaranthite lies off the trend. This work hints that complexity may hold a relationship to stability but it is difficult to foresee a numerical, quantitative use of such relationship. Examination of other systems may help to resolve this issue.

5. Conclusions

We have determined the thermodynamic properties of all $\text{Fe}(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})_x$ phases. All calculated phase diagrams, be they for the relationships with aqueous solutions (Fig. 9), air moisture (Fig. 8) or for elevated temperatures and pressures (Fig. 10), generate reasonable topologies. The examination of the relationship between stability of the phases studied and their complexity showed vague results and called for inspection of other systems of related phases.

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