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THE CRYSTAL STRUCTURE OF VLADIMIRITE, WITH A REVISED CHEMICAL FORMULA, $Ca_4(AsO_4)_2(AsO_3OH)\cdot 4H_2O$

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ABSTRACT

Two samples of vladimirite, one from Bou Azzer, Morocco, and the other from a new occurrence in Copiapó, Chile (designated as R100075 and R080001, respectively), were examined with an electron microprobe, single-crystal X-ray diffraction, and Raman spectroscopy. Our results show that vladimirite is monoclinic with space group $P2_1/c$ and unit-cell parameters *a* 5.8279(2), *b* 10.1802(4), *c* 22.8944(10) Å, β 96.943(2)°, and *V* 1348.35(9) Å^3 for R100075 and *a* 5.8220(1), *b* 10.1750(2), *c* 22.8816(6) Å, β 96.902(1)°, and *V* 1345.66(5) Å^3 for R080001. The structure determinations, with R_1 = 0.022 and 0.023 for R100075 and R080001, respectively, yielded an ideal chemical formula $Ca_4(AsO_4)_2(AsO_3OH)\cdot 4H_2O$ (Z = 4) for this mineral, in contrast to $Ca_5(AsO_4)_2(AsO_3OH)_2\cdot 5H_2O$ (Z = 3) documented in the literature. The chemical compositions for R100075 and R080001 are $Ca_{4.03}(AsO_4)_2(As_{0.99}O_3OH)\cdot 4H_2O$ and $Ca_{3.97}(AsO_4)_2(As_{1.01}O_3OH)\cdot 4H_2O$, with trace Zn and Mn, respectively. The structure is characterized by undulating layers formed by the four nonequivalent, rather irregular Ca polyhedra [$Ca1O_6(H_2O)$, $Ca2O_6(H_2O)$, $Ca3O_4(H_2O)_3$, and $Ca4O_5(H_2O)_3$] linked through the sharing of edges and vertices. These undulating layers are parallel to (010) and are interconnected by AsO_4 and AsO_3OH tetrahedra, as well as hydrogen bonds, along the **b** axis. Vladimirite is remarkable inasmuch as one of the hydrogen-bonded O–H···O distances (O12H–H···O3) is only 2.465(2) Å, which is the shortest donor–acceptor distance of all known Ca-bearing arsenate minerals, similar to the short donor–acceptor distances observed in several synthetic compounds containing AsO_3OH groups.

Keywords: vladimirite, arsenate, crystal structure, X-ray diffraction, Raman spectra.

SOMMAIRE

Nous avons examiné deux échantillons de vladimirite, dont un de Bou Azzer, au Maroc, et l'autre d'un nouvel indice à Copiapó, au Chili (designés R100075 et R080001, respectivement), avec une microsonde électronique, diffraction X sur monocristal and spectroscopie Raman. D'après nos résultats, la vladimirite serait monoclinique, groupe spatial $P2_1/c$, avec les paramètres réticulaires *a* 5.8279(2), *b* 10.1802(4), *c* 22.8944(10) Å, β 96.943(2)°, et *V* 1348.35(9) Å^3 pour R100075 et *a* 5.8220(1), *b* 10.1750(2), *c* 22.8816(6) Å, β 96.902(1)°, et *V* 1345.66(5) Å^3 pour R080001. Les déterminations de la structure, jusqu'à un résidu R_1 de 0.022 et 0.023 pour R100075 et R080001, respectivement, ont mené à une formule chimique idéale $Ca_4(AsO_4)_2(AsO_3OH)\cdot 4H_2O$ (Z = 4), contrairement à $Ca_5(AsO_4)_2(AsO_3OH)_2\cdot 5H_2O$ (Z = 3), tel qu'indiqué dans la littérature. La formule chimique de R100075 et R080001 est $Ca_{4.03}(AsO_4)_2(As_{0.99}O_3OH)\cdot 4H_2O$ et $Ca_{3.97}(AsO_4)_2(As_{1.01}O_3OH)\cdot 4H_2O$, respectivement, avec traces de Zn et Mn. La structure contient des couches ondulantes formées de quatre polyèdres plutôt irréguliers non équivalents, [$Ca1O_6(H_2O)$, $Ca2O_6(H_2O)$, $Ca3O_4(H_2O)_3$, et $Ca4O_5(H_2O)_3$], liés par partage de coins et d'arêtes. Ces couches ondulantes sont parallèles à (010); elles sont interconnectées grâce aux tétraèdres AsO_4 et AsO_3OH, ainsi qu'aux liaisons hydrogène, le long de l'axe **b**. La vladimirite est remarquable par la faible longueur d'une des liaisons hydrogène O–H···O, O12H–H···O3, qui est seulement 2.465(2) Å. Il s'agit de la plus courte distance entre donateur et accepteur de tous les arsenates de Ca connus comme minéraux; elle ressemble aux distances entre donateur et accepteur établies dans le cas de composés synthétiques contenant le groupe AsO_3OH.

