

Thermodynamic properties of mansfieldite ($\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$), angelellite ($\text{Fe}_4(\text{AsO}_4)_2\text{O}_3$) and kamarizaite ($\text{Fe}_3(\text{AsO}_4)_2(\text{OH})_3 \cdot 3\text{H}_2\text{O}$)

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ABSTRACT

Thermodynamic data for the arsenates of various metals are necessary to calculate their solubilities and to evaluate their potential as arsenic storage media. If some of the less common arsenate minerals have been shown to be less soluble than the currently used options for arsenic disposal (especially scorodite and arsenical iron oxides), they should be further investigated as promising storage media. Furthermore, the health risk associated with arsenic minerals is a function of their solubility and bioavailability, not merely their presence. For all these purposes, solubilities of such minerals need to be known. In this work, a complete set of thermodynamic data has been determined for mansfieldite, $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$; angelellite, $\text{Fe}_4(\text{AsO}_4)_2\text{O}_3$; and kamarizaite, $\text{Fe}_3(\text{AsO}_4)_2(\text{OH})_3 \cdot 3\text{H}_2\text{O}$, using a combination of high-temperature oxide-melt calorimetry, relaxation calorimetry, solubility measurements, and estimates where possible and appropriate. Several choices for the reference compounds for As for the high-temperature oxide-melt calorimetry were assessed. Scorodite was selected as the best one. The calculated Gibbs free energy of formation (all data in $\text{kJ} \cdot \text{mol}^{-1}$) is -1733.4 ± 3.5 for mansfieldite, -2319.2 ± 7.9 for angelellite and -3056.8 ± 8.5 for kamarizaite. The solubility products for the dissolution reactions are -21.4 ± 0.5 for mansfieldite, -43.4 ± 1.5 for angelellite and -50.8 ± 1.6 for kamarizaite. Available, but limited, chemical data for the natural scorodite–mansfieldite solid-solution series hint at a miscibility gap; hence the non-ideal nature of the series. However, no mixing parameters were derived because more data are needed. The solubility of mansfieldite is several orders of magnitude higher than that of scorodite. The solubility of kamarizaite, on the other hand, is comparable to that of scorodite, and kamarizaite even has a small stability field in a pH–pe diagram. It is predicted to form under mildly acidic conditions in acid drainage systems that are not subject to rapid neutralization and sudden strong supersaturation. The solubility of angelellite is high, and the mineral is obviously restricted to unusual environments, such as fumaroles. Its crystallization may be enhanced *via* its epitaxial relationship with the much more common hematite. The use of the scorodite–mansfieldite solid solution for arsenic disposal, whether the solid solution is ideal or not, is not practical. The difference in

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solubility products of the two end-members (scorodite and mansfieldite) is so large that almost any system will drive the precipitation of essentially pure scorodite, leaving the aluminium in the aqueous phase.

KEYWORDS: mansfieldite, angelellite, kamarizaite, high-temperature oxide-melt calorimetry, relaxation calorimetry.

Introduction

ARSENIC is a commonly assumed or proven culprit of environmental problems, and therefore is a subject of anxious monitoring by public authorities and scientists. Indeed, arsenic has been shown to be abundant at mine sites and in contaminated soil profiles (e.g. Hebbard *et al.*, 2017; Rahman *et al.*, 2017; Drahota *et al.*, 2018; Akopyan *et al.*, 2018; Gamble *et al.*, 2018; Cui *et al.*, 2018), or in aquifers and rivers (e.g. Bozau *et al.*, 2017; Shen *et al.*, 2018; Bhowmick *et al.*, 2018). There is less appreciation (by the public) of the fact that the mere presence of arsenic does not automatically present an acute health danger. It is the solubility and bioavailability of the arsenic that determines the level of threat, not just its presence. Solubility, at equilibrium with an aqueous solution, is a variable that can be determined and predicted from thermodynamic data. Arsenic is not only of interest because it raises a red flag due to its toxicity. The crystal chemistry of arsenic is particularly rich; even today, new arsenate structures are being synthesized and solved (e.g. Đorđević *et al.* 2017; Schwendtner and Kolitsch 2017; Alcantar *et al.* 2017; Krivovichev *et al.*, 2018).

An integral component of the quest for better options for long-term disposal of arsenic-bearing waste, soils and sediments is the measurement and evaluation of thermodynamic data for various arsenates of common metals, such as iron or aluminium. If some of these could be shown to have lower solubility than the currently used options – i.e. scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) and As-bearing ferrihydrite (Riveros *et al.*, 2001) – the practical sides (e.g. ease and economic viability of synthesis, kinetic inertness, filtration and dewatering) could be considered to utilize such a phase or phases for large-scale applications.

The thermodynamic properties of arsenic oxides, aqueous species and arsenates have been reviewed by Nordstrom *et al.* (2014). They prove that scorodite indeed is the phase with the lowest As solubility in most chemical systems. Other phases with low solubilities are mimetite and mimetite–pyromorphite solid solutions (Flis *et al.*, 2011), but they require the presence or addition of lead to the

polluted sediments or waste form. Substitution of arsenic into common sulfates, such as jarosite (Savage *et al.*, 2005; Johnston *et al.*, 2012; Forray *et al.*, 2014) or alunite/natroalunite (Vinals *et al.*, 2010; Luo *et al.*, 2015; Sunyer *et al.*, 2016) has also been considered, and may be applicable in systems with low pH and high sulfate concentrations (Welham *et al.*, 2000). Kocourková *et al.* (2011) argued against jarosite/alunite as an arsenic-storage medium, stating that “beudantite and scorodite represent a long-term option for immobilization of arsenic, but arsenic stored in jarosite can be mobilized relatively easily”. In cementitious or ash systems with alkaline pH, calcium arsenates, sulfate-arsenates, or adsorption of arsenic on C-S-H phases plays the dominant role (e.g. Kumarathasan *et al.*, 1990; Cornelis *et al.*, 2008; Prasanna and Kamath, 2009). In systems dominated by arsenic, secondary arsenates precipitate under oxidizing conditions, and their bulk chemistry is dictated by the primary composition and the properties of the fluids, especially their pH.

In this work, for the first time, the thermodynamic properties of the minerals mansfieldite, kamarizaite and angelellite were measured by a combination of high-temperature oxide-melt calorimetry, relaxation calorimetry and solubility measurements. Limited chemical data on the natural mansfieldite–scorodite solid solution are also presented. The samples, either synthetic or natural, were characterized by powder X-ray diffraction and electron microprobe analysis. For mansfieldite, solid state ^{27}Al nuclear magnetic resonance (NMR) spectroscopy was used to check the sample purity with respect to a possible amorphous admixture.

Materials

Synthetic samples

The mansfieldite was synthesized hydrothermally. A solution made by mixing 0.57 g of AlCl_3 and 15 mL of deionized water was mixed with a solution of 1.00 g $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ dissolved in 15 mL of deionized water. The resulting clear liquid

was poured into a 125 mL Teflon container, inserted into a Paar stainless steel autoclave, sealed, and heated at 180°C for four days. Afterwards, the autoclave was allowed to slowly cool to room temperature, and the suspension was filtered and dried. A white powder was obtained.

A sample that mostly contained angelellite was synthesized after a modified procedure of Wright *et al.* (2000). Briefly, 4.182 g (18.2 mmol) of anhydrous As_2O_5 and 29.943 g (74.1 mmol) $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 500 mL of 2 M nitric acid (HNO_3) (65%) and boiled under a fume hood to dryness. The residue was ground and heated at 700°C for 36 h. After cooling, the dark reddish-brown powder obtained was washed with 500 mL of deionized water and air-dried.

To remove an FeAsO_4 impurity (cf. Wright *et al.*, 2000), the dried sample was mixed with 200 mL of 18% (by mass) hydrochloric acid (HCl), and the suspension was stirred at room temperature for 2 h. The solution turned increasingly yellow, indicating liberation of Fe^{3+} from the sample. After 2 h, the suspension was filtered and washed with 500 mL of deionized water and air-dried. As the impurity could still be detected by powder X-ray diffraction, although its quantitative proportion was reduced, the extraction procedure with HCl was repeated two more times. After a total of 6 h of HCl extraction, the angelellite yield was reduced by more than 50%, but no further reflections of the impurity were detected.

For the synthesis of scorodite, a modified procedure of Baghurst *et al.* (1995) was used, as in our previous work on this phase (Majzlan *et al.*, 2012). Each of the chemicals: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (6.758 g, 25.0 mmol), As_2O_5 (2.873 g, 12.5 mmol) and NaOH (1.000 g, 25 mmol) were dissolved in a separate batch of 50 mL deionized H_2O . After dissolution, the solutions were mixed. In contrast to Majzlan *et al.* (2012), the pH of the final solution was not adjusted. Solution was added to make a volume of 250 mL, and a portion thereof poured into a Teflon-lined steel autoclave. The autoclave was closed tightly and kept at 145°C for three days. After cooling, the precipitate was filtered and washed with deionized H_2O .

Natural samples

A natural kamarizaite sample was used, because no synthesis protocol has been reported for this phase so far. The sample was collected *in situ* by one of the authors (U.K.) underground from the 3rd level of the Hilarion Mine at Agios Konstantinos

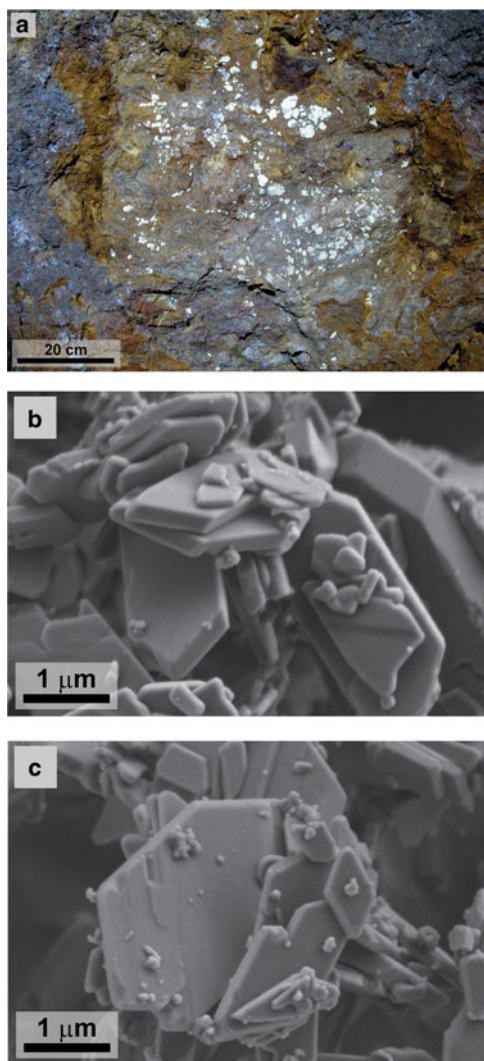


FIG. 1. (a) Aggregates of pale beige, fine-grained kamarizaite, embedded in a dark brown limonite-jarosite (-scorodite) matrix, the result of complete weathering of primary ores. Photo of a wall in the kamarizaite-containing stope on the 3rd level of the Hilarion Mine, Kamariza. Photo by Stefan Moser. (b and c) Back-scattered electron images of kamarizaite crystals.

(Kamariza), Lavrion District, Greece; a site known for its rich secondary mineralogy (Skarpelis and Argyraki, 2009, Kolitsch *et al.*, 2014). The samples consist of aggregates (up to 1.5 cm in diameter, Fig. 1a) of fine-grained kamarizaite (platy crystals 1–2 µm large, but <0.2 µm thick; Fig. 1b,c) embedded in a

heterogeneous matrix of fine-grained jarosite [$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$], scorodite and iron oxides. The crystallography of these and other kamarizaite samples from Lavrion was described in detail by Kolitsch *et al.* (2016). In the vicinity of the kamarizaite-bearing sites, somewhat larger crystals of scorodite grow on quartz relics in the gossan. Primary ore minerals have not been found here, but it could have been dominated by arsenopyrite, a fairly common ore mineral in Lavrion (Voudouris *et al.*, 2008). The underground stope with the kamarizaite aggregates had previously been primarily known for its excellent specimens of lavendulan [$\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$]. This mineral is thought to form here because the stope, located at the second lowest level of the mine, is close to sea level (currently at the fourth and lowest level). The current oxidation front at Kamariza is located at sea level (Skarpelis and Argyraki 2009).

The samples of the scorodite–mansfieldite solid solution were collected by one of the authors (M.Š.) at Ľubietová-Svätodušná, Slovakia. These samples were collected on the dumps, as the old mining works are now inaccessible. There are three historically mined deposits at Ľubietová, but only Podlipa has been the subject of modern systematic research (Luptáková *et al.*, 2016, Števko *et al.*, 2016, 2017). Svätodušná and Kolba received limited attention, apart from the identification of secondary minerals. Svätodušná is the type locality, and is still known particularly for its excellent crystals of euchroite [$\text{Cu}_2(\text{AsO}_4)(\text{OH})\cdot 3\text{H}_2\text{O}$], which are a product of the weathering of tennantite [$\text{Cu}_6[\text{Cu}_4(\text{Fe,Zn})_2]\text{As}_4\text{S}_{13}$], as well as other primary As minerals (arsenopyrite and Co–Ni–sulfides/sulfosalts) (Majzlan *et al.*, 2016). Aggregates of scorodite and mansfieldite are rare. The Fe-dominated members (scorodite) are chemically homogeneous, but the Al-dominated members (mansfieldite) show strong zonation, with variations in the ratio of $\text{Fe}/(\text{Fe} + \text{Al})$ (Fig. 2a). They either occur separately or are overgrown by younger olivenite [$\text{Cu}_2(\text{AsO}_4)(\text{OH})$] (Fig. 2b) on the fractures of the host rocks (gneisses and granite porphyries) or in the vugs of deeply weathered tennantite (also see Borčinová Radková *et al.*, 2017).

Methods

Characterization of the solids

Powder X-ray diffraction (PXRD) analyses were conducted using a Bruker D8 Advance diffractometer in the angular range of $5\text{--}90^\circ 2\theta$ at room

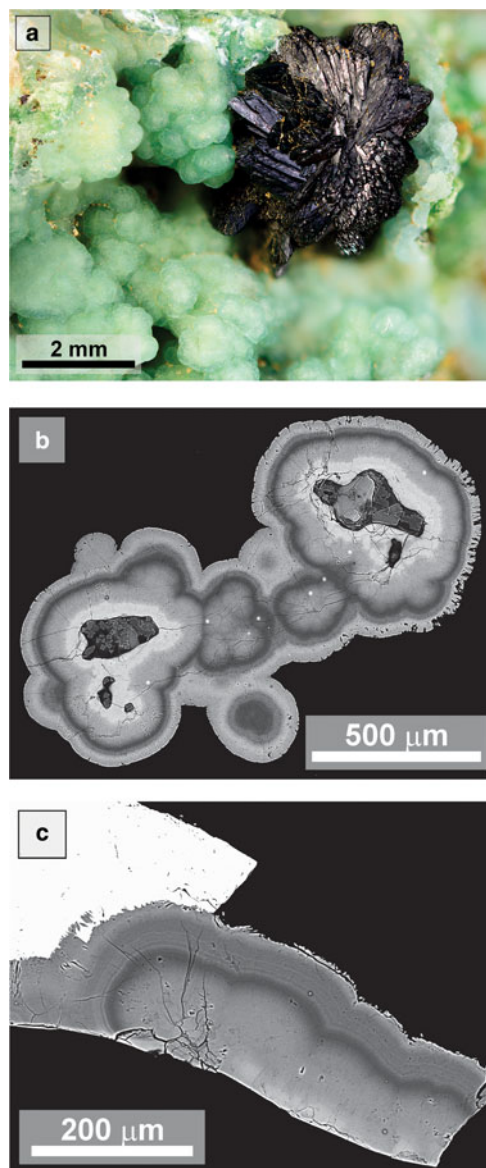


FIG. 2. Images of minerals from Ľubietová-Svätodušná. (a) Photograph of a botryoidal mansfieldite crust (light green) with a younger olivenite (dark green) crystal aggregate. Photo by Pavel Škacha. (b) Back-scattered electron (BSE) image of zoned aggregate of mansfieldite, with pronounced variations in the $\text{Fe}/(\text{Fe} + \text{Al})$ ratio. (c) BSE image of a mansfieldite aggregate (shades of grey), overgrown by a crystal of olivenite (white).

temperature. The step size was set to $0.01^\circ 2\theta$ and the dwell time to 1 s per step. In order to reduce the noise of the Fe fluorescence, excited by the Cu

emission radiation from the Fe-rich samples, the energy window of the Lynxeye detector was set to 0.18–0.25 V.

The images of selected carbon-coated samples were acquired with a Zeiss Ultra Plus field-emission gun scanning electron microscope (SEM) with an accelerating voltage of 2 kV. Semiquantitative energy-dispersive (EDX) analyses were carried out with the same instrument using an acceleration voltage of 20 kV.

Thermogravimetric (TG) and differential thermal (DT) analyses were carried out with a TG 92 Setaram TG/DTA instrument. The samples were heated from room temperature to 900°C in a flow of argon using a 10°C/min heating rate. The samples were also analysed for their water content with a Karl-Fischer NC2/66 titration system (University of Bochum, Germany). The samples were heated to 600°C, the escaping water was absorbed by water-free methanol, and determined quantitatively by titration with I_2 and SO_2 .

The solid-state ^{27}Al MAS NMR experiments were performed on a 600 MHz Agilent NMR spectrometer using a 3.2 mm triple resonance MAS NMR probe, and spinning speeds of 15 and 18 kHz. The ^{27}Al NMR spectra are referenced to 1 M aqueous solution of Al^{3+} chloride ($\delta_{iso}(^{27}Al) = 0$ ppm).

The compositions of the minerals in thin sections were 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, a beam current of 15 nA and a spot size of 10 μm . The wavelength-dispersive X-ray spectrometers were used to measure the elements and X-ray lines of $MgK\alpha$, $AlK\alpha$, $SK\alpha$, $CaK\alpha$, $FeK\alpha$, $ZnK\alpha$, $MnK\alpha$ and $AsL\alpha$. To improve the count-rate statistics, the counting times were 30 s on each peak and 15 s on the background. The standards were MgO for Mg; Al_2O_3 for Al; apatite for Ca; baryte 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 were (in wt.%): Mg 0.03, Ca 0.04, Al 0.02, Fe 0.01, S 0.04, Mn 0.04, As 0.02 and Zn 0.02.

Solubility experiments

For the solubility experiments, from 10 to 25 mg of synthetic mansfieldite was placed in 15 mL

polypropylene centrifugation tubes. The tubes and two procedural blanks were filled with solutions made of 12 mL ultrapure water (resistivity $< 18 M\Omega \cdot cm^{-1}$) and HNO_3 solutions (Suprapur, Merck), with different HNO_3 molarities (between 1 mM and 1 M). The tubes were then capped with paraffin sheets and sealing screw caps. The solutions were shaken moderately (100 rpm) and continuously for a period of 20 weeks at constant room temperature ($24 \pm 1^\circ C$). At the end of the experiments the suspensions in the tubes were centrifuged for 10 min at 4000 rpm, and the pH values were measured. The supernatant was filtered through nylon filters with a pore size of 0.2 μm (ProFill).

The pH values of the solutions were measured by a SenTix®41 and pH/ION 3310 multimeter (WTW, Germany). Calibration WTW solutions 1.679 ± 0.02 ($25^\circ C$) and 4.006 ± 0.02 ($25^\circ C$) were used before the measurements to calibrate the instrument. The samples were submitted for elemental analysis (As, Al) by inductively coupled plasma mass spectrometry (ICP-MS, ThermoScientific XSeries II quadrupole). The NO_3 was analysed by high-performance liquid chromatography (HPLC; Dionex ICS-2000). The residual solids were analysed by PXRD using a PANalytical X'Pert Pro diffractometer (settings: $CuK\alpha$ radiation, 40 kV and 30 mA, 2θ range $5-80^\circ$, step size 0.02° , and counting time of 150 s using an X'Celerator multichannel detector).

Thermodynamic modelling of the aqueous solutions was performed with the *PHREEQC* software suite (Parkhurst and Appelo, 1999). The log K values for the As(V) species were taken from Nordstrom *et al.* (2014); the values for the Al(III) and the Al(III)-As(V) species were retained from the original database.

Calorimetry

High-temperature oxide melt calorimetry has been described in detail by Navrotsky (1997, 2014). The evaluation of experimental data requires empirical calibration, using ~ 15 mg pellets of $\alpha-Al_2O_3$ (Alfa Aesar, 99.997 wt.% metals basis). The samples, in the form of ~ 15 mg pellets, were dissolved in the calorimetric solvent ($3Na_2O \cdot 4MoO_3$) at 975 K. The measured heat effect is the heat of drop solution ($\Delta_{dsol}H$); that is, the sum of heat content ($H_{975} - H_{298}$) and heat of solution ($\Delta_{sol}H$) at 975 K. To expel the water vapour evolved from the sample during dissolution in the calorimetric solvent, the calorimetric assembly was flushed with argon (65 mL/min). The accuracy of the calorimetric

measurements with the molten solvent inside the setup was checked by frequent measurements of $\Delta_{\text{dsol}}H$ for hematite, $\alpha\text{-Fe}_2\text{O}_3$. Majzlan (2017) showed that the value of $95.63 \pm 0.50 \text{ kJ}\cdot\text{mol}^{-1}$ satisfies the constraints of an appropriate closed thermochemical cycle. In this work, the measured $\Delta H_{\text{dsol}}(\alpha\text{-Fe}_2\text{O}_3)$ value was $95.10 \pm 0.73 \text{ kJ}\cdot\text{mol}^{-1}$, in good agreement with the previous number.

The heat capacity of mansfieldite between 2 and 300 K was measured by relaxation calorimetry using a commercial Physical Properties Measurement System (PPMS, from Quantum Design, San Diego, California, USA) at the University of Salzburg, Austria. With due care, the accuracy can be within 1% from 5–300 K, and 5% from 0.7–5 K (Kennedy *et al.* 2007). Powdered samples were wrapped in a thin Al foil and compressed to produce a pellet $\sim 0.5 \text{ mm}$ thick, 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).

Results

The samples were screened for their phase purity with PXRD. All samples used for calorimetry were found to be pure, their unit-cell parameters are listed in Table 1. For the synthetic samples (mansfieldite, angelellite), the chemical content on the cationic (Fe, Al) and the anionic (As) sites was assumed to correspond to the nominal formula.

Cursory EDX analyses did not show the presence of any other cations or anions.

For kamarizaite, the composition was determined by electron microprobe, and is listed in Table 2. The only metal in any substantial concentration was Fe. Kolitsch *et al.* (2016) also reported minor Al in their kamarizaite samples and samples of related minerals. In our case, the Fe/(Fe + Al) ratio was always $>99.4\%$. On the tetrahedral sites, As dominates, however the concentration of P is not negligible, with an average As/(As + P) ratio of 92.2%. The elements S, Se and Si could also be present at this site, but their concentrations are deemed too low to influence the calorimetric results; therefore, they are ignored in the evaluation of the calorimetric data.

In terms of water content of the samples, no assumptions were made. High-temperature oxide-melt calorimetry is particularly sensitive to the variations in H_2O content; therefore, significant effort was expended for its precise determination. Thermogravimetric (TG) analyses did not always lead to satisfactory results. The TG analyses for scorodite and angelellite (Fig. 3a) show a plateau at high temperatures and allow for a precise determination of the volatile content in these samples. Similar behaviour was observed for angelellite (Fig. 3b) although, as expected, the mass loss was very small. The TG results for kamarizaite (Fig. 3c) show the loss of volatiles, probably in the form of H_2O gas; but with steady mass loss at higher temperatures ($>400^\circ\text{C}$). The high-temperature changes could perhaps be attributed to either O_2 loss (during reduction of As_2O_5 to As_2O_3) or volatilization of arsenic species. These changes,

TABLE 1. Space group, unit-cell parameters and water content of the phases investigated in this work*.

Phase	Angelellite	Mansfieldite	Kamarizaite	Scorodite
Space group	$P\bar{1}$	$Pbca$	$P\bar{1}$	$Pcab$
Reference to structural model	Moore and Araki (1978)	Harrison (2000)	Kolitsch <i>et al.</i> (2016)	Hawthorne (1976)
Unit-cell dimensions ($\text{\AA}$)	$a = 6.4736(4)$ $b = 6.6006(4)$ $c = 5.0358(3)$	$a = 8.7917(9)$ $b = 9.7902(9)$ $c = 10.084(1)$	$a = 7.6841(15)$ $b = 8.0662(15)$ $c = 10.193(2)$	$a = 8.9512(9)$ $b = 10.3247(9)$ $c = 10.0438(9)$
Unit-cell angles ($^\circ$), if not constrained by symmetry	$\alpha = 106.23(1)$ $\beta = 98.41(1)$ $\gamma = 108.77(1)$		$\alpha = 68.336(9)$ $\beta = 75.379(11)$ $\gamma = 63.641(9)$	
Unit-cell volume V ($\text{\AA}^3$)	188.90(2)	867.9(2)	523.12(18)	928.2(1)
Water content measured (wt.%)	0.22	18.75	15.36	16.83
Water content nominal (wt.%)	0	17.84	14.73	15.61

*Water content was determined by Karl-Fischer titration and is reported in wt.%.

TABLE 2. Composition of the natural kamarizaite sample (in wt.%), determined by electron microprobe*.

Constituent	wt. %	Constituent	wt. %
Fe ₂ O ₃	40.29(118)	CdO	0.00(1)
As ₂ O ₅	36.46(94)	Sb ₂ O ₅	0.01(1)
P ₂ O ₅	1.90(8)	PbO	0.03(3)
SiO ₂	0.42(12)	HgO	0.01(1)
SO ₃	0.57(3)	CoO	0.05(1)
SeO ₂	0.26(8)	NiO	0.00(0)
Al ₂ O ₃	0.05(3)	CuO	0.03(1)
CaO	0.05(2)	ZnO	0.01(1)
Ag ₂ O	0.01(2)	MnO	0.01(1)
Bi ₂ O ₃	0.02(4)	Total	80.18(186)

*Average of 25 spot analyses; one standard deviation in parentheses.

however, interfered with the loss of H₂O and precluded precise determination of the water content of the sample. Our results are in broad agreement with the TG data for type kamarizaite by Chukanov *et al.* (2010) who observed, using a heating rate of 4°C/min, complete dehydration and dehydroxylation in a vacuum in the 110–420°C temperature range, with a weight loss of 15.3(1)%. The TG measurements of Kolitsch *et al.* (2016), conducted in N₂ and using a heating rate of 5°C/min, were also similar. They revealed a one-step weight loss of 14.6 wt% in the 99–500°C range for kamarizaite; in very good agreement with the calculated value of 14.73 wt%. After $T_{\max}$ (900°C) of the thermal treatment, the decomposition products of kamarizaite were hematite, arsenolite and an unknown FeAsO₄ phase (ICDD 21-910) (Kolitsch *et al.*, 2016).

The water contents of the samples were determined by Karl-Fischer titration, a technique that measures H₂O content chemically, and therefore is not influenced by other volatile species (Table 1).

A common problem with the calorimetry of aluminium oxides and oxysalts is the presence of an amorphous impurity. Such impurities, in small to moderate amounts, can escape the detection by PXRD, but can introduce significant systematic errors into the calorimetric results. Hence, we applied solid state ²⁷Al MAS NMR to screen the mansfieldite sample for amorphous substances. The ²⁷Al MAS NMR spectrum of mansfieldite contains a single ²⁷Al NMR resonance in the region for octahedral Al [$\delta_{\text{iso}}(^{27}\text{Al}) = 0.6(5)$ ppm]. The resonance has a distinct line shape, which could either originate from a single site with a second order quadrupole line shape, or two ²⁷Al sites with

similar chemical shift and relative intensity. To distinguish between these two possibilities, a ²⁷Al 3QMAS NMR spectrum was recorded (Fig. 4). This experiment removes the second order quadrupole line broadening in the F1 dimension, and for each site gives a featureless line shape. A single ²⁷Al resonance is observed, confirming the presence of one crystallographic Al site in mansfieldite, and thus the sample purity. It is characterized by a moderate quadrupole coupling interaction [$\delta_{\text{iso}}(^{27}\text{Al}) = 0.6(5)$ ppm, $C_Q = 2.7(2)$ MHz, $\eta = 0.15(5)$], as obtained from analysis of the ²⁷Al single pulse and 3QMAS NMR spectra.

Calorimetric determination of enthalpies of formation

None of the phases studied in this work dissolved in 5 N HCl, the calorimetric solvent routinely used in our laboratory (Majzlan, 2017). However, the iron arsenates dissolve rapidly in a high-temperature oxide melt, and are therefore suitable for high-temperature oxide-melt calorimetry. Mansfieldite presents a set of specific difficulties which will be discussed briefly later; these difficulties precluded any solution calorimetry work on this phase.

High-temperature oxide-melt calorimetry of arsenical compounds

The high-temperature oxide-melt calorimetry of arsenical compounds was tested and shown to be feasible by Forray and Navrotsky (2005) and Forray *et al.* (2014). These authors performed a set of experiments with the well characterized As₂O₃ and As₂O₅ to show that reliable enthalpies of formation

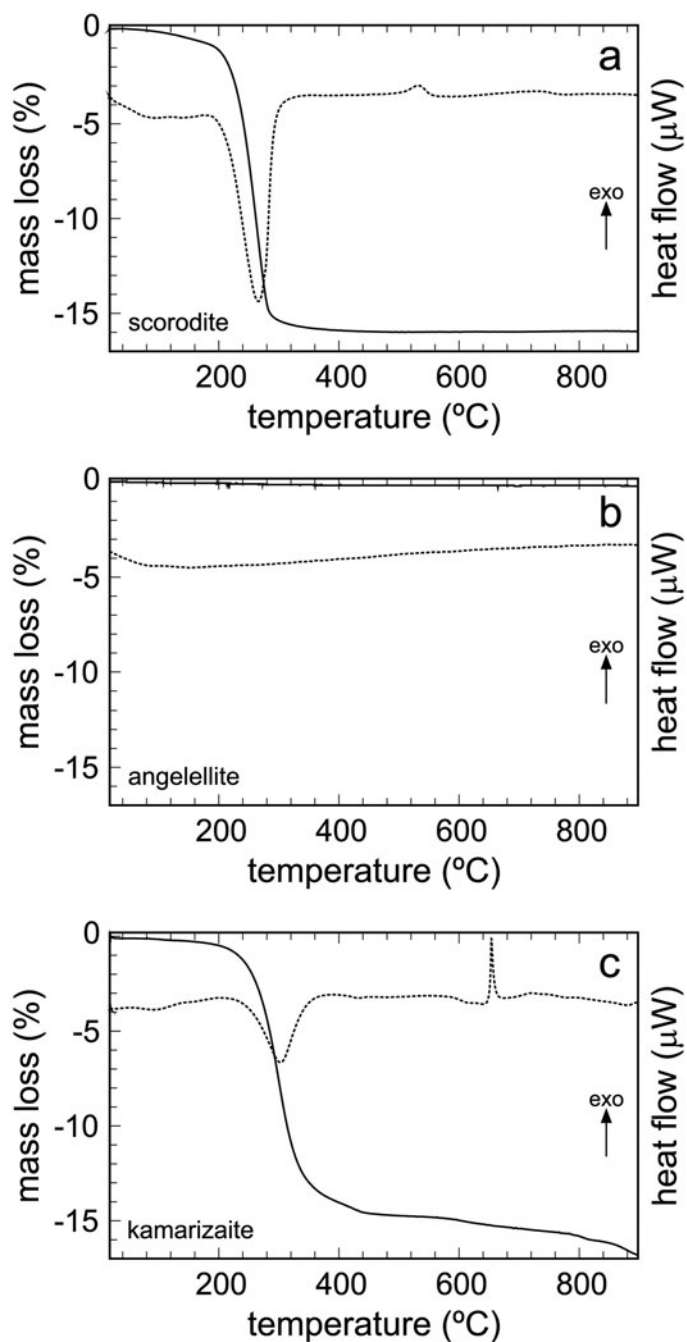


FIG. 3. Thermogravimetric (TG) and differential thermal (DT) traces for the samples used for high-temperature oxide-melt calorimetry in this work. TG traces are shown as solid lines, with the corresponding mass loss on the left-hand side vertical axis. DT traces are shown as dashed lines.

can be obtained if the dissolution enthalpies of these two phases in a calorimetric solvent (a near-eutectic mixture of Na_2MoO_4 and MoO_3 , Navrotsky and Kleppa, 1968) are measured. They also tested the experimental system for arsenic that may escape the high-temperature zone of the calorimeter, concluding that arsenic is completely retained in the melt. Later, Majzlan (2017) showed that the oxidation state of arsenic in the melt is predominantly maintained as As^{5+} ; the sodium molybdate melt has a tendency to oxidize most elements into their highest oxidation state and tolerate such oxidation processes without parasitic reactions (Navrotsky, 1997).

Hence, it may seem that high-temperature oxide-melt calorimetry on arsenical compounds is an established technique, working flawlessly and yielding good results. Yet, the enthalpy of formation of As_2O_3 from Forray *et al.* (2014), $-652.6 \text{ kJ}\cdot\text{mol}^{-1}$, deviates greatly from other recommended values, with the exception of the datum of $-653.9 \text{ kJ}\cdot\text{mol}^{-1}$ in SGTE (1999). All the other values cluster around $-657 \text{ kJ}\cdot\text{mol}^{-1}$. Contrary to the statement of Forray *et al.* (2014) that the origin of these values is unclear because they can be traced to Wagman *et al.* (1968), who gave no references, these thermodynamic data can be tracked back to a set of solubility and heat capacity studies with excellent mutual agreement and tight errors. The derivation of the last recommended value, $-657.06 \text{ kJ}\cdot\text{mol}^{-1}$, was detailed in

Nordstrom *et al.* (2014). Hence, there is a difference of $4.46 \text{ kJ}\cdot\text{mol}^{-1}$ between the value derived by Forray *et al.* (2014) and that recommended by Nordstrom *et al.* (2014). Such a discrepancy is not satisfactory.

Selection of reference compounds for high-temperature oxide-melt calorimetry: Scorodite and KH_2AsO_4

In this work, we carried out additional tests to judge the feasibility of high-temperature oxide-melt calorimetry on arsenical compounds. Instead of using As_2O_3 , a strongly hygroscopic and difficult-to-control compound, scorodite ($\text{FeAsO}_4\cdot 2\text{H}_2\text{O}$) was chosen for these tests. Scorodite appears, in relation to thermodynamic data, to be the best known As(V) phase. The solubility studies (Langmuir *et al.*, 2006) and calorimetric work (Majzlan *et al.*, 2012) on scorodite converge almost perfectly (cf. Nordstrom *et al.*, 2014). Scorodite is easy to prepare, maintain and handle – and therefore is an excellent reference compound.

Chemical analyses of the synthetic scorodite sample used in this study showed that the composition is $\text{FeAsO}_4\cdot 2.19\text{H}_2\text{O}$. This information is important in that the high-temperature oxide-melt calorimetry (in contrast to the acid-solution calorimetry) is very sensitive to the H_2O content of the samples. The heat effect due to 1 mole of H_2O is

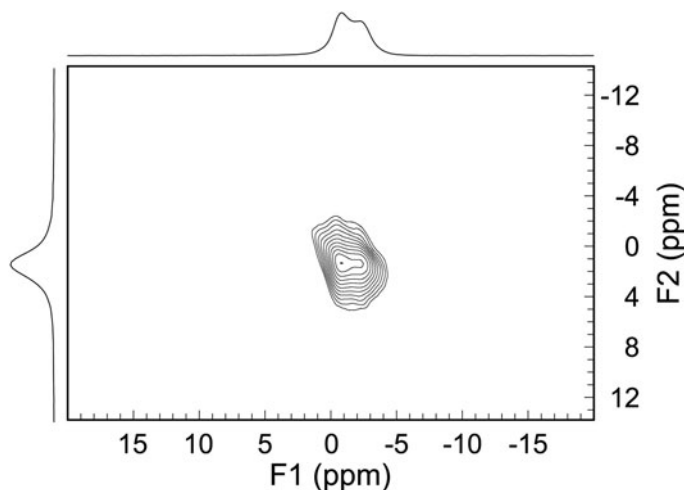


FIG. 4. ^{27}Al MAS NMR spectrum of synthetic mansfieldite with projection showing the single pulse ^{27}Al MAS NMR spectrum (F2, above) and the single resonance in the indirect dimension (F1, left), where the second order quadrupole interaction is removed. The spectrum was recorded at 14.1 T using 18 kHz spinning and the three pulse z-filtered sequence.

69 kJ·mol⁻¹ for the high-temperature calorimetry, but only -0.54 kJ·mol⁻¹ for the acid-solution calorimetry (for both types of calorimetry experiments with temperature and solvents were as outlined in Majzlan, 2017). As the nominal composition of scorodite is FeAsO₄·2H₂O, and its crystal structure (Hawthorne, 1976) has no free or exchangeable H₂O molecules (such as in zeolites, for example), it can be assumed that the excess water is adsorbed physically onto the surfaces of the particles or occluded within them. Therefore, the excess water can be thermodynamically handled as bulk water.

A thermodynamic cycle for scorodite with the composition FeAsO₄·2.19H₂O is listed in Table 3. Assuming that the excess water is loosely bound liquid water, the calculated enthalpy of formation for FeAsO₄·2H₂O is -1512.7 ± 1.8 kJ·mol⁻¹, differing by 3.8 kJ·mol⁻¹ from the calorimetrically determined value of -1508.9 ± 2.9 kJ·mol⁻¹ (Majzlan *et al.*, 2012) and is recommended by Nordstrom *et al.* (2014). This difference is also not any reason for excessive rejoicing, but it shows the true magnitude of the discrepancies if many crosschecks are performed.

Another test was carried out with KH₂AsO₄, a simple compound presumably with a nominal composition. The data, already collected and briefly discussed by Majzlan *et al.* (2012), lead to

an enthalpy of formation for this phase of -1184.9 ± 2.8 kJ·mol⁻¹; differing by 3.7 kJ·mol⁻¹ from the acid-solution calorimetric value of -1181.2 ± 2.0 kJ·mol⁻¹ (cf. Majzlan, 2017).

These tests show that in both cases, the values determined by high-temperature oxide-melt calorimetry deviate by 3.7–3.8 kJ·mol⁻¹ from the better constrained thermochemical data. This difference hints that there may be a systematic error of this magnitude included in the data for As₂O₅, either in the drop solution enthalpy or the enthalpy of formation. Therefore, in this work, the thermochemical cycles for the arsenates are not constructed with As₂O₅ as the reference compound.

It seems that the most accurately known enthalpy of formation of the arsenates is that for scorodite. Therefore, this phase was chosen as the reference phase for arsenic in the thermochemical cycles for the other iron arsenates investigated. A proper combination of the enthalpies of reactions 1, 2 and 5 (-ΔH₁ + ΔH₂ - 0.19ΔH₅, see Table 3) gives the enthalpy of drop solution of stoichiometric FeAsO₄·2H₂O in molten 3Na₂O·4MoO₃ at 975 K, as +289.27 ± 1.46 kJ·mol⁻¹. This value will be used in the following thermochemical cycles.

Angelellite

The enthalpy of formation of angelellite was determined *via* the thermochemical cycle in

TABLE 3. Thermochemical cycle for scorodite*.

FeAsO ₄ ·2.19H ₂ O (cr,l, 298) = FeAsO ₄ ·2H ₂ O (cr, 298) + 0.19H ₂ O (l, 298)	1
FeAsO ₄ ·2.19H ₂ O (cr,l, 298) = 0.5Fe ₂ O ₃ (sol, 975) + 0.5As ₂ O ₅ (sol, 975) + 2.19H ₂ O (g, 975)	2
α-Fe ₂ O ₃ (cr, 298) = Fe ₂ O ₃ (sol, 975)	3
As ₂ O ₅ (cr, 298) = As ₂ O ₅ (sol, 975)	4
H ₂ O (l, 298) = H ₂ O (g, 975)	5
2Fe (cr, 298) + 1.5O ₂ (g, 298) = α-Fe ₂ O ₃ (cr, 298)	6
2As (cr, 298) + 2.5O ₂ (g, 298) = As ₂ O ₅ (cr, 298)	7
H ₂ (g, 298) + 0.5O ₂ (g, 298) = H ₂ O (l, 298)	8
Fe (cr, 298) + As (cr, 298) + 3O ₂ (g, 298) + 2H ₂ (g, 298) = FeAsO ₄ ·2H ₂ O (cr, 298)	
ΔH ₁ = 0 (with the assumption that the excess water is liquid bulk water)	
ΔH ₂ = 302.20 ^a ± 1.46 ^b (5) ^c	
ΔH ₃ = 95.63 ± 0.50 (see Majzlan, 2017)	
ΔH ₄ = 76.7 ± 0.8 (Forray <i>et al.</i> , 2005)	
ΔH ₅ = 68.93 (calculated from Robie and Hemingway, 1995)	
ΔH ₆ = -826.2 ± 1.3 (Robie and Hemingway, 1995)	
ΔH ₇ = -925.5 ± 1.0 (Wagman <i>et al.</i> , 1968)	
ΔH ₈ = -285.8 ± 0.1 (Robie and Hemingway, 1995)	
Δ _r H ⁰ (scorodite) = ΔH ₁ - ΔH ₂ + 0.5ΔH ₃ + 0.5ΔH ₄ + 2.19ΔH ₅ + 0.5ΔH ₆ + 0.5ΔH ₇ + 2ΔH ₈	

*All enthalpy values in kJ·mol⁻¹. Abbreviations of phases: cr = crystalline, l = liquid, g = gas, sol = solution in the calorimetric solvent. Temperature of each participating reactant or product is specified in K.

^a Mean; ^b two standard deviations of the mean; ^c number of measurements.

Table 4. Chemical analysis gave the formula $\text{Fe}_4(\text{AsO}_4)_2\text{O}_3 \cdot 0.017\text{H}_2\text{O}$. The small amount of water is certainly physisorbed, but even this small amount accounts for a correction of $1.2 \text{ kJ} \cdot \text{mol}^{-1}$. The possibility of structural OH groups was entertained by Moore and Araki (1978), but rejected by detailed neutron diffraction studies (Wright *et al.*, 2000). The calculated enthalpy of formation from the elements at standard conditions is $-2625.7 \pm 7.3 \text{ kJ} \cdot \text{mol}^{-1}$ for the composition $\text{Fe}_4(\text{AsO}_4)_2\text{O}_3$.

Kamarizaite

The enthalpy of formation of kamarizaite was determined via the thermochemical cycle in Table 5. Chemical analysis gave the formula $\text{Fe}_3[(\text{AsO}_4)_{0.922}(\text{PO}_4)_{0.078}]_2(\text{OH})_3 \cdot 3.159\text{H}_2\text{O}$. As with scorodite and angelellite, the small amount of excess H_2O ($0.159\text{H}_2\text{O}$) is treated as physisorbed water in the thermochemical cycle (Table 5). Thermodynamic properties are therefore reported for the composition $\text{Fe}_3[(\text{AsO}_4)_{0.922}(\text{PO}_4)_{0.078}]_2(\text{OH})_3 \cdot 3\text{H}_2\text{O}$. The enthalpy of formation for this composition is $-3640.4 \pm 7.9 \text{ kJ} \cdot \text{mol}^{-1}$.

Mansfieldite

The dissolution of mansfieldite in 5 N HCl was so slow that a calorimetric determination of a reliable dissolution enthalpy was unattainable. Mansfieldite may dissolve in the molten $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$, but corundum, the reference phase of choice for aluminium, does not. Corundum dissolves readily in molten lead

borate ($2\text{PbO} \cdot \text{B}_2\text{O}_3$), but this solvent has never been tested as an alternative for calorimetry on arsenical compounds. An alternative approach was chosen, specifically the experimental determination of the solubility product and measurement of low-temperature heat capacity. These data sets also allow for derivation of the enthalpy of formation.

Determination of solubility product of mansfieldite

To obtain the thermodynamic data for mansfieldite, its solubility was studied directly in aqueous solutions. Two sets of experiments were performed, under similar conditions, in Jena and Prague, and the results are summarized in Table 6.

The aqueous concentrations of Al(III), As(V), NO_3^- , together with the pH (Table 6), served for the calculation of the solubility product, using the software package *PHREEQC*. The data are shown graphically in Fig. 5 as an apparent saturation index for an assumed value of the solubility product ($\log K_{\text{sp}} = -21.4$, see below) of mansfieldite. In a well-conducted experiment, the data over a certain pH range would plot as a plateau whose mean defines the solubility product. However, in the case of mansfieldite, as the pH decreases, the data progressively deviate from such a plateau. Nevertheless, because of the hydrolysis of metals such as Fe or Al, solubility data for Al or Fe arsenates are preferably taken at low pH (cf. Langmuir *et al.*, 2006). At higher pH, the

TABLE 4. Thermochemical cycle for angelellite*.

$\text{Fe}_4(\text{AsO}_4)_2\text{O}_3 \cdot 0.017\text{H}_2\text{O}$ (cr, 1, 298) = $\text{Fe}_4(\text{AsO}_4)_2\text{O}_3$ (cr, 298) + $0.017\text{H}_2\text{O}$ (l, 298)	9
$\text{Fe}_4(\text{AsO}_4)_2\text{O}_3 \cdot 0.017\text{H}_2\text{O}$ (cr, 1, 298) = $2\text{Fe}_2\text{O}_3$ (sol, 975) + As_2O_5 (sol, 975) + $0.017\text{H}_2\text{O}$ (g, 975)	10
$\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ (cr, 298) = $0.5\text{Fe}_2\text{O}_3$ (sol, 975) + $0.5\text{As}_2\text{O}_5$ (sol, 975) + $2\text{H}_2\text{O}$ (g, 975)	11
Fe (cr, 298) + As (cr, 298) + 3O_2 (g, 298) + 2H_2 (g, 298) = $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ (cr, 298)	12
4Fe (cr, 298) + 2As (cr, 298) + 5.5O_2 (g, 298) = $\text{Fe}_4(\text{AsO}_4)_2\text{O}_3$ (cr, 298)	
$\Delta H_f = 0$ (with the assumption that the excess water is liquid bulk water)	
$\Delta H_{10} = 324.47^a \pm 2.94^b(7)^c$	
$\Delta H_{11} = 289.27 \pm 1.46$ (calculated as $-\Delta H_1 + \Delta H_2 - 0.19\Delta H_5$, see text)	
$\Delta H_{12} = -1508.9 \pm 2.9$ (Majzlan <i>et al.</i> 2012)	
$\Delta_f H^\circ(\text{angelellite}) = \Delta H_9 - \Delta H_{10} + 2\Delta H_{11} + \Delta H_3 + (0.017-4) \Delta H_5 + \Delta H_6 - 4\Delta H_8 + 2\Delta H_{12}$	

*All enthalpy values in $\text{kJ} \cdot \text{mol}^{-1}$. Abbreviations of phases: cr = crystalline, l = liquid, g = gas, sol = solution in the calorimetric solvent. Temperature of each participating reactant or product is specified in K. The reactions 3, 5, 6, and 8 are listed in Table 3, together with their enthalpies. Note that the enthalpy of formation of scorodite (reaction 12) is not that calculated from the thermochemical cycle in Table 3 but that reported by Majzlan *et al.* (2012); for explanation, see text.

^a mean; ^b two standard deviations of the mean; ^c number of measurements.

TABLE 5. Thermochemical cycle for kamarizaite (natural sample with composition $\text{Fe}_3[(\text{AsO}_4)_{0.922}(\text{PO}_4)_{0.078}]_2(\text{OH})_3 \cdot 3.159\text{H}_2\text{O}$)*.

$\text{Fe}_3(\text{AsO}_4)_{2a}(\text{PO}_4)_{2-2a}(\text{OH})_3 \cdot (3+x)\text{H}_2\text{O}$ (cr, 298) = $\text{Fe}_3(\text{AsO}_4)_{2a}(\text{PO}_4)_{2-2a}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ (cr, 298) + $x\text{H}_2\text{O}$ (l, 298)	13
$\text{Fe}_3(\text{AsO}_4)_{2a}(\text{PO}_4)_{2-2a}(\text{OH})_3 \cdot (3+x)\text{H}_2\text{O}$ (cr, 298) = $1.5\text{Fe}_2\text{O}_3$ (sol, 975) + $a\text{As}_2\text{O}_5$ (sol, 975) + $(1-a)\text{P}_2\text{O}_5$ (sol, 975) + $x\text{H}_2\text{O}$ (g, 975)	14
P_2O_5 (cr, 298) = P_2O_5 (sol, 975)	15
2P (cr, 298) + 2.5O_2 (g, 298) = P_2O_5 (cr, 298)	16
3Fe (cr, 298) + $2a\text{As}$ (cr, 298) + $2(1-a)\text{P}$ (cr, 298) + 7O_2 (g, 298) + 4.5H_2 (g, 298) = $\text{Fe}_3(\text{AsO}_4)_{2a}(\text{PO}_4)_{2-2a}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ (cr, 298)	
$\Delta H_{13} = 0$ (with the assumption that the excess water is liquid bulk water)	
$\Delta H_{14} = 673.93^{a \pm 5.16^{b(c)}}$	
$\Delta H_{15} = -164.6 \pm 0.85$ (Ushakov et al. 2001)	
$\Delta H_{16} = -1504.9 \pm 0.5$ (Robie and Hemingway 1995)	
$\Delta_f H^\circ(\text{kamarizaite}) = \Delta H_{13} - \Delta H_{14} + x\Delta H_5 + 2a(\Delta H_{11} + \Delta H_{12}) + (1-a)(\Delta H_{15} + \Delta H_{16}) + 0.5(3-2a)(\Delta H_3 + \Delta H_6) + 0.5(9-8a)(\Delta H_5 + \Delta H_8)$	

*For this composition, the variables in reactions 13, 14, and the formation reaction for kamarizaite are: $x = 0.159$ and $a = 0.922$. Note that the thermochemical cycle generates the enthalpy of formation for the composition

$\text{Fe}_3[(\text{AsO}_4)_{0.922}(\text{PO}_4)_{0.078}]_2(\text{OH})_3 \cdot 3\text{H}_2\text{O}$, treating the excess H_2O ($0.159\text{H}_2\text{O}$) as physisorbed water (reaction 13). All enthalpy values in $\text{kJ} \cdot \text{mol}^{-1}$. Abbreviations of phases: cr = crystalline, l = liquid, g = gas, sol = solution in the calorimetric solvent. The reactions 3, 5, 6, 8, 11, and 12 are listed in Tables 3 and 4, together with their enthalpies.

^a Mean; ^b two standard deviations of the mean; ^c number of measurements

dissolution tends to be incongruent, as is also documented in our data (Table 6).

The systematic changes of the apparent solubility product at low pH values are difficult to comprehend. They could be caused if another phase, Al hydroxide or arsenate, becomes the solubility-controlling phase. However, the PXRD data after the solubility experiments show no additional crystalline impurity at all. Amorphous material, in turn, cannot be considered because its solubility is higher than the solubility of crystalline mansfieldite.

In this situation, we tentatively chose $\log K_{sp} = -21.4 \pm 0.5$ as the best value for mansfieldite for

the dissolution reaction $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$ (cr) = Al^{3+} (aq) + AsO_4^{3-} (aq) + $2\text{H}_2\text{O}$ (aq). This datum is derived as the mean of two data points with congruent dissolution, which belong to the plateau in Fig. 5. These two experiments are highlighted in bold in Table 6. For data at higher pH, the dissolution is clearly incongruent. At lower pH, a systematic change of the ion activity product with pH is observed. The choice of this value is also to some extent supported by thermodynamic data from other studies, as discussed below. Using the appropriate thermodynamic data for the aqueous ions and liquid water, the Gibbs free energy of

TABLE 6. Results of mansfieldite solubility measurements in Jena and Prague*.

Solubility experiments in Jena									
pH	1.00	1.50	2.00	2.37	2.73	3.07	3.48	3.73	4.07
Al	43.4	19.7	6.5	15.1	8.2	4.24	2.42	1.48	0.68
As	118	54.2	17.3	33.8	14.0	5.59	2.08	0.702	0.306
NO_3	8080	1965	536	279.8	129.2	62.21	32.11	15.6	6.46
Solubility experiments in Prague									
pH	0.35	0.40	1.01	1.29	1.34	1.91	2.33	3.03	
Al	160	136	51	32.1	29.8	18.5	8.0	2.2	
As	440	376	145	83.9	77.6	49.4	21.5	50.9	
NO_3	31,015	15,574	6203	3101	1551	620	310	62.0	

*pH in standard units, chemical species in mg/L. Two experiments marked in bold were used to estimate the $\log K_{sp}$ for mansfieldite.

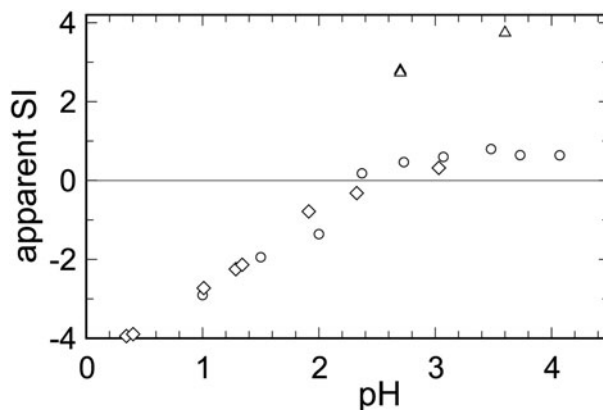


FIG. 5. Calculated apparent saturation indices for assumed $\log K_{sp}$ (mansfieldite) = -21.4 . Circles: mansfieldite dissolution, this work (experiments in Jena); diamonds: mansfieldite dissolution, this work (experiments in Prague); triangles: dissolution of amorphous $\text{AlAsO}_4 \cdot 3.5\text{H}_2\text{O}$ (Pantuzzo *et al.*, 2014).

formation of mansfieldite at standard conditions is $-1733.4 \pm 3.5 \text{ kJ} \cdot \text{mol}^{-1}$.

Determination and estimation of the standard entropies

Having measured $\Delta_f H^\circ$ or $\log K_{sp}$ (and hence, also $\Delta_f G^\circ$) of the studied phases, a complete thermodynamic data set for each phase can be obtained if the standard entropies are known. Two approaches were followed for this purpose. For the iron arsenates, the entropies were estimated. Estimates of entropies are relatively robust, especially if entropies of similar phases have been previously measured. This is the case with arsenates of ferric iron (e.g. Majzlan *et al.*, 2012). For mansfieldite, the low-temperature heat capacity was measured experimentally, and the entropy calculated from these data.

The basis for the estimation of entropies is Kopp's rule which states that the entropy of a phase is simply a linear combination of the entropies of its components, if these components are crystal-chemically comparable to that phase. For example, this means that the entropy of $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ could be estimated as the linear combination of entropies of $0.5\text{Fe}_2\text{O}_3$, $0.5\text{As}_2\text{O}_5$ and $2\text{H}_2\text{O}$; the latter not in the form of liquid water but of metastable ice instead. Our results (e.g. Majzlan *et al.*, 2012) show that the experimental entropies of the oxides (Fe_2O_3 , As_2O_5 , P_2O_5), in combination with the entropy of metastable ice at $T = 298.15 \text{ K}$, yield good results. The numerical values are $S^\circ(\alpha\text{-Fe}_2\text{O}_3) = 87.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $S^\circ(\text{P}_2\text{O}_5) = 114.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ (Robie and

Hemingway, 1995), $S^\circ(\text{As}_2\text{O}_5) = 105.44 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ (Nordstrom and Archer, 2003) and $S^\circ(\text{H}_2\text{O}, \text{cr}) = 41.94 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ (Majzlan *et al.*, 2012). Taking these values, the estimated standard entropy for angelellite [for the composition $\text{Fe}_4(\text{AsO}_4)_2\text{O}_3$] is $280.2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. For kamarizaite, with the nominal composition $\text{Fe}_3(\text{AsO}_4)_2(\text{OH})_3 \cdot 3\text{H}_2\text{O}$, the estimate is $425.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; and for the natural kamarizaite $[\text{Fe}_3[(\text{AsO}_4)_{0.922}(\text{PO}_4)_{0.078}]_2(\text{OH})_3 \cdot 3\text{H}_2\text{O}]$ it is $426.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

Low-temperature heat-capacity data for mansfieldite, measured by relaxation calorimetry from 2–300 K, are shown in Fig. 6 and also listed in Supplementary Table S1. At the low-temperature end, heat capacity was extrapolated to 0 K by an extended Debye polynomial $C_p = A_3 T^3 + A_5 T^5$. The remaining data were fitted with orthogonal polynomials. The differential scanning calorimetry data, measured between 280–300 K, compared very well with the relaxation data (Fig. 6). As expected, no anomalies or phase transitions are detectable in the data. Thermodynamic functions, calculated from smoothed polynomials that fit the data, are listed in Table 7. The standard entropy at $T = 298.15 \text{ K}$ is $148.2 \pm 1.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

Discussion

Critical evaluation of the thermodynamic data and estimates for nominal compositions

A complete thermodynamic data set for each phase studied in this work is listed in Table 8. The solubility products ($\log K_{sp}$) can be inserted

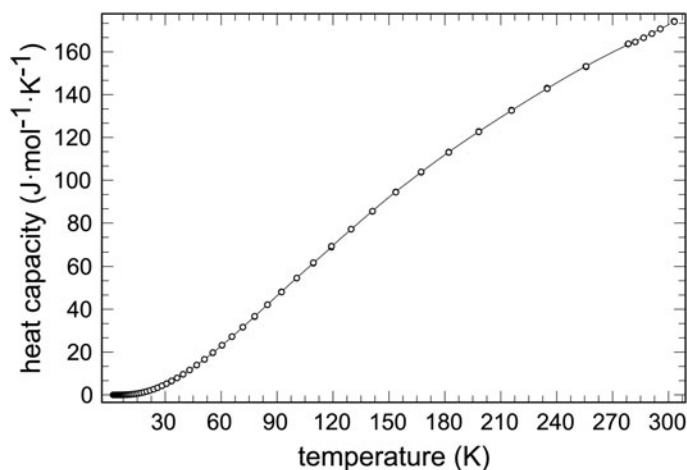


FIG. 6. Low-temperature heat capacity data for synthetic mansfieldite, $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$, molecular mass $201.931 \text{ g} \cdot \text{mol}^{-1}$. The lines are the fits for integration and calculation of molar thermodynamic functions (Table 7).

directly into common geochemical codes such as *PHREEQC* or *The Geochemists' Workbench* (<https://www.gwb.com/>). Variation of the solubility products with temperature (over a limited temperature range) can be calculated with the enthalpies of dissolution reactions ($\Delta_r H^\circ$), which are also given in Table 8.

The calculated solubility over a wide pH range is displayed graphically in Fig. 7. Note that the

solubility curves were calculated by ignoring the other intervening phases, such as Fe oxides (cf. Langmuir *et al.*, 2006; Majzlan *et al.*, 2012). The incongruent nature of dissolution of the phases investigated will be discussed later.

Mansfieldite

The solubility product of mansfieldite was estimated from the solubility data generated in this

TABLE 7. Thermodynamic functions for mansfieldite, $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$ (molecular mass $201.931 \text{ g} \cdot \text{mol}^{-1}$).

T K	C_p $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$H_T - H_0$ $\text{J} \cdot \text{mol}^{-1}$	S° $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$G_T - H_0$ $\text{J} \cdot \text{mol}^{-1}$	T K	C_p $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$H_T - H_0$ $\text{J} \cdot \text{mol}^{-1}$	S° $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$G_T - H_0$ $\text{J} \cdot \text{mol}^{-1}$
0	0	0	0	0	160	98.87	6592	64.42	-3716
10	0.1544	0.3671	0.04844	-0.1173	170	105.5	7614	70.61	-4391
20	1.578	7.38	0.4801	-2.222	180	111.9	8701	76.82	-5128
30	4.960	38.57	1.699	-12.39	190	117.9	9850	83.04	-5927
40	9.889	111.7	3.770	-39.05	200	123.7	11060	89.23	-6789
50	15.94	240.1	6.608	-90.34	210	129.4	12320	95.41	-7712
60	22.84	433.3	10.11	-173.4	220	134.9	13650	101.6	-8697
70	30.38	699.0	14.19	-294.5	230	140.3	15020	107.7	-9743
80	38.29	1042	18.76	-458.9	240	145.5	16450	113.7	-10850
90	46.31	1465	23.74	-671.1	250	150.5	17930	119.8	-12020
100	54.23	1968	29.03	-934.7	260	155.3	19460	125.8	-13250
110	61.99	2549	34.56	-1253	270	159.8	21040	131.7	-14530
120	69.64	3207	40.28	-1627	280	164.1	22660	137.6	-15880
130	77.25	3942	46.16	-2059	290	168.2	24320	143.5	-17290
140	84.78	4752	52.16	-2550	298.15	171.8	25700	148.2	-18470
150	92.05	5637	58.26	-3102	300	172.7	26020	149.2	-18750

TABLE 8. Summary of thermodynamic data for the phases studied. All enthalpies and Gibbs free energies in $\text{kJ}\cdot\text{mol}^{-1}$, entropies in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The estimated values for the nominal composition of kamarizaite are given without uncertainties, because they are not known.

	Mansfieldite $\text{AlAsO}_4\cdot 2\text{H}_2\text{O}$	Angelellite $\text{Fe}_4(\text{AsO}_4)_2\text{O}_3$	Kamarizaite $\text{Fe}_3[(\text{AsO}_4)_{0.922}(\text{PO}_4)_{0.078}]_2(\text{OH})_3\cdot 3\text{H}_2\text{O}$	Kamarizaite $\text{Fe}_3(\text{AsO}_4)_2(\text{OH})_3\cdot 3\text{H}_2\text{O}$
$\Delta_f H^\circ$	-1969.8 ± 3.5	-2625.6 ± 7.3	-3640.4 ± 7.9	-3579.0
S°	148.2 ± 1.1	280.2	426.0	425.3
$\Delta_f S^\circ$	-792.6 ± 1.4	-1027.9	-1751.6	-1751.5
$\Delta_f G^\circ$	-1733.4 ± 3.5	-2319.2 ± 7.9	-3118.2 ± 8.5	-3056.8
$\Delta_r G^\circ$	122.1 ± 2.9^a	247.6 ± 8.8^b	292.5 ± 9.1^c	290.0^d
$\log K_{\text{sp}}$	-21.4 ± 0.5^a	-43.4 ± 1.5^b	-51.2 ± 1.6^c	-50.8^d
$\Delta_f H^\circ$	-32.4 ± 4.1^a	-216.3 ± 8.9^b	-70.2 ± 8.6^c	-70.4^d

^a for reaction $\text{AlAsO}_4\cdot 2\text{H}_2\text{O} (\text{cr}) = \text{Al}^{3+} (\text{aq}) + \text{AsO}_4^{3-} (\text{aq}) + 2\text{H}_2\text{O} (\text{l})$

^b for reaction $\text{Fe}_4(\text{AsO}_4)_2\text{O}_3 (\text{cr}) + 6\text{H}^+ (\text{aq}) = 4\text{Fe}^{3+} (\text{aq}) + 2\text{AsO}_4^{3-} (\text{aq}) + 3\text{H}_2\text{O} (\text{l})$

^c for reaction $\text{Fe}_3[(\text{AsO}_4)_{0.922}(\text{PO}_4)_{0.078}]_2(\text{OH})_3\cdot 3\text{H}_2\text{O} (\text{cr}) + 3\text{H}^+ (\text{aq}) = 3\text{Fe}^{3+} (\text{aq}) + 1.844\text{AsO}_4^{3-} (\text{aq}) + 0.156\text{PO}_4^{3-} (\text{aq}) + 6\text{H}_2\text{O} (\text{l})$

^d for reaction $\text{Fe}_3(\text{AsO}_4)_2(\text{OH})_3\cdot 3\text{H}_2\text{O} (\text{cr}) + 3\text{H}^+ (\text{aq}) = 3\text{Fe}^{3+} (\text{aq}) + 2\text{AsO}_4^{3-} (\text{aq}) + 6\text{H}_2\text{O} (\text{l})$

work (Fig. 5). A more precise determination would be desirable; however, several lines of evidence show that the accuracy, even for such an estimate, was not compromised greatly.

Solubility of a crystalline phase is expected to be lower than its amorphous counterpart. In other words, the amorphous counterpart imposes an upper limit on the solubility of the crystalline phase. Pantuzzo *et al.* (2014) measured the solubility of amorphous $\text{AlAsO}_4\cdot 3.5\text{H}_2\text{O}$ and determined it as $\log K_{\text{sp}} = -18.06 \pm 0.05$. The value was calculated from a single point at $\text{pH} = 2.7$, measured in triplicate. Another measurement at $\text{pH} = 3.5$ was not used because the dissolution was found to be incongruent. Hence, there are no data at lower pH , and it is not clear if the solubility of this material would also show the behaviour observed in our samples. The tight error on the result is the consequence of using a triplicate of a single point, not an excellent agreement over a pH range. Despite this, the solubility of the amorphous $\text{AlAsO}_4\cdot 3.5\text{H}_2\text{O}$ is, as expected, several orders of magnitude higher than the solubility of mansfieldite from this work.

A lower limit on the solubility of mansfieldite can be found by comparison with the isostructural scorodite. Le Berre *et al.* (2007) have carried out a series of syntheses and leaching experiments on mansfieldite, scorodite, and the solid-solution members between them. They found that the leachability systematically increases from scorodite to mansfieldite. They reported that mansfieldite has

“at least 10 times higher solubility than that of scorodite”. Although kinetic and thermodynamic arguments are mixed in their work (because the U.S. Environmental Protection Agency Toxicity Characterization Leaching Procedure cannot determine solubility, but only leachability over a certain time), our data support their conclusion. Calculated solubility curves (Fig. 7) are in agreement with their statement. At $\text{pH} = 4$, the solubility of mansfieldite is ~ 10 times higher than that of scorodite. At $\text{pH} = 6$, their solubilities are similar, but this pH region is irrelevant because both phases undergo incongruent dissolution. Congruent dissolution and efficient arsenic retention at this pH cannot be reached, either in the laboratory or in the field.

Older datum of $\log K_{\text{sp}} = -15.8$ for $\text{AlAsO}_4\cdot 2\text{H}_2\text{O}$ (Chukhlantsev, 1956) seems to complicate matters. However, the synthesis product was not characterized in that case, and it is not clear what was actually measured. These early measurements have been discussed and questioned in the literature, not only with respect to the Al arsenate but also to the arsenates of other metals (e.g. Pantuzzo *et al.*, 2014 and references therein).

Kamarizaite

In this work, we derived the thermodynamic properties of a natural sample of kamarizaite, with the composition $\text{Fe}_3[(\text{AsO}_4)_{0.922}(\text{PO}_4)_{0.078}]_2(\text{OH})_3\cdot 3\text{H}_2\text{O}$. Even though the currently used geochemical codes easily operate with such

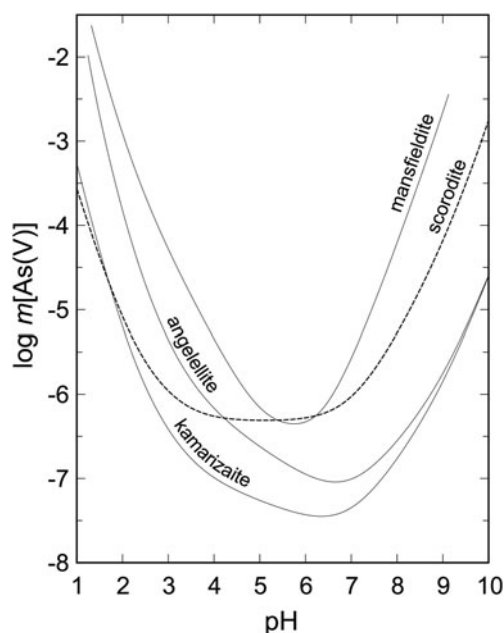


FIG. 7. Calculated solubility for the phases studied, compared to the solubility of scorodite. Note that in this figure no other phases are considered. All of the phases shown, however, dissolve incongruently at mildly acidic to alkaline pH. The solubility curves for the natural kamarizaitite and the nominal-composition kamarizaitite essentially overlap. Therefore, only that for the natural kamarizaitite is shown.

mixed compositions, it would be desirable to have a $\log K_{sp}$ value for the end-member composition $\text{Fe}_3(\text{AsO}_4)_2(\text{OH})_3 \cdot 3\text{H}_2\text{O}$. The reason is the ability to calculate a saturation index for this mineral from routine chemical analyses of aqueous samples. In our work, we have seen countless chemical analyses of natural and contaminated waters with the Fe and As concentration reported, but without measured P concentrations. From such analytical data, a saturation index for the composition of our natural sample cannot be calculated.

In the absence of additional thermodynamic data for the solid solution of kamarizaitite and tinctite (its phosphate analogue), we turn to the chemically similar and crystal-chemically related solid-solution series scorodite–strengite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ – $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$). The $\log K_{sp}$ for scorodite (Langmuir *et al.*, 2006; Majzlan *et al.*, 2012) was recalculated by Nordstrom *et al.* (2014) to be -25.68 . The $\log K_{sp}$ of strengite was determined by Nriagu (1972) and re-evaluated by Iuliano *et al.*

(2007) as -28.4 . Hence, the difference is 2.72 log units per one As/P site. For a 7.8% PO_4 substitution for AsO_4 in natural kamarizaitite and 2 As/P sites, the difference in $\log K_{sp}$ between our natural composition and end-member composition for kamarizaitite would be 0.4 log units. Using this datum and the thermodynamic functions of the natural kamarizaitite, the solubility product ($\log K_{sp}$) for the nominal composition of kamarizaitite $[\text{Fe}_3(\text{AsO}_4)_2(\text{OH})_3 \cdot 3\text{H}_2\text{O}]$ is estimated as -50.8 .

Solid solution between mansfieldite and scorodite

Scorodite is the most common secondary arsenate, but mansfieldite is rare. Intermediate compositions are seldom found. The abundance of scorodite could be a consequence of the fact that the primary minerals that weather to produce arsenates are dominated by pyrite (FeS_2) and arsenopyrite (FeAsS). On the other hand, there are no aluminium sulfides in nature, owing to their instability in contact with water. Yet, acidic mine drainage solutions commonly mobilize a large amount of aluminium by chemical attack of phyllosilicates (e.g. Lintnerová *et al.*, 1999).

Synthetic intermediate members of the scorodite–mansfieldite solid solution were prepared (at 160°C) and characterized by Le Berre *et al.* (2007). They observed that all solids had a higher Fe/(Fe + Al) ratio than the starting solution. This fact is easily explained by the large difference in $\log K_{sp}$ values between scorodite and mansfieldite, thus forcing the solids to take up much more Fe than Al, compared to the mother aqueous solution. The few experiments, in combination with the synthesis temperature that is not applicable to natural samples of these minerals, preclude a quantitative statement about the thermodynamics of this solid solution. Additionally, the unusual scatter of the lattice parameters and the unit-cell volumes (Fig. 8) hint that the synthesis products may have been heterogeneous, with Fe-rich cores and Fe-depleted rims. We have been trying to circumvent such problems by biological synthesis of this solid solution at lower temperatures (cf. Gonzalez-Contreras *et al.*, 2010), but so far with limited success.

An occurrence with both scorodite and mansfieldite was reported from Krásno (Czech Republic) by Sejkora *et al.* (2006). There, scorodite is common, while mansfieldite is rare; however, they may occur together. Semiquantitative (EDX) analyses showed that the Al–Fe substitution in Krásno mansfieldite is limited, unlike the As–P

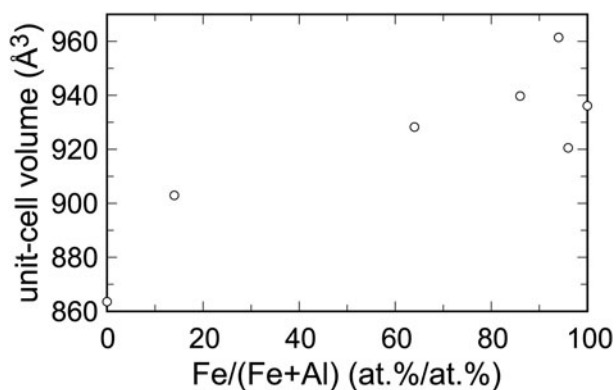


FIG. 8. Unit-cell volumes of the synthetic members of the mansfieldite–scorodite solid-solution series. Calculated from Le Berre *et al.* (2007).

substitution that is characterized by a wide variation of the As/(As + P) ratio. In some locations analysed, P predominates over As.

Natural members of the scorodite–mansfieldite solid solution were encountered within this work at the Ľubietová-Svätodušná locality (Fig. 2). Chemical analyses of these aggregates define two clusters (Fig. 9). The first cluster consist of compositions very close to scorodite in terms of the Fe/(Fe + Al) ratio, although with ~4 mol.% of a FePO₄ component. The other cluster contains intermediate compositions where Al predominates over Fe, but the Fe/(Fe + Al) ratios scatter widely. They have a lower P content than the compositions in the first cluster. These two clusters, clearly divided from each other by a gap, are an indication of the thermodynamic non-ideal nature of the

scorodite–mansfieldite solution. Yet, the limited number of analyses and the interfering phosphate component disqualify the use of these data for a quantitative thermodynamic analysis. Such analysis must await more data from natural systems or a successful synthesis of homogeneous intermediate compositions.

Solubility and stability of the phases studied

Stability and scarcity of kamarizaite

As mentioned above, scorodite is one of the preferred phases for arsenic immobilization in mining waste because of its low solubility, long-term stability, high As fraction in the solid, easy filtration, and low cost of the ingredients needed to make it (e.g. Swash and Monhemius, 1998).

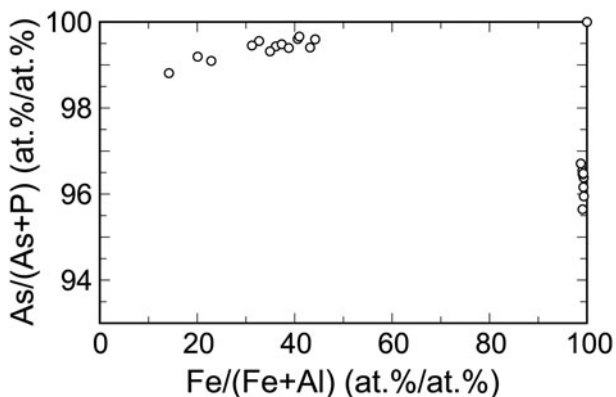


FIG. 9. Projection of the composition of the members of scorodite–mansfieldite solid-solution series from Ľubietová-Svätodušná. All data determined by electron microprobe spot analyses.

Scorodite undergoes incongruent dissolution at $\text{pH} > \sim 4$ (e.g. Majzlan *et al.* 2012) and releases much more As into the solution than that predicted from congruent dissolution (shown in Fig. 7). All phases in Fig. 7 show similar behaviours of incongruent dissolution and large As escape into the aqueous solution. Hence, only a comparison of their solubilities in the acidic region make sense. Kamarizaitite is predicted to have a very similar solubility to scorodite, making it a phase of potential interest for further research. The low solubility of kamarizaitite is supported, albeit only qualitatively, by our observation that this phase dissolved very sluggishly in hydrochloric or nitric acid, similarly to scorodite. Although dissolution rates cannot be directly equated to thermodynamic stability, there is a theoretical link between the two variables.

An intriguing question is then the massive presence of scorodite at many mine drainage sites and oxidation zones with copious Fe and As, compared to the dire scarcity of kamarizaitite. A partial answer to this question may be very prosaic. Even at the site that yielded our kamarizaitite specimen, collectors had erroneously identified this mineral as pale jarosite and thus disregarded it. Therefore, kamarizaitite, as an inconspicuous companion of iron sulfates or arsenates (cf. also Kolitsch *et al.*, 2016) might typically have been overlooked. Perhaps this mineral is not as rare as is thought of today.

Surprisingly, kamarizaitite has a small stability field in a pH-pe diagram, in a pH range between ~ 5 and 7 (Fig. 10). Other Fe arsenates or sulfate-arsenates such as parascorodite, kaňkite, bukovskýite, zýkaite, tooeleite, or angelellite do not appear because they are metastable. Kamarizaitite would then form as a stable phase from mildly acidic solutions. Under such conditions, however, active acid mine-drainage systems produce hydrous ferric oxide with adsorbed arsenate or schwertmannite, depending on the As/S concentration (Jambor, 1994). It is, however, important to note that acid mine-drainage systems reach very high supersaturation states *via* rapid neutralization and dilution. An oxidation zone, such as that in Kamariza, does not need to support such rapid reactions far away from equilibrium. Slow neutralization of locally acidic fluids may sustain them near equilibrium with stable, crystalline phases; one of them being kamarizaitite. Skarpelis and Argyraki (2009) stated that “[at Lavrion] mineral deposition in the supergene ore took place under near-neutral to mildly acidic conditions”, as a product of the influx of acidic, metal-laden fluids into the host carbonate rocks. This statement, however, is a generalization as not only marble is in direct contact with the mineralization, but also dark schists, which locally allow for very low pH in weathering solutions. In and on sulfide-rich ore lenses embedded in marble, highly

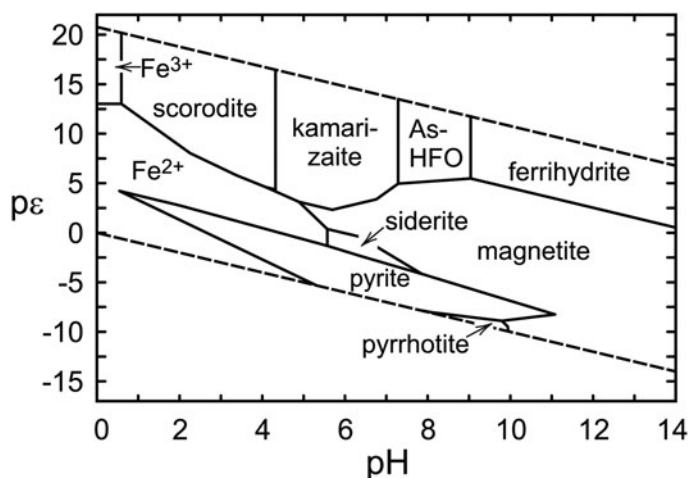


FIG. 10. A pe-pH diagram constructed at $T = 298.15$ K, assuming the activity of 10^{-3} for dissolved Fe, 10^{-4} for dissolved As, 10^{-5} for dissolved S, and 10^{-2} for dissolved C species. Coarse-grained, bulk goethite and hematite are suppressed from the calculation because their formation is kinetically hindered. Hence, although their stability would account for large fields of either bulk hematite or goethite in this diagram, they are rarely encountered in this form in acid drainage systems. As-HFO = arsenical hydrous ferric oxide.

acidic conditions can prevail. In the kamarizaite-bearing stope, no marble was encountered. The stope is fairly dry and no acid mine drainage can be observed. In conclusion, kamarizaite could be expected as an *in situ* supergene phase in oxidation zones and gossans after massive sulfide/arsenide mineralization where the host rocks have a substantial neutralization capacity or the mineralizing solutions are sufficiently diluted to result in an only mildly acidic environment.

Stability and scarcity of angelellite

Angelellite is a rare mineral species. The type specimen was found in the Vela Yareta tin mine in Argentina, and assumed to be of exhalative origin (Ramdohr *et al.*, 1959). Angelellite was presumably also found in arsenic-polluted soils (Gomez-Parrales *et al.*, 2011) and in Fe–As sludges (Pinisakul *et al.*, 2002). However, in both cases the quantity of angelellite was very small and the identification somewhat questionable. Therefore, it seems that angelellite is restricted to specific high-temperature environments where Fe and As can be transported in a gas phase. In addition, its crystallization can be aided by pre-existing hematite as these minerals are capable of epitaxial intergrowths (Weber, 1959, Moore and Araki, 1978).

The predicted solubility of angelellite is substantially higher than that of scorodite (Fig. 7), making it an unsuitable candidate for arsenic disposal. In our work, we have found that arsenic can be incorporated in hematite in the form of angelellite-like nanoclusters (Bolan *et al.*, 2013). This option could be further explored, and we are currently working on the thermodynamic description of such samples.

Stability and usefulness of scorodite–mansfieldite solid solution for arsenic disposal

The solubility of mansfieldite is much higher than that of scorodite, a fact that had been established for mansfieldite quite some time ago (cf. Le Berre *et al.*, 2007). Solid solutions (for example, scorodite–mansfieldite), because of their additional stabilization *via* the entropy of mixing or possibly also the enthalpy of mixing, are also of interest as candidates (with lower solubilities than the currently used options). In the case of mansfieldite–scorodite, the quantitative thermodynamic data were not determined in this work, but some evidence indicates that the solid solution may be non-ideal. Whether ideal or not, the difference

between the solubilities of the end-members (scorodite and mansfieldite) is so large that the practical use of this solid solution is difficult to imagine. In order to produce intermediate members of this solid solution, the waste forms would have to be doped with massive amounts of soluble aluminium. Much of this aluminium, however, would not enter the solid arsenate, and instead would remain in the aqueous phase, potentially causing additional environmental problems.

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Supplementary material

To view supplementary material for this article, please visit <https://doi.org/10.1180/mgm.2018.107>

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