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RESEARCH

Guérinite $Ca_6(HAsO_4)_3(AsO_4)_2·10.5H_2O$ – a revision of the mineral formula

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Abstract

A single crystal of guérinite from the Plaka Mine, Lavrion, Greece, was examined by X-ray diffraction. The mineral crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters $a = 17.628$ (2), $b = 6.728$ (1), $c = 23.384$ (3) Å, $\beta = 90.68$ (1)°, $V = 2773.4$ (6) $Å^3$. The originally reported mineral formula $Ca_5(HAsO_4)_2(AsO_4)_2·9H_2O$, Z = 5 should be revised to $Ca_6(HAsO_4)_3(AsO_4)_2·10.5H_2O$, Z = 4. Accordingly, guérinite is no longer considered a polymorph to ferrarisite. The structure is characterized by complex layers consisting of corner- and edge sharing of CaO_n ($n = 7$, 8) polyhedra and arsenate groups. The connection between these units is achieved exclusively via hydrogen bonding.

Keywords Guérinite · $Ca_6(HAsO_4)_3(AsO_4)_2·10.5H_2O$ · Mineral formula · Lavrion

Introduction

Guérinite was discovered as a new mineral on two museum specimen labelled to originate from Schneeberg, Saxony and Richelsdorf, Hessia (Nefedov 1961) and named after the chemist Henri Guérin, Paris-Sud University, Orsay, France, who had synthesized and identified (Guérin 1941) the phase as $5CaO·2As_2O_5·10H_2O$. The chemical analysis of a sample from the Sainte-Marie-aux-Mines, Alsace, was considered in agreement with the formula $Ca_5H_2(AsO_4)_4·9H_2O$ (Pierrot 1964).

The crystal structure was first described by Catti and Ferraris (1974) from a tiny synthetic sample (supplied by Guérin) in space group $P2_1/n$, with unit cell parameters $a = 17.63$ (1), $b = 6.734$ (3), $c = 23.47$ (2) Å, β = 90.6 (1)°, refined to $R = 0.13$. These authors characterized the material as very poor, commonly occurring twinned or as intergrown aggregates. Their structure analysis – due to the low scattering power of the sample - was ambiguous and several structure models were discussed. Finally the description as $Ca_5(HAsO_4)_2(AsO_4)_2·9H_2O$, Z = 5, assuming "empty" cavities that accommodate not fully occupied additional Ca^{2+} atoms was suggested as the most likely solution. Using this very formula, the mineral species ferrarisite (Catti et al. 1980) was later described as being a polymorph to guérinite.

The guérinite specimen, recently found at Lavrion, allowed a more detailed examination of its crystal structure. This led to a slight change in the proposed mineral formula, as will be discussed in the work presented now.

Sample and experimental

Guérinite, forming acicular to wedge-shaped, colorless crystals as rosettes and spherulites (Fig. 1), was collected from a banded, vein-type mineralization of the Plaka mine No. 145 during a sampling excursion in April 2019. The veins known as "vein 80" or "Filoni 80" are up to two meters wide and extend 1 km from East to West between Plaka and Adami Valley (Conophagos 1980; Skarpelis 2007; Voudouris et al. 2008). Hydrothermally altered hornfels and skarnoids are rich in Pb-As-Sb-Zn-Cu-Ag, sourced from a contact metamorphic zone. The mineralogy of the oxidation zone comprises rauenthalite, marcasite, pharmacolite, stergiouite, arsenopyrite, chalcopyrite, sphalerite, pyrite, calcite, fluorite, and quartz (Rieck and Rieck 1999; Wendel and Rieck 1999a; Wendel