(Traduit par la Rédaction)

Mots-clés: vladimirite, arsenate, structure cristalline, diffraction X, spectres Raman.

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Introduction

Because of the biological and geochemical importance of arsenic, especially its role in water and waste management, the crystal chemistry of As-bearing minerals has been a subject of extensive investigations (Smedley & Kinniburgh 2002, Vaughan 2006, O'Day 2006). Under oxidizing conditions, arsenic commonly exists as As^{5+} in water, with $(AsO_4)^{3-}$, $(HAsO_4)^{2-}$, $(H_2AsO_4)^{1-}$, and $(H_3AsO_4)^0$ being the prevailing aqueous species in different pH ranges. When such solutions interact with surrounding rocks, especially limestones, a series of Ca-bearing arsenates may form. Currently, there are eleven species of Ca arsenate in the list of IMA-accepted minerals, including ferrarisite $Ca_5(AsO_3OH)_2(AsO_4)_2•9H_2O$, guérinite $Ca_5(AsO_3OH)_2(AsO_4)_2•9H_2O$, haidingerite $Ca(AsO_3OH)•H_2O$, johnbaumite $Ca_5(AsO_4)_3OH$, pharmacolite $Ca(AsO_3OH)•2H_2O$, phaunouxite $Ca_3(AsO_4)_2•11H_2O$, rauenthalite $Ca_3(AsO_4)_2•10H_2O$, sainfeldite $Ca_5(AsO_4)_2(AsO_3OH)_2•4H_2O$, švenekite $CaH_4(AsO_4)_2$, vladimirite $Ca_5(AsO_4)_2(AsO_3OH)_2•5H_2O$, and weilite $Ca(AsO_3OH)$. Among these minerals, the crystal structures of all but vladimirite have been determined (Ferraris & Chiari 1970, Chiari & Ferraris 1971, Ferraris & Abbona 1972, Ferraris *et al.* 1971, 1972a, 1972b, Catti & Ferraris 1974, Catti *et al.* 1980, Catti & Ivaldi 1983, Lee *et al.* 2009).

Vladimirite is a secondary mineral formed in the oxidized zone of arsenic-bearing mineral deposits (Anthony *et al.* 2000). It was first described by Nefedov (1953, 1955), with the composition (wt.%) As_2O_5 48.30, CaO 34.26, H_2O 17.87, sum 100.43, or an ideal chemical formula $Ca_3(AsO_4)_2•4H_2O$ and a monoclinic cell with *a* 5.80(5), *b* 10.17(5), *c* 22.7(1) Å, β 82.68°. However, a further analysis by Pierrot (1964) of two different samples of vladimirite (one of the type material from Tuva Auton, Russia, and the other from the Irhtem mine, Morocco) produced, respectively, As_2O_5 53.31, 52.1, CaO 34.0, 33.2, H_2O 12.1, 12.1, sum 99.4, 97.4 (wt.%). These results are significantly different from those given by Nefedov (1953), leading Pierrot (1964) to propose a chemical formula of $Ca_5H_2(AsO_4)_4•5H_2O$ (Z = 3) for this mineral, which brings the calculated density of 3.17 g/cm^3 into accord with the measured one of 3.14(2) g/cm^3. From the powder X-ray-diffraction data, Pierrot (1964) also suggested space group $P2_1/c$ for vladimirite with the cell parameters *a* 5.81, *b* 10.19, *c* 22.7 Å, β 82.7°. Yakhontova & Stolyarova (1970) re-analyzed samples of vladimirite from the type locality and obtained (wt.%) As_2O_5 53.44, CaO 33.65, H_2O 12.63, sum 99.72, confirming the chemical formula given by Pierrot (1964). Since then, no further detailed crystallographic or chemical study has been reported for vladimirite. We present the first determination of the structure of vladimirite from single-crystal X-ray-diffraction data, and demonstrate that the ideal chemical formula of this mineral is $Ca_4(AsO_4)_2(AsO_3OH)•4H_2O$ (Z = 4) rather than $Ca_5H_2(AsO_4)_4•5H_2O$ (Z = 3), as documented in the earlier literature.

