Original paper

Giftgrubeite, CaMn$_2$Ca$_2$(AsO$_4$)$_2$(AsO$_3$OH)$_2$·4H$_2$O, a new member of the hureaulite group from Sainte-Marie-aux-Mines, Haut-Rhin Department, Vosges, France

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Giftgrubeite, ideally CaMn$_2$Ca$_2$(AsO$_4$)$_2$(AsO$_3$OH)$_2$·4H$_2$O, is a new mineral occurring at the Giftgrube Mine, St Jacques vein, Rauenthal, Sainte-Marie-aux-Mines, Haut-Rhin Department, Grand Est, France and named after the type-locality. Giftgrubeite is mostly associated with Mn-bearing calcite, native arsenic, löllingite, and picropharmacolite. It is a recent secondary mineral, formed by alteration of the arsenical vein minerals after mining. Giftgrubeite occurs in colorless, rarely pearl white to pale yellow rosettes of brittle tabular crystals flattened on {1 0 0} and up to 0.2 mm in size. Hardness (Mohs) is 3 ½, D_{meas} is 3.23(2) g·cm^{-3}, D_{calc} is 3.24 g·cm^{-3}. The new mineral is biaxial negative without pleochroism. Measured 2V angle is ~72° and calculated 2V angle is 75.1°; the refractive indices measured in white light are: α = 1.630(2), β = 1.640(2) and γ = 1.646(2). The most prominent Raman bands are at 902, 885, 864, 851, 824, 797 and 759 cm^{-1}. The empirical chemical formula is (Ca$_{3.04}$Mn$_{1.30}$Mg$_{0.38}$Fe$_{0.28}$)$_{\Sigma5.00}$(AsO$_4$)$_{1.99}$(AsO$_3$OH)$_2$·4H$_2$O. Giftgrubeite is monoclinic, C2/c, Z = 4, with a = 18.495(7) Å, b = 9.475(4) Å, c = 9.986(4) Å, β = 96.79(3)° and V = 1737.7(12) Å^3. The six strongest lines in the X-ray powder diffraction pattern are [d in Å (I)(hkl)]: 3.33 (100)(–2 2 2), 3.18 (80)(2 2 2), 2.414 (60)(7 1 1), 4.80 (50)(–3 1 1), 4.65 (50)(–2 0 2) and 3.05 (50)(1 1 3). The structure of giftgrubeite was solved from the crystal retrieved from the type specimen by the charge-flipping algorithm. Giftgrubeite contains a well-known structure type parent to the hureaulite group of minerals, which is based upon an octahedral edge-sharing pentamers of M^{2+}-polyhedra, pentamers linked into a loose framework by sharing corners with octahedra in adjacent pentamers and further by AsO$_4$ and AsO$_3$OH tetrahedra. There are three distinct octahedral sites: M1, M2, and M3. In the case of giftgrubeite, two of the M sites were found to be fully occupied by Ca; namely M1 and M3. The M2 site was then found to contain Mg besides dominant Mn. Considering the refined site occupancies, the structural formula for giftgrubeite is Ca$_3$Mn$_{1.30}$Mg$_{0.70}$(AsO$_4$)$_2$(AsO$_3$OH)$_2$(H$_2$O)$_4$. Giftgrubeite is an ordered intermediate member between villyaellenite, MnMn$_2$Ca$_2$(AsO$_3$OH)$_2$(AsO$_4$)$_2$·4H$_2$O and sainfeldite, CaCa$_2$Ca$_2$(AsO$_4$)$_2$(AsO$_3$OH)$_2$·4H$_2$O.

1. Introduction

The Sainte-Marie-aux-Mines ore district, with its long mining and mineralogical history, is famous due to the unusual occurrence of Ca- and Mg-bearing arsenates. The St. Jacques vein, locally enriched by native arsenic and Fe–Ni–Co arsenides, is the type-locality for several Ca-bearing arsenates: ferrarisite (Bari et al. 1980a), fluckite (Bari et al. 1980b), mcnearite (Sarp et al. 1981), phaunouxite (Bari et al. 1982), rauenthalite (Pierrot 1964), sainfeldite (Pierrot 1964), villyaellenite (Sarp 1984), weilite (Herpin and Pierrot 1963) and giftgrubeite (this study).

Giftgrubeite is named after the type locality, the Giftgrube Mine close to Sainte-Marie-aux-Mines (Vosges, France). Name "Giftgrube" originates from the German "Gift" = poisonous, and "Grube" = mine; the mine was in operation namely for mining silver, copper and native arsenic. The mineral and its name were approved by Commission on New Minerals, Nomenclature and Classification (CNMNC) in April 2017 (IMA2016-102) (Hålenius et al. 2017). One holotype and one part of them, defined as co-type, specimens are deposited in the mineral collection of the Musée cantonal de géologie, University of Lausanne, Anthropole, Dorigny, CH-1015 Lausanne, Switzerland, catalog numbers MGL n° 080133 and 080134, respectively.