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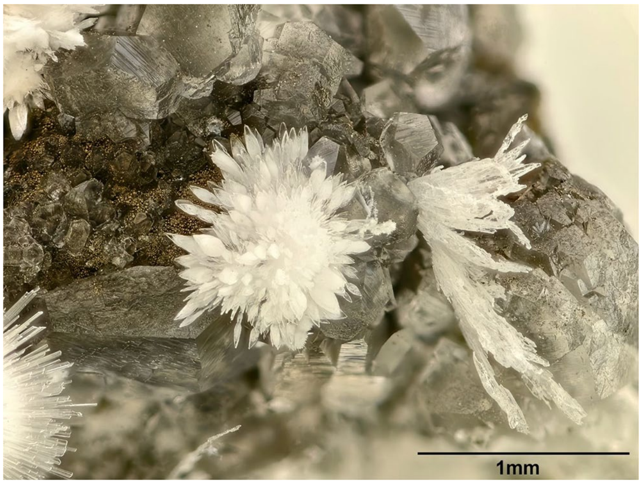

Fig. 1 Guérinite rosette, associated with white, needle-like rauenthalite (lower left) and deformed pharmacolite (right) on calcite matrix that is partially covered by tiny marcasite crystals (mainly left of guérinite). White-light optical image

and Rieck 1999b; Skarpelis 2007; Voudouris et al. 2008; Rieck et al. 2018; Rieck et al. 2020).

The chemical analysis of guérinite was performed on a WDS (wavelength dispersive spectrometer), an electron probe microanalyzer JEOL Hyperprobe JXA8530F. Nine spot analyses (30 µm beam diameter) were averaged, measurement conditions 10 kV and 20 nA. Wollastonite $Ca_3(Si_3O_9)$, InAs and MgO were used as reference materials.

For the single crystal X-ray diffraction study, a selected crystal lamella of guérinite, 0.15 × 0.05 × 0.02 mm^3 in size, was mounted on a MiTeGen loop with silicone grease. The measurement was carried out at room temperature on a Bruker APEXII diffractometer equipped with a charge-coupled device (CCD) area detector and an Incoatec Microfocus Source IµS (30 W; multilayer mirror; Mo-K_α). Fifteen sets of phi- and omega-scans with 1° scan width were combined at a crystal-detector distance of 40 mm to achieve respective full sphere data up to to 70° 2θ. Data handling with integration and absorption correction by evaluation of multi-scans was done with the Bruker Apex5 suite (Bruker 2023). The structure was solved by direct methods (SHELXT; Sheldrick 2015a); subsequent difference Fourier syntheses and least-squares refinements yielded the positions of the remaining hydrogen atoms using the SHELXL software (Sheldrick 2015b) implemented in the shelXle GUI tool (Hübschle et al. 2011). Non-hydrogen atoms were refined with anisotropic displacement parameters and the labelling scheme of these atoms was chosen in accordance to Catti and Ferraris (1974) except for the H_2O molecules which have been renamed to O_w. OH and H_2O groups were refined applying moderate geometrical restraints [O-H = 0.90(2) Å; H-H = 1.50 (5) Å]. The crystallographic data as well as details of the measurements and refinements are listed in Table 1.

Table 1 Crystal data and details of the intensity measurements and structure refinement for guérinite

Crystal Data	
Formula	$Ca_6(HAsO_4)_3(AsO_4)_2 \cdot 10.5H_2O$
Space group	$P2_1/n$
a (Å)	17.628 (2)
b (Å)	6.728 (1)
c (Å)	23.384 (3)
β (°)	90.68 (1)
V (Å^3)	2773.4 (6)
Z	4
ρ_{calc} (g cm^{-3})	2.70
µ (Mo$K\alpha$) (mm^{-1})	7.19
Data collection and refinement	
Unique data	13,480
Data with $F_o > 4\sigma(F_o)$	9577
Variables, restraints	455 / 36
$R1$ [for $F_o > 4\sigma(F_o)$] [1]	0.0495
$wR2$ [for all F_o^2] [1]	0.0902
a, b[1]	0.013, 14.4
$\Delta\rho_{min / max}$ (eÅ^{-3})	-1.28 / 1.53

[1] $R1 = \Sigma F_o - F_c / \Sigma F_o$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{½}$; $w = 1 / [\sigma^2(F_o^2) + (a \times P)^2 + b \times P]$; $P = \{[\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2\} / 3$

Results

The WDS analytical data of guérinite from Lavrion are given in Table 2. Apart from a small amount of magnesium, substituting for calcium, no other trace elements could be detected within the measurement accuracy. The H_2O content was assumed by difference. The chemical composition obtained is very similar to the ones reported in the literature for the mineral as well as for the synthetic analogues.

The single-crystal X-ray diffraction analysis confirmed the monoclinic space group $P2_1/n$ with unit cell parameters $a = 17.628$ (2), $b = 6.728$ (1), $c = 23.384$ (3) Å, $\beta = 90.68$ (1)°, $V = 2773.4$ (6) Å^3, close to those given by Catti and Ferraris (1974), i.e. $a = 17.63$ (1), $b = 6.734$ (3), $c = 23.47$ (2) Å, $\beta = 90.6$ (1)°, $V = 2785.5$ Å^3. Final structure parameters are quoted in Table S1 in the electronic supplementary material, relevant interatomic bond distances and bond angles are compiled in Table 3, supplemented by bond-valences Σv (valence units) calculated according to Brese and O'Keeffe (1991). The proposed hydrogen bonding system is listed in Table 4. Further details of the crystal structure data may be obtained from the joint CCDC/FIZ Karlsruhe online deposition service: https://www.ccdc.cam.ac.uk/structures/ by quoting the CSD deposition number 2377340.

Table 2 Chemical analysis of guérinite from Lavrion (1) in comparison with chemical data reported in literature (2–4) as well as ideal chemical compositions derived from the respective proposed mineral formulae (5–7)

	1	2	3	4	5	6	7
As_2O_5	51.21	49.76	51.74	50.31	50.97	49.95	51.38
CaO	30.01	30.06	30.64	30.29	29.85	30.47	30.09
H_2O	18.72	19.18	17.62	19.40	19.18	19.58	18.53
MgO	0.06						
sum	100.00	99.00 *	100.00	100.00	100.00	100.00	100.00

1 Present study, Plaka mine No. 145, Lavrion

2 Pierrot (1964), Sainte-Marie-aux-Mines, Alsace, * 0.40 wt% insoluble

3 Catti and Ferraris (1974), synthetic sample supplied by H. Guérin

4 Catti and Ferraris (1974), sample synthesized according to Pierrot (1964)

5 $Ca_6(HAsO_4)_3(AsO_4)_2 \cdot 10.5H_2O$ (present study)

6 $Ca_5H_2(AsO_4)_4 \cdot 9H_2O$ Pierrot (1964), Catti and Ferraris (1974), model (1)

7 $Ca_6H_3(AsO_4)_5 \cdot 10H_2O$ Catti and Ferraris (1974), model (2)

Table 3 Selected interatomic bond lengths (Å) and bond strengths ν (v.u.; according to Brese and O'Keeffe 1991) for guérinite

		ν			ν			ν
As1-O1	1.654 (3)	1.36	As2-O5	1.683 (2)	1.25	As3-O9	1.667 (2)	1.31
As1-O2*	1.734 (3)	1.09	As2-O6	1.667 (2)	1.31	As3-O10	1.697 (2)	1.21
As1-O3	1.682 (3)	1.26	As2-O7	1.698 (3)	1.21	As3-O11	1.683 (3)	1.25
As1-O4	1.660 (3)	1.33	As2-O8	1.677 (3)	1.28	As3-O12	1.694 (3)	1.22
< As1$^{[4]}$-O>	< 1.682>	Σ5.04	< As2$^{[4]}$-O>	< 1.681>	Σ5.05	< As3$^{[4]}$-O>	< 1.685>	Σ4.99
As4-O13	1.664 (3)	1.32	As5-O17	1.669 (3)	1.30			
As4-O14*	1.754 (3)	1.04	As5-O18*	1.736 (3)	1.08			
As4-O15	1.674 (3)	1.29	As5-O19	1.665 (3)	1.32			
As4-O16	1.663 (2)	1.32	As5-O20	1.678 (3)	1.27			
< As4$^{[4]}$-O>	< 1.690>	Σ4.97	< As5$^{[4]}$-O>	< 1.688>	Σ4.97			
						Ca3-O1	2.554 (3)	0.21
Ca1-O3	2.373 (3)	0.33	Ca2-O3	2.459 (3)	0.27	Ca3-O3	2.565 (3)	0.20
Ca1-O4	2.347 (3)	0.36	Ca2-O6	2.284 (3)	0.43	Ca3-O5	2.410 (3)	0.30
Ca1-O6	2.558 (3)	0.20	Ca2-O13	2.322 (2)	0.38	Ca3-O7	2.378 (3)	0.33
Ca1-O7	2.476 (2)	0.25	Ca2-O13	2.430 (3)	0.29	Ca3-O10	2.409 (2)	0.30
Ca1-O15	2.365 (3)	0.34	Ca2-O16	2.402 (3)	0.31	Ca3-O17	2.812 (4)	0.10
Ca1-O16	2.395 (3)	0.32	Ca2-O$_w$1	2.462 (3)	0.26	Ca3-O20	2.440 (3)	0.28
Ca1-O$_w$3	2.452 (4)	0.27	Ca2-O$_w$2	2.496 (3)	0.24	Ca3-O$_w$1	2.563 (3)	0.20
< Ca1$^{[7]}$-O>	< 2.423>	Σ2.07	< Ca2$^{[7]}$-O>	< 2.408>	Σ2.18	< Ca3$^{[8]}$-O>	< 2.516>	Σ1.92
Ca4-O1	2.328 (3)	0.38	Ca5-O5	2.344 (3)	0.36	Ca6-O9	2.270 (3)	0.44
Ca4-O5	2.805 (3)	0.10	Ca5-O8	2.342 (3)	0.36	Ca6-O14	2.493 (3)	0.24
Ca4-O7	2.409 (3)	0.30	Ca5-O10	2.443 (3)	0.28	Ca6-O$_w$2	2.505 (3)	0.23
Ca4-O11	2.318 (3)	0.39	Ca5-O10	2.728 (3)	0.13	Ca6-O$_w$6	2.410 (4)	0.30
Ca4-O17	2.419 (3)	0.30	Ca5-O12	2.365 (3)	0.34	Ca6-O$_w$7	2.390 (4)	0.32
Ca4-O20	2.458 (3)	0.27	Ca5-O12	2.448 (3)	0.27	Ca6-O$_w$8	2.358 (5)	0.34
Ca4-O$_w$4	2.371 (4)	0.34	Ca5-O$_w$5	2.429 (3)	0.29	Ca6-O$_w$9	2.513 (5)	0.23
< Ca4$^{[7]}$-O>	< 2.444>	Σ2.08	< Ca5$^{[7]}$-O>	< 2.443>	Σ2.03	< Ca6$^{[7]}$-O>	< 2.420>	Σ2.10

* Protonated oxygen ligands

Discussion

Crystal structure

According to the structure solution and refinement, the asymmetric unit of guérinite contains – excluding hydrogen atoms – six Ca^{2+} and five As^{5+} cations, further 30 O^{2-} anions, all located at general sites and fully occupied. In addition, one more site may (based on the observed residual electron density of ~5e $Å^{-3}$) probably be interpreted as a half-occupied oxygen atom of a H_2O molecule. By edge-, corner- and face-sharing of $Ca(O, O_w)_n$ ($n = 7,8$) polyhedra as well as AsO_4 and $HAsO_4$ tetrahedral groups a complex layered structure parallel to $(\bar{1}01)$ is formed, as illustrated