Experimental Procedures

Two samples of vladimirite were used in this study: one from the Ait Ahmane vein No. 53, Bou Azzer, Morocco and the other from the Corbriza mine, Copiapó, Chile [designated as R100075 (http://rruff.info/R100075) and R080001 (http://rruff.info/R080001), respectively]. It should be pointed out that this is the first report of vladimirite from Copiapó, Chile. The work by Pierrot (1964) and Yakhontova & Stolyarova (1970) demonstrates that the Moroccan material is the same as the type material. Vladimirite measured from R080001 is optically biaxial (+), with n_α = 1.660, n_β = 1.663, n_γ = 1.665, and $2V_{meas}$ = 90.6°, as compared to those reported by Nefedov (1953, 1955): biaxial (+), with n_α = 1.650, n_β = 1.656, n_γ = 1.661, and $2V_{meas}$ = 70°.

The two samples were analyzed with a Cameca SX100 electron microprobe with an acceleration potential of 15 kV and a beam current of 8 nA. Standards included diopside for Mg, apatite for Ca, Zn metal for Zn, rhodonite for Mn, and As_2O_3 for As. The resultant chemical formulas, calculated on the basis of 11.5 O atoms, are $Ca_{4.03}(As_{0.99}O_3OH)(AsO_4)_2•4H_2O$ for R100075 (average of 10 points) and $Ca_{3.97}(As_{1.01}O_3OH)(AsO_4)_2•4H_2O$ for R080001 (average of 15 points), both of which can be simplified as $Ca_4(AsO_4)_2(AsO_3OH)•4H_2O$ (Table 1).

On the basis of our optical examination and X-ray-diffraction peak profiles, nearly equidimensional crystals (~0.06 × 0.06 × 0.07 mm for R100075 and ~0.04 × 0.05 × 0.05 mm for R080001) were selected and mounted on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized Mo*K*α radiation. The detailed experimental procedures were similar to those described by Yang *et al.* (2011). Observed reflections with $I_{obs} > 2\sigma(I)$ were indexed on the basis of a monoclinic unit-cell (Table 2). No satellite or superlattice reflections were observed. Observed systematic absences of reflections for both samples indicate the unique space-group $P2_1/c$. The structure was solved and refined using the program SHELX97 (Sheldrick 2008). The positions of all atoms were refined with anisotropic displacement parameters, except for H atoms, which were refined with a fixed isotropic displacement parameter (U_{eq} = 0.03). The ideal composition, $Ca_4(AsO_4)_2(AsO_3OH)•4H_2O$, was assumed for both samples during the structure refinements, as the overall effects of the trace amounts of Zn and Mn (Table 1) on the final structure results are negligible. Final refined coordinates and displacement parameters of atoms are listed in Table 3, and selected bond-lengths in Table 4. Because of the rather similar