2. Occurrence

The new mineral was found in an old stope on the St. Jacques vein, in the Giftgrube Mine, the Rauenthal Valley, Sainte-Marie-aux-Mines, Haut-Rhin Department, Grand Est, France.

Giftgrubeite is a supergene mineral, formed by alteration of the As-bearing hypogene minerals and its formation is connected with the post-mining alteration processes. The Giftgrube Mine was first mined for Ag (and Cu) during the 16–17th century. Some galleries were reopened later, especially during the 18th century. Arsenic has been exploited only slightly during early 20th century at the same time as Gabe Gottes Mine (1932–1940) in the same vein. That is why there are loose pieces of native arsenic on the ground and walls of the mine (left by miners), in old works. The associated minerals occurring with giftgrubeite are gangue quartz and multi-stage deposition carbonates, Mn–Fe-bearing calcite (up to 5 mol. % $MnCO_3$ and up to 2 mol. % $FeCO_3$) and Fe–Mn-bearing dolomite, as well as native arsenic, löllingite, tetrahedrite, skutterudite, and chalcopyrite. Associated oxidized post-mining minerals are arsenolite, picropharmacolite, pharmacolite ± haidingerite, chongite and scorodite.
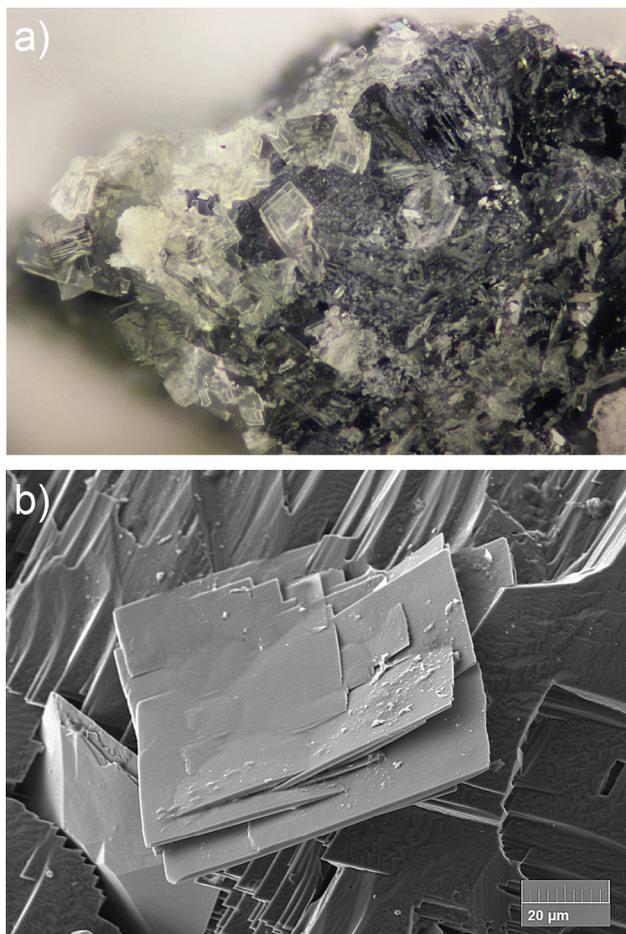
3. Physical and optical properties

Giftgrubeite occurs in crystals forming rosette-like aggregates having up to 0.2 mm across (Fig 1a). Crystals are flattened {100} (Fig 1b), with following crystal forms (by decreasing importance): {100}, {001}, {110}. Crystals are transparent with a vitreous luster. The mineral has a white streak. It is non-fluorescent under both long- and short-wave UV. The Mohs hardness is about 3 ½. Crystals are brittle without visible cleavage and have a curved fracture. The density was measured by floatation of crystals in diiodomethane/1-chloronaphtalene system (at 20 °C), giving 3.23(2) $g \cdot cm^{-3}$. The calculated density is 3.24 $g \cdot cm^{-3}$ based on the empirical formula.

Optically, giftgrubeite is biaxial (–), with $\alpha = 1.630(2)$, $\beta = 1.640(2)$, $\gamma = 1.646(2)$ (measured in white light at 22 °C, with refractive index liquids controlled with a Leitz–Jelley micro-refractometer after measurements). The measured $2V$ is ~72°; the calculated $2V$ is 75.1°. No pleochroism was observed.

4. Chemical composition

A crystal aggregate of giftgrubeite was analyzed (Tab. 1) using a Cameca SX100 electron microprobe (Masaryk University, Brno), operating in WDS mode with an accelerating voltage of 15 kV, beam current of 10 nA, and a 8 μm beam diameter. The following X-ray lines (standards) were used: K_α lines: Mg (diopside), Ca (wollastonite), Mn (rhodonite), Fe (almandine); L_α line: As (lammerite, $Cu_3(AsO_4)_2$). Other likely elements, such as Si, Al, S, P, K, V, and F were also sought, but their contents were below the detection limits (~0.05–0.15 wt. % with the analytical conditions used). The counting times were 10 or 20 s on peak and half of this on each background. The raw data were reduced using the $X–\varphi$ matrix correction routine (Merlet 1994). Because insufficient material was available for a direct determination of H_2O, the amount of water was calculated on the basis of charge balance and O = 19 *apfu*, obtained by the crystal structure analysis.

The empirical formula is: $(Ca_{3.04}Mn_{1.30}Mg_{0.38}Fe_{0.28})_{5.00}(AsO_4)_{1.99}(AsO_3OH)_2 \cdot 4H_2O$ and the simplified structural formula is $Ca_3Mn_2(AsO_4)_2(AsO_3OH)_2 \cdot 4H_2O$, which requires CaO 19.57, Mn 16.50, As_2O_5 53.46, H_2O 10.48, total 100 wt. %.

Fig. 1a – Tabular crystals of giftgrubeite on black, tarnished native arsenic affected by alteration. Horizontal width of photograph is 1.6 mm. **b** – Flattened {100} crystals aggregate of giftgrubeite (SEM image).

The Gladstone-Dale compatibility $1 - (Kp/Kc)$ for the empirical formula, is 0.011 in the range of excellent.

5. Raman spectroscopy

Raman spectrum of giftgrubeite (Fig. 2) was collected on Jobin–Yvon Labram HR, using a grid of 600 lines/mm, 100× objective lens and utilizing 633 nm laser. Spectral calibration was done on Ne-emission lines using the low-pressure Ne-discharge lamp. Raman spectrum of giftgrubeite (Fig. 2) is dominated by the stretching vibrations of AsO_4 and $AsO_3(OH)$ groups, respectively. The most prominent bands at 902, 885, 864, 851, 824, 797 and 759 cm^{-1} are attributed to overlapping ν_3 antisymmetric and the ν_1 symmetric As–O vibrations of the AsO_4 and $AsO_3(OH)$ groups; the bands of the lower energy can be assigned more favorably to the protonated $AsO_3(OH)$. A weak shoulder at 696 cm^{-1} may be related to the out-of-plane bending vibration of As–OH. Sharp bands of the medium intensity at 433, 384, 359 and 342 cm^{-1} are related to the ν_4 (δ) O–As–O and ν_2 (δ) O–As–O bending vibrations. The bands at the lowest energies are related to the lattice modes. The broad bands of the low intensity in the range 2798–3448 cm^{-1} are attributed to the ν O–H vibrations of the hydrogen-bonded water molecules. The bands at 2300–2500 cm^{-1} most probably reflect organic impurities due to resin and glue to which the examined crystals were mounted.

Tab. 1 Results of WDS analyses of giftgrubeite from Sainte-Marie-aux-Mines

Constituent	Wt. %	Range	Stand. Dev.	Probe Standard
MgO	1.82	1.31–2.21	0.37	diopside
CaO	20.26	19.49–20.72	0.44	wollastonite
MnO	11.02	10.35–11.94	0.50	rhodonite
FeO	2.43	1.14–3.89	0.97	almandine
As_2O_5	54.54	54.23–55.01	0.26	lammerite
H_2O^*	10.70	–	–	–
Total	100.77			

H_2O^* contents were calculated from structure model

6. Powder X-ray diffraction (XRD)

Powder XRD data were collected using a Gandolfi Camera (114.6 mm diameter; CuK_α/Ni-filtered; Si as external standard) and are given in Tab. 2. Unit-cell parameters refined from the powder data using the program UNIT-CELL (Holland and Redfern 1997) are as follows: $a = 18.67(2)$ Å, $b = 9.62(1)$ Å, $c = 10.09(1)$ Å, $\beta = 96.59(6)°$, $V = 1800(5)$ Å^3, $Z = 4$.

7. Single-crystal X-ray diffraction

7.1. Experiment and the refinement

A single-crystal extracted from the type specimen was used for the single-crystal X-ray study on a Rigaku SuperNova diffractometer with mirror-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) from a microfocus X-ray source detected by Atlas S2 CCD detector. Crystallo-
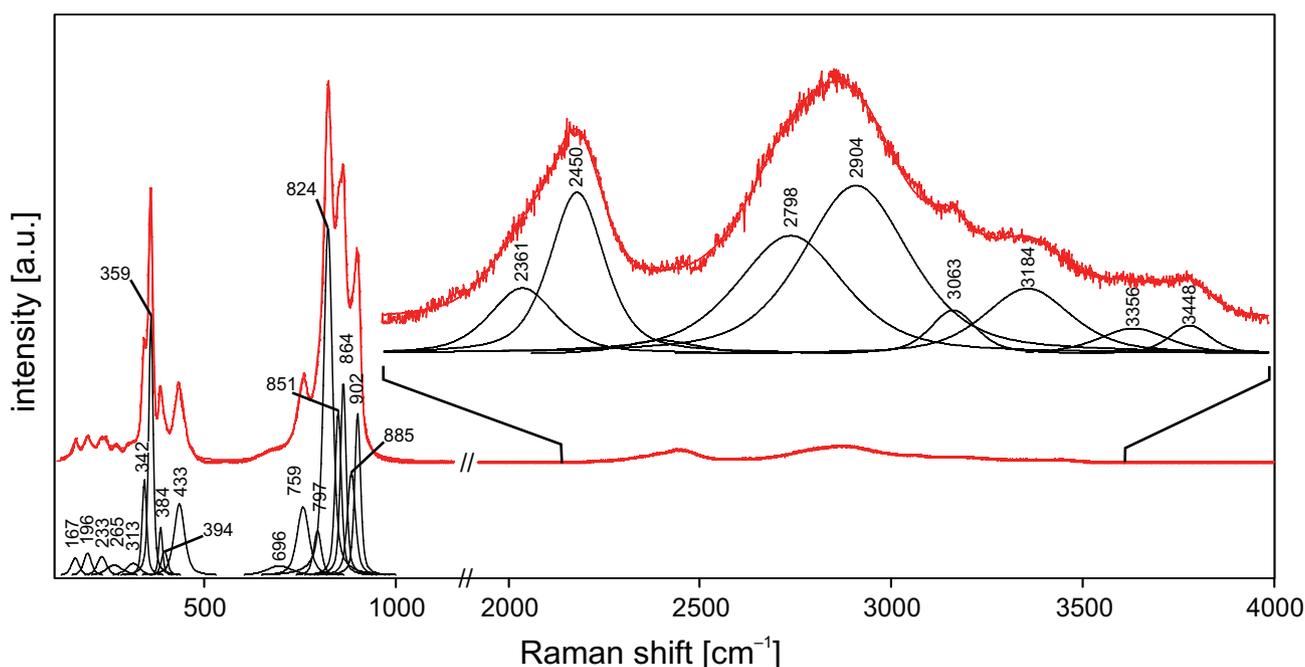
Fig. 2 The Raman spectrum of giftgrubeite.

Tab. 2 Powder-diffraction data for giftgrubeite from Sainte-Marie-aux-Mines (d_{hkl} values quoted in Å)

I_{obs} *	d_{obs}	I_{calc}	d_{calc}	h	k	l
20	9.35	24	9.19	2	0	0
40	8.54	46	8.42	1	1	0
10	6.68	17	6.60	−1	1	0
10	6.28	10	6.25	1	1	1
50	4.80	14	4.76	−3	1	1
50	4.65	38	4.60	−2	0	2
40	4.43	35	4.39	3	1	1
20	4.25	15	4.16	2	0	2
30	4.01	17	3.95	−2	2	1
40	3.85	24	3.80	2	2	1
30	3.46	21	3.43	0	2	2
30	3.38	57	3.35	−5	1	1
100	3.33	100	3.30	−2	2	2
30	3.24	21	3.21	−4	2	1
80	3.18	68	3.13	2	2	2
50	3.05	35	3.02	1	1	3
20	2.78	14	2.74	−3	3	1
20	2.70	10	2.66	3	3	1
50	2.488	15	2.479	0	0	4
60	2.414	20	2.386	7	1	1

* observed intensities might be affected by the preferred orientation effects

Tab. 3 Summary of data collection conditions, crystallographic details and structure refinement for giftgrubeite

Structural formula	$Ca_3Mn_{1.30}Mg_{0.70}(AsO_4)_2(AsO_3OH)_2(H_2O)_4$
	$a = 18.495(7)$ Å
	$b = 9.475(4)$ Å
	$c = 9.986(4)$ Å
	$\beta = 96.79(3)$ °
V [Å^3]	1737.7(12)
Z	4
Space group	$C2/c$
$D_{calc.}$ [g.cm^{-3}]	3.205 (for the above given formula)
Temperature	282 K
Wavelength	MoK_a, 0.71073 Å
Crystal dimensions	$46 \times 26 \times 21$ µm^3
Limiting θ angles	3.26–28.57°
Limiting Miller indices	$-24 \le h \le 22, -9 \le k \le 12, -8 \le l \le 13$
No. of reflections	3398
No. of unique reflections	1907
No. of observed reflections (criterion)	542 [$I > 3\sigma(I)$]
Absorption coefficient (mm^{-1}), method	9.54, analytical + empirical scaling
T_{min}/T_{max}	0.783/0.885
R_{int}	0.126
F_{000}	1572
Parameters refined, constraints, restraints	133, 9, 0
R, wR (obs)	0.0699, 0.1634
R, wR (all)	0.2163, 0.2610
GOF (obs, all)	1.22, 0.99
Weighting scheme	$1/(\sigma^2(I) + 0.0049000001I^2)$
$\Delta\rho_{min}, \Delta\rho_{max}$ (e . Å^{-3})	−2.43, 4.41

graphic parameters and data collection details are given in Tab. 3. Integration of the data, including corrections for background, polarization, and Lorentz effects, were carried out with the CrysAlis *RED* program. The absorption correction was finalized in the Jana2006 program (Petříček et al. 2014). The giftgrubeite structure was solved by the charge-flipping algorithm using the SHELXT program (Sheldrick 2015) and subsequently refined by the least-squares algorithm of the Jana2006 software (Petříček et al. 2014) based on F^2. Nearly all atom sites were found by the solution, missing positions of the remaining O atoms

were located on the difference-Fourier maps. All atoms were refined using anisotropic displacement parameters, and the $M2$ site was refined as a Mn/Mg mixed site. Nevertheless, the refinement converged to somewhat higher R values (Tab. 3) compared to e.g. refinement of structurally related miguelromeroite by Kampf (2009); the higher
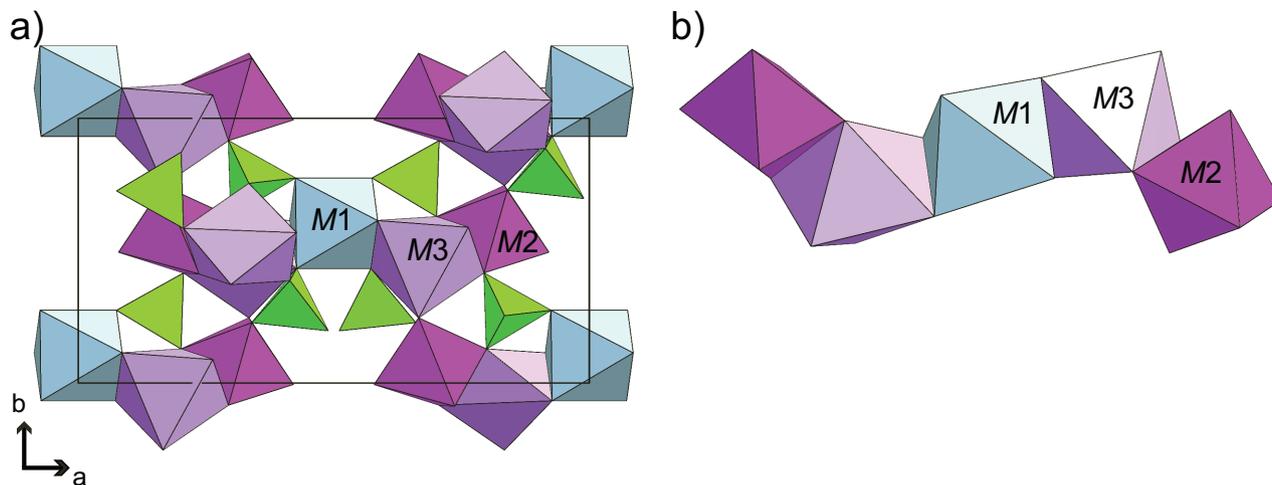
Fig. 3a – The crystal structure of giftgrubeite viewed down *c*. The As^{5+}tetrahedra are green, two Ca-based polyhedra are pale blue (*M*1) and lavender (*M*3), Mn/Mg polyhedra (*M*2) are pink. The unit-cell edges are displayed in solid black lines. For clarity, only half of the cell content along *c* is shown. **b** – The pentamer of edge-sharing octahedra, which is characteristic of the hureaulite group of minerals.

obtained *R* values are namely due to weak signal caused by the poor quality of crystals. Atom coordinates, displacement parameters, and bond-valence sums (calculated by DIST procedure in Jana2006 using bond–valence parameters from Gagné and Hawthorne 2015) are listed in Tab. 4, anisotropic displacement parameters in supplementary Tab. S1 and selected interatomic distances are provided in Tab. 5. The original crystallographic information file (cif) for giftgrubeite is provided as Supplementary material and can be downloaded from the Journal web site *http://jgeosci.org*.

Tab. 4 Atom positions and equivalent displacement parameters (U_{eq}, in Å^2) for giftgrubeite

Atom	Occ.	x/a	y/b	z/c	$U_{eq/iso}$	BV
#1						
As1		0.66020(13)	0.7682(3)	0.6221(2)	0.0325(8)	5.2(1)
As2		0.58408(13)	0.6878(3)	0.0894(2)	0.0335(9)	5.3(1)
M1		0.5	0.3891(7)	0.25	0.029(2)	2.20(4)
M2	0.65(2)/0.35(2)	0.6840(2)	0.9164(5)	0.3139(4)	0.0330(17)	1.79(3)
M3		0.6756(3)	0.4689(5)	0.8613(4)	0.0343(17)	2.04(4)
O1		0.7367(8)	1.0882(16)	0.4706(14)	0.037(6)	0.46(1)
O2		0.5749(8)	0.7743(16)	0.6478(14)	0.035(5)	1.78(6)
O3		0.6660(8)	0.7541(16)	0.4548(13)	0.031(5)	1.95(7)
O4		0.7061(9)	0.9158(16)	0.6754(14)	0.041(6)	1.93(7)
O5		0.6606(8)	0.7724(17)	0.1412(15)	0.038(6)	1.68(6)
O6(OH)		0.5108(9)	0.803(2)	0.0793(15)	0.052(7)	1.09(5)
O7		0.7013(9)	0.6281(17)	0.7005(16)	0.048(6)	1.99(7)
O8		0.5859(8)	0.6135(17)	−0.0604(14)	0.037(6)	2.07(5)
O9		0.5790(10)	1.006(2)	0.3325(16)	0.052(7)	0.35(1)
O10		0.5728(8)	0.5678(18)	0.2018(14)	0.042(6)	2.24(7)

In giftgrubeite *M*1 and *M*3 site are occupied by Ca^{2+}, *M*2 is a mix Mn/Mg site.

7.2. General crystal-structure features

The structure of giftgrubeite (Fig. 3a) is a well-known type of the hureaulite group of minerals (Ferraris and Abona 1972; Moore and Araki 1973; Kampf 2009). The fundamental building block that these minerals contain is an octahedral edge-sharing pentamer (Fig. 3b). Pentamers are linked into a loose framework by sharing corners with octahedra in adjacent pentamers, and they are further linked *via* AsO$_4$ and AsO$_3$OH tetrahedra. There are three distinct octahedral sites designated *M*1, *M*2, and *M*3 (Tab. 4; Fig. 3a–b). In the case of giftgrubeite two of the *M* sites were found to be fully occupied by Ca^{2+} (*M*1 and *M*3 sites). The *M*2 site is occupied by Mg^{2+} additionally to the dominant Mn^{2+}. The site-scattering refinements provided fractions of 0.35(2) Mg (crystal #1) and 0.29(2) Mg (crystal #2) at the *M*2 site, giving 0.70 and 0.58 Mg apfu, respectively. The presence of Fe, documented by the electron-microprobe study, was, however, neglected in the refinement, namely due to the increased number of parameters against the poorer data quality. The Mg content obtained from the refinement is then a result of a combination of (Mg + Fe) mixing at the site. The average <*M*2–Φ> bond-length of 2.20 and 2.21 Å, respectively, corresponds well with the Mn–O distances observed in the Mn-dominant member of the hureaulite group, miguelromeroite (Kampf 2009). Considering the refined site occupancies, the structural formula for giftgrubeite is Ca$_3$Mn$_{1.30}$Mg$_{0.70}$(AsO$_4$)$_2$(AsO$_3$OH)$_2$(H$_2$O)$_4$ (crystal #1), for *Z* = 4. This formula in line with the empirical formula obtained from the electron microprobe; however, we were not able to distinguish between Mg and Fe in our structure refinement.

Tab. 5 Selected interatomic distances (in Å) in the giftgrubeite structure

#1			
As1–O2	1.63(2)	As2–O5	1.65(2)
As1–O3	1.69(1)	As2–O6(OH)	1.73(2)
As1–O4	1.69(2)	As2–O8	1.65(1)
As1–O7	1.68(2)	As2–O10	1.63(2)
<As1–O>	1.67	<As2–O>	1.68
M1–O2^{iii}	2.38(2)		
M1–O2^{iv}	2.38(2)		
M1–O8^{v}	2.33(2)		
M1–O8^{vi}	2.33(1)		
M1–O10	2.25(2)		
M1–O10^{vii}	2.25(2)		
<M1–O>	2.32		
M2–O1	2.39(2)	M3–O1^{viii}	2.46(1)
M2–O3	2.14(2)	M3–O3^{vi}	2.33(2)
M2–O4^{i}	2.18(2)	M3–O4^{viii}	2.32(2)
M2–O5	2.21(2)	M3–O7	2.29(2)
M2–O7^{ii}	2.19(2)	M3–O8^{ix}	2.36(2)
M2–O9	2.15(2)	M3–O10^{vi}	2.36(1)
<M2–O>	2.21	<M3–O>	2.35

Symmetry codes: (i) *x*, −*y*+2, *z*−1/2; (ii) −*x*+3/2, −*y*+3/2, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) *x*, −*y*+1, *z*−1/2; (v) −*x*+1, −*y*+1, −*z*; (vi) *x*, −*y*+1, *z*+1/2; (vii) −*x*+1, *y*, −*z*+1/2; (viii) −*x*+3/2, *y*−1/2, −*z*+3/2; (ix) *x*, *y*, *z*+1.

8. Discussion

8.1. Giftgrubeite and other As-bearing members of the hureaulite group

Giftgrubeite is a new member of the hureaulite group of minerals, structurally closely related to As-members of the group: miguelromeroite, MnMn$_2$Mn$_2$(AsO$_3$OH)$_2$(AsO$_4$)$_2$·4H$_2$O (Kampf 2009), villyaellenite, MnMn$_2$Ca$_2$(AsO$_3$OH)$_2$(AsO$_4$)2·4H$_2$O (Kampf

Tab. 6 Comparative data for the members of the hureaulite group of minerals

	giftgrubeite	villyaellenite	miguelromeroite	sainfeldite
type locality	Sainte-Marie-aux-Mines, France	Sainte-Marie-aux-Mines, France	Ojuela mine, Mexico	Sainte-Marie-aux-Mines, France
reference	this paper	Sarp (1984), Kampf (2009)	Kampf (2009)	Pierrot (1964), Ferraris and Abona (1972)
$M1$ (1 *apfu*)	Ca	Mn, Ca	Mn	Ca
$M2$ (2 *apfu*)	Ca	Mn	Mn	Ca
$M3$ (2 *apfu*)	Mn	Ca	Mn	Ca
Me (ideal.)	Ca_2CaMn_2	Mn_3Ca_2	Mn_5	Ca_5
Me (meas.)	$Ca_{3.04}Mn_{1.30}Mg_{0.38}Fe_{0.28}$	$(Mn_{2.69}Ca_{2.07})_{\Sigma 4.76}$	$Mn_{4.63}Zn_{0.32}Ca_{0.08}Fe_{0.01}$	Ca_5
space group	$C2/c$	$C2/c$	$C2/m$	$C2/m$
a	18.495(7)	18.400(2)	18.030(1)	18.781(7)
b	9.475(4)	9.4778(10)	9.2715(5)	9.820(4)
c	9.986(4)	9.9594(12)	9.7756(5)	10.191(4)
β	96.79(3)	96.587(3)	96.266(2)	97.02(3)
V	1737.7(12)	1725.4(3)	1624.4(2)	1865.4
Z	4	4	4	4
R_{obs}, R_{all} (%)	6.99/21.63	10.26/12.33	3.83/4.02	3.90
strongest lines	8.54/40	8.476/90	8.279/28	8.7
in XRD	4.80/50	4.761/40	3.734/15	4.86
	4.65/50	4.606/50	3.357/33	4.64
powder pattern	3.33/100	3.811/40	3.234/100	4.45
(d Å/I_{obs})	3.18/80	3.297/100	3.074/68	3.37/100
	3.05/50	3.132/60	2.97/39	3.18/50

2009) sainfeldite, $CaCa_2Ca_2(AsO_4)_2(AsO_3OH)_2 \cdot 4H_2O$ (Ferraris and Abona 1972), and chongite $CaMg_2Ca_2(AsO_4)_2(AsO_3OH)_2 \cdot 4H_2O$ (Kampf et al. 2015). Comparative data for these species are presented in Tab. 6. Giftgrubeite, $CaMn_2Ca_2(AsO_4)_2(AsO_3OH)_2 \cdot 4H_2O$ is an ordered intermediate member between villyaellenite, $MnMn_2Ca_2(AsO_3OH)_2(AsO_4)2 \cdot 4H_2O$, and sainfeldite, $CaCa_2Ca_2(AsO_3OH)_2(AsO_4)2 \cdot 4H_2O$, and corresponds to the unnamed mineral phase mentioned by Kampf (2009) from Gozaisho Mine in Japan. As noted by Kampf (2009) the $M1$ site is capable of accepting a full range of Ca and Mn occupancies. The $M2$ site is then capable of accepting a distinct proportion of Mn, Mg and Ca occupancies, leading to end-members: giftgrubeite (Mn), chongite (Mg) and sainfeldite (Ca). The Mg content in giftgrubeite corresponds to chongite component; its presence suggests that at least a limited solid-solution between these two end-members exists and Mn-chongite, with atomic ratio Ca : Mg : Mn = 66 : 19 : 16 was observed intimately associated with giftgrubeite. Noteworthy, the substitutions that take place in the structure of giftgrubeite and related As-bearing members of the hureaulite group, lead to an increasing unit-cell volume with an increasing portion of Ca^{2+} entering the structure (Fig. 4). The [6]-coordinated Ca^{2+} is larger (1 Å) than [6]-coordinated Mn^{2+} (0.83 Å), while considering their ionic radii (Shannon 1976).
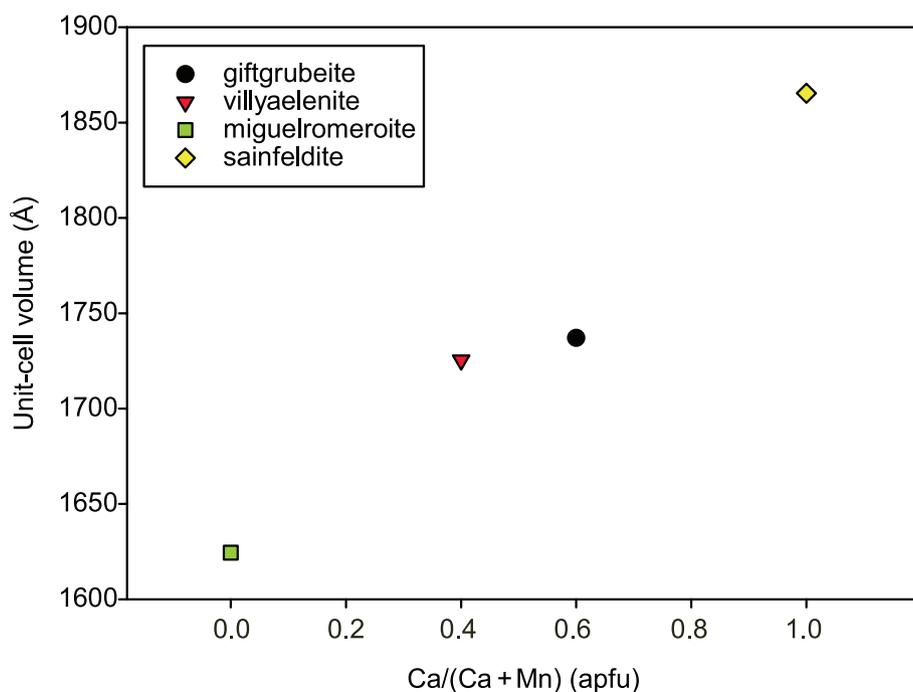
Fig. 4 Dependence of the unit-cell volume on the fraction of Ca^{2+} in the structures of As-bearing members of the hureaulite group of minerals.

8.2. Formation of giftgrubeite

Careful micro- and macroscopic study of the giftgrubeite mineral association showed that the new mineral formed *via* atmospheric oxidation weathering of native arsenic in the wet environment of the abandoned mine. The formation involves several steps. The first is represented by oxidation weathering of massive or disseminated native arsenic to arsenic (III) oxide, As_2O_3, which is thermodynamically favored (Majzlan et al. 2014). As_2O_3 in contact with humid air or oxygen-rich descending (meteoric) water subsequently oxidizes into highly hygroscopic arsenic (V) oxide, As_2O_5, dissolves and this leads to the formation of solutions containing various arsenate anion species, depending on corresponding pH (in an increasing order), e.g.: $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-} or $(AsO_3OH)^{2-}$ (see Pierrot 1964; Majzlan et al. 2014). Such solutions then attack gangue carbonates, here mostly the Mn–Fe-bearing calcite and dolomite, which proceeds with the shift in pH to more alkaline (see model 3Aa of Markl et al. 2014), and subsequent formation of giftgrubeite (as the main Ca–Mn-bearing arsenate) and picropharmacolite (as the main Mg-bearing arsenate) from locally oversaturated solutions.

Electronic supplementary material. Supplementary crystallographic data and table of anisotropic displacement parameters in giftgrubeite is available online at the Journal web site (*http://dx.doi.org/10.3190/jgeosci.276*).

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