Table 4 Hydrogen bonding scheme [Å, °] for guérinite

D–H	d(D–H)	D–H···A	d(D–A)	∠(D–H···A)	(H–D–H)	∠(H–D–H)
O$_w$1–H1a	0.90(3)	O$_w$1–H1A···O12	2.668(4)	159(4)	H1A–O$_w$1–H1b	109(4)
O$_w$1–H1b	0.89(2)	O$_w$1–H1b···O8	2.860(4)	152(5)		
O$_w$2–H2a	0.88(3)	O$_w$2–H2a···O15	2.788(4)	139(5)	H2a–O$_w$2–H2b	112(4)
O$_w$2–H2b	0.89(4)	O$_w$2–H2b···O4	2.719(4)	141(4)		
O$_w$3–H3a	0.89(5)	O$_w$3–H3a···O20	2.709(5)	149(6)	H3a–O$_w$3–H3b	115(5)
O$_w$3–H3b	0.89(4)	O$_w$3–H3b···O$_w$10	2.761(5)	177(7)		
O$_w$4–H4a	0.89(6)	O$_w$4–H4a···O$_w$6	3.109(6)	157(6)	H4a–O$_w$4–H4b	115(5)
O$_w$4–H4b	0.90(4)	O$_w$4–H4b···O19	2.773(5)	158(6)		
O$_w$5–H5a	0.89(2)	O$_w$5–H5a···O17	2.780(4)	154(4)	H5a–O$_w$5–H5b	110(4)
O$_w$5–H5b	0.90(3)	O$_w$5–H5b··O9	2.687(4)	171(5)		
O$_w$6–H6a	0.89(5)	O$_w$6–H6a···O19	2.665(5)	164(6)	H6a–O$_w$6–H6b	103(4)
O$_w$6–H6b	0.90(4)	O$_w$6–H6b···O$_w$2	3.050(5)	131(5)		
		O$_w$6–H6b···O4	3.107(5)	137(5)		
O$_w$7–H7a	0.90(5)	O$_w$7–H7a···O$_w$9	3.020(7)	164(7)	H7a–O$_w$7–H7b	114(5)
O$_w$7–H7b	0.89(4)	O$_w$7–H7b···O$_w$5	2.740(5)	166(6)		
O$_w$8–H8a	0.89(6)	O$_w$8–H8a···O18	3.079(7)	149(8)	H8a–O$_w$8–H8b	120(6)
O$_w$8–H8b	0.89(6)	O$_w$8–H8b···O18	2.923(6)	145(7)		
O$_w$9–H9a	0.93(6)				H9a–O$_w$9–H9b	96(4)
O$_w$9–H9b	0.92(5)	O$_w$9–H9b···O15	2.752(6)	141(5)		
O$_w$10–H10a	0.90(5)	O$_w$10–H10a···O2	3.151(6)	137(5)	H10a–O$_w$10–H10b	120(4)
O$_w$10–H10b	0.89(4)	O$_w$10–H10b···O19	2.790(5)	111(5)		
O$_w$11–H11a	0.95(12)	O$_w$11–H11a···O$_w$11	2.84(2)	169(16)	H11a–O$_w$11–H11b	108(6)
O$_w$11–H11b	0.90(12)	O$_w$11–H11b···O$_w$8	2.706(12)	148(12)		
O2–H2	0.89(2)	O2–H2···O$_w$10	2.794(6)	157(6)		
O14–H14	0.88(2)	O14–H14···O8	2.699(4)	175(4)		
O18–H18	0.90(2)	O18–H18···O11	2.635(4)	158(4)		

in Fig. 2. This is consistent with the morphology of the crystals, which exhibit dominant thin lamellae of $\{\bar{1}01\}$. These layers are linked to each other via hydrogen bonding only, involving also the intercalated, free H_2O molecules O$_w$10 and half-occupied O$_w$11.

While the five mean $<As^{5+}$-O$>$ distances differ only slightly (1.681–1.690Å), three monoprotonated $(HAsO_4)^{2-}$ and two deprotonated $(AsO_4)^{3-}$ groups can be differentiated based on individual As-O distances (see again Table 3): the monoprotonated arsenates each show one significantly longer bond distance As-OH (1.734, 1.736 and 1.754 Å). This is also proven by the calculated bond strengths ν, which are – not taking contributions of hydrogen atoms into account – 1.09, 1.08, and 1.28 v.u. (valence units) for O2, O18 and O14, respectively.

Revision of the mineral formula

Catti and Ferraris (1974) recognized – under consideration of the assumed guérinite formula $Ca_5(HAsO_4)_2(AsO_4)_2{\cdot}9H_2O$ with $Z=5$ – that the resulting 25 Ca atoms per unit cell cannot be accommodated on full positions in the space group $P2_1/n$. Accordingly, these authors discussed several approaches to solve the above problem. Derived from results of the crystal structure refinement with six Ca and five As sites in the asymmetric unit, they developed two suggestions for the guérinite formula. Model (1):$Ca_5(HAsO_4)_2(AsO_4)_2{\cdot}9H_2O$ with $Z=5$, assigning two residual electron-density peaks as disordered, additional calcium positions with site occupation factors of 0.17 and 0.08, respectively, which in total would represent one more calcium atom per the unit cell. Model (2): $Ca_6H_3(AsO_4)_5{\cdot}10H_2O$ with $Z=4$, and therefore a different As/Ca ratio as well as total water content.

Although Catti and Ferraris (1974) were well aware that the respective mineral formulae only had slight differences in overall chemistry (see Table 2), probably within the range of experimental error, they ultimately favored model (1) due to results of TGA analyses. In view of the present study – it shows one order of magnitude higher accuracy, for example at interatomic distances – model (1) proposed by Catti and Ferraris (1974) should be revised, in particular for the following reasons. (a) A mineral formula with $Z=5$ in the space group $P2_1/n$ seems to be unlikely, especially as in this case two partially occupied atomic positions for Ca as well as a mixed arsenate group were used. (b) Based on bond lengths and bond strengths, three acidic and two deprotonated arsenate groups are clearly differentiated. This is consistent with the balance of charges for six observed Ca^{2+} cations. (c) The partially occupied Ca position called "St(1)" as postulated

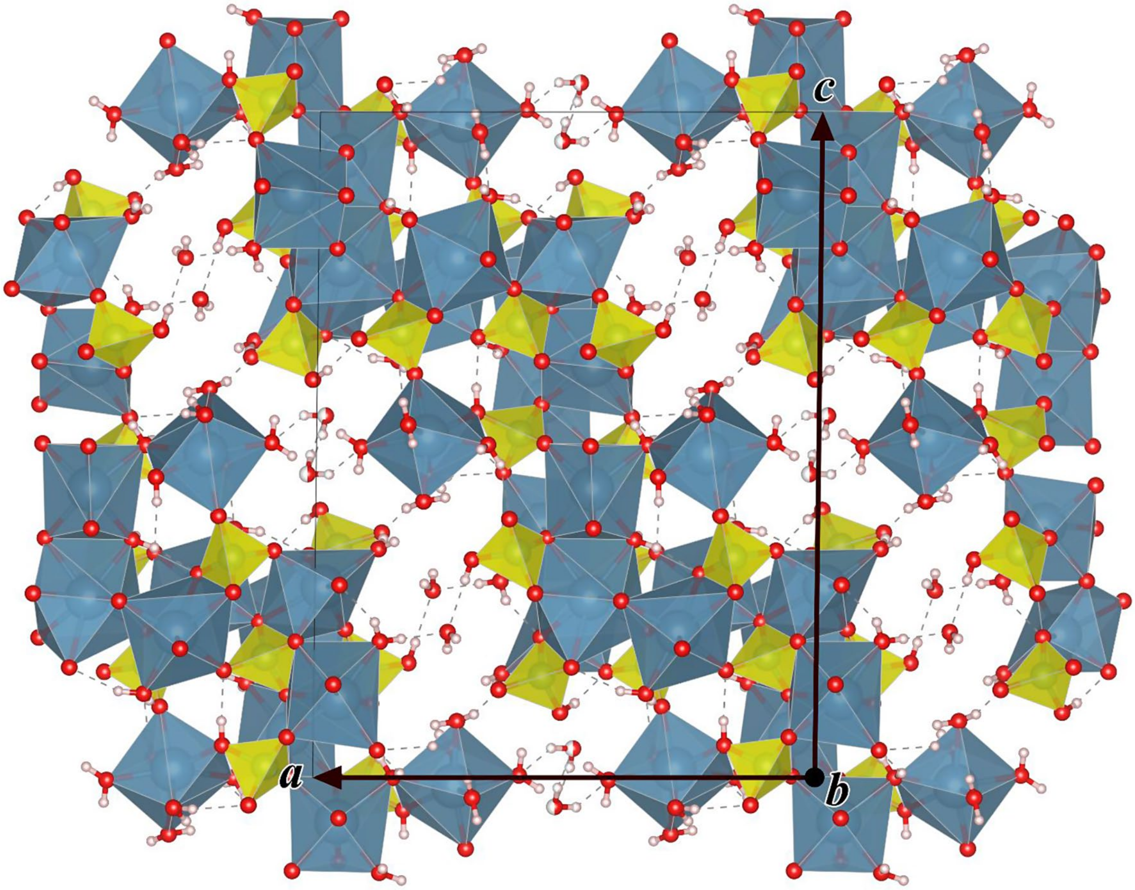

Fig. 2 Sketch of the crystal structure of guérinite projected along [010]. CaO_n polyhedra are shown in blue, the arsenate groups in yellow, oxygen atoms as red spheres, and hydrogens grey

by Catti and Ferraris (1974) can alternatively be explained by one half-occupied H_2O molecule, specifically O_w11.

Taking into account six fully occupied Ca sites, the presence of three protonated arsenate groups and assuming that the residual electron peak is a partially occupied H_2O molecule, then the chemical formula of of guérinite results as $Ca_6(HAsO_4)_3(AsO_4)_2{\cdot}10.5H_2O$. Therefore, guérinite should no longer be considered a polymorph to ferrarisite.

Hydrogen bonding system

The crystal structure of guérinite features a complex system of hydrogen bonds. A likely model – based on bond strength calculations, interatomic O - O distances (ignoring edges of coordination polyhedra) and the approximate location of the protons in final difference Fourier syntheses – is listed in Table 4. Essentially, it corresponds to the suggestions of Catti and Ferraris (1974), cf. their Table 3. Very strong hydrogen bonds are missing, the D-A contacts range from typical lengths to weak ones (2.63 to 3.15 Å). The H_2O molecules O_w1 – O_w9 are ligands of CaO_n polyhedra, resulting in the following coordinations: $Ca1O_6(O_w)_1$, $Ca2O_5(O_w)_2$, $Ca3O_7(O_w)_1$, $Ca4O_6(O_w)_1$, $Ca5O_6(O_w)_1$, and $Ca6O_2(O_w)_5$. The calculated bond strengths ν for the oxygen atoms of these H_2O molecules are < 0.5 v.u. Oxygen atoms acting as acceptors are in the range of 1.32 to 1.83 v.u., that not involved in hydrogen bonding vary from 1.92 to 2.09 v.u.

Related structures

Guérinite belongs to a group of calcium arsenates, the vast majority of which are known as minerals. A list of these representatives is compiled in Table 5, providing details about atomic arrangement and crystal chemistry. The respective calcium atoms are found in different coordination figures; distorted CaO_6 octahedra or irregular 7- or 8-coordinations often occur. In the case of guérinite, 7-coordinations are predominant, the average Ca-O bond lengths correspond to expectations; the calculated bond strength sums are in the range from 1.92 to 2.18 v.u. Geometrical analysis of the arsenate groups clearly shows that the As-O distances to protonated ligands in general are noticeably longer with

Table 5 Compilation of Ca-arsenate minerals and synthetic compounds

Mineral	Proposed Formula	S.G.	$<$ Ca$^{[6]}$-O$>$	$<$ Ca$^{[7]}$-O$>$	$<$ Ca$^{[8]}$-O$>$	$<$ As$^{[4]}$-O$>$	As-O$_h$	Reference
Synthetic [a]	$Ca_2(As_2O_7)$	*C*2/*m*	2.349			1.673	(1.712) [b]	Pertlik (1980)
Synthetic	$Ca_3(AsO_4)_2$	*R*3*c*	2.29	2.44	2.52, 2.55	1.65–1.69		Gopal and Calvo (1971)
Segerstromite	$Ca_3(AsO_4)_2[As^{3+}(OH)_3]_2$	$I2_13$			2.548	1.684		Yang et al. (2018)
Johnbaumite [c]	$Ca_5(AsO_4)_3OH$	$P6_3/m$			2.464, 2.597 [d]	1.689		Lee et al. (2009)
Weilite	$Ca(HAsO_4)$	$P\overline{1}$		2.463	2.546	1.655–1.674	1.702,1.716	Ferraris and Chiari (1970)
Švenekite	$Ca(HAsO_4)_2$	$P\overline{1}$			2.503	1.684, 1.686	1.722,1.736	Ondruš et al. (2013)
Haidingerite	$Ca(HAsO_4)\cdot H_2O$	*Pcnb*		2.452		1.687	1.756	Ferraris et al. (1972)
Pharmacolite	$Ca(HAsO_4)\cdot 2H_2O$	*Ia*			2.515	1.686	1.729	Ferraris et al. (1971)
Synthetic	$Ca(HAsO_4)\cdot 3H_2O$	*Pbca*	2.334			1.680	1.734	Catti and Ferraris (1973)
Sainfeldite	$Ca_5(HAsO_4)_2(AsO_4)_2\cdot 4H_2O$	*C*2/*c*	2.346–2.381			1.689, 1.690	1.726	Ferraris and Abbona (1972)
Synthetic [e]	$Ca_5(HAsO_4)_2(AsO_4)_2\cdot 5H_2O$	$P\overline{1}$	2.35	2.42–2.45		1.68, 1.70	1.73	Catti and Ivaldi (1981)
Vladimirite	$Ca_4(HAsO_4)(AsO_4)_2\cdot 4H_2O$	$P2_1/c$		2.421–2.458	2.523	1.688–1.690	1.747	Yang et al. (2011)
Jeankempite	$Ca_5(HAsO_4)_2(AsO_4)_2\cdot 7H_2O$	$P\overline{1}$	2.391	2.421–2.464		1.693–1.705	1.719–1.786	Olds et al. (2020)
Guérinite	$Ca_6(HAsO_4)_3(AsO_4)_2\cdot 10½H_2O$	$P2_1/n$		2.408–2.444	2.516	1.681–1.690	1.734–1.754	Present study
Synthetic guérinite	"$Ca_5(HAsO_4)_2(AsO_4)_2\cdot 9H_2O$"	$P2_1/n$		2.40–2.51	2.52	1.61–1.69	1.69–1.79	Catti and Ferraris (1974)
Ferrarisite	$Ca_5(HAsO_4)_2(AsO_4)_2\cdot 9H_2O$	$P\overline{1}$	2.340	2.427, 2.439		1.687, 1.688	1.739	Catti et al. (1980)
Dobšináite [f]	$Ca_3(AsO_4)_2\cdot 2H_2O$	$P2_1/c$						Sejkora et al. (2021)
Rauenthalite	$Ca_3(AsO_4)_2\cdot 10H_2O$	$P\overline{1}$		2.424, 2.468	2.532	1.670, 1.685		Catti and Ivaldi (1983)
Phaunouxite	$Ca_3(AsO_4)_2\cdot 11H_2O$	$P\overline{1}$		2.412–2.434	2.518	1.684, 1.685		Catti and Ivaldi (1983)

[a] Thortveitite structure type; [b] bridging oxygen; [c] apatite structure type; [d] 6+3 coordination; [e] dehydration product of ferrarisite; [f] roselite structure type, no structure refinement

values above 1.70 Å; this is also the case with guérinite (1.734–1.754 Å). A comparable increase in bond length can also be seen with bridging oxygens of As_2O_7 groups.

Layered structures of different complexity are predominant (e.g. in švenekite; haidingerite, pharmacolite, guérinite, ferrarisite, rauenthalite, phaunouxite, weilite, vladimirite, synth. $Ca_5(HAsO_4)_2(AsO_4)_2\cdot 5H_2O$, or in jeankempite). The higher degree of hydration in these compounds is likely a responsible factor. For topological similarities of the crystal structure of guérinite with those of jeankempite and other calcium arsenates the reader is referred to the work of Olds et al. (2020).

Conclusions

The crystal structure of guérinite was examined in more detail for the first time on natural material from Lavrion. It turned out that the mineral formula, as previously stated in the literature, needs to be revised slightly. The likely formula, based on chemical analysis and single-crystal X-ray structure refinement is now: $Ca_6(HAsO_4)_3(AsO_4)_2\cdot 10.5H_2O$.

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