TABLE 1. THE COMPOSITION OF VLADIMIRITE FROM DIFFERENT LOCALITIES

Locality	Tuva, Russia	Tuva, Russia	Irhtem, Morocco	Tuva, Russia	Bou Azzer, Morocco	Copiapó, Chile
As_2O_5 wt.%	48.30	53.31	52.1	53.44	52.05	52.05
CaO	34.26	34.0	33.2	33.65	34.19	33.54
ZnO					0.01	0.02
MnO						0.02
H_2O	17.87	12.1	12.1	12.63	12.41	12.41
Sum	100.43	99.4	97.4	99.72	98.66	98.04
Ca *apfu*	4.23	3.95	3.95	3.91	4.03	3.97
As	2.91	3.02	3.02	3.03	2.99	3.01
Proposed formula	$Ca_3(AsO_4)_2$ •$4H_2O$	$Ca_5H_2(AsO_4)_4$ •$5H_2O$		$Ca_5H_2(AsO_4)_4$ •$5H_2O$	$Ca_4(AsO_4)_2(AsO_3OH)$ •$4H_2O$	
Reference	(1)	(2)	(2)	(3)	(4)	(4)

The number of cations is normalized on the basis of 11.5 atoms of oxygen. References: (1) Nefedov (1953), (2) Pierrot (1964), (3) Yakhontova & Stolyarova (1970), (4) this work.

TABLE 2. SUMMARY OF CRYSTAL DATA AND REFINEMENT RESULTS FOR VLADIMIRITE

	Vladimirite (Morocco, R100075)	Vladimirite (Chile, R080001)
Analytical chemical formula	$Ca_{4.03}(AsO_4)_2$ $(As_{0.99}O_3OH)$•$4H_2O$	$Ca_{3.97}(AsO_4)_2$ $(As_{1.01}O_3OH)$•$4H_2O$
Space group	$P2_1/c$ (no. 14)	
a (Å)	5.8279(2)	5.8220(1)
b (Å)	10.1802(4)	10.1750(2)
c (Å)	22.8944(10)	22.8816(6)
β (°)	96.943(2)	96.902(1)
V (Å^3)	1348.35(9)	1345.66(5)
Z	4	4
ρ_{calc} (g/cm^3)	3.203	3.209
μ (mm^{-1})	9.002	9.020
2θ range for data collection	≤66.28	≤65.25
No. of reflections collected	21477	17331
No. of independent reflections	5120	4226
No. of reflections with I > 2σ(I)	4298	3574
No. of parameters refined	236	236
R_{int}	0.033	0.037
Final R_1, wR_2 factors [I > 2σ(I)]	0.022, 0.043	0.023, 0.046
Final R_1, wR_2 factors (all data)	0.033, 0.045	0.032, 0.055
Goodness-of-fit	1.026	1.064

structural data between the two samples, we will only use the data of R100075, which are apparently of a better quality than those of R080001, for the discussion hereafter, unless otherwise stated. A table of structure factors and a cif file are available from the Depository of Unpublished Data [document Vladimirite CM49_1055].

The Raman spectra of vladimirite were collected from a randomly oriented crystal at 100% power on a Thermo Almega microRaman system, using a solid-state laser with a wavenumber of 532 nm, and a thermo-electrically cooled CCD detector. The laser is partially polarized with 4 cm^{-1} resolution and a spot size of 1 μm.

Discussion

Crystal structure and chemical formula

The crystal structure of vladimirite contains 23 distinct non-hydrogen atomic sites, with four occupied by Ca^{2+}, three by As^{5+}, eleven by O^{2-}, one by OH^-, and four by H_2O (Table 3), giving rise to a structure formula $Ca_4(AsO_4)_2(AsO_3OH)$•$4H_2O$ (Z = 4), rather than $Ca_5H_2(AsO_4)_4$•$5H_2O$ (Z = 3) as given in the current list of IMA-defined minerals. Its main building units are AsO_4 (As1 and As2) and AsO_3OH (As3) tetrahedra, plus CaO_7 (Ca1, Ca2, and Ca3) and CaO_8 (Ca4) polyhedra. The most striking feature of the vladimirite structure is manifested in its undulating layers formed by the four nonequivalent Ca polyhedra that share vertices and edges. These undulating layers are parallel to (010) and are interconnected by isolated AsO_4 and AsO_3OH tetrahedra, as well as hydrogen bonds, along [010] (Fig. 1).

Among the three AsO_4 tetrahedra in vladimirite, the protonated AsO_3OH tetrahedron is expectedly the most distorted (Ferraris & Ivaldi 1984), as measured in terms of the tetrahedron quadratic elongation (TQE) and tetrahedron angle variance (TAV) (Robinson *et al.* 1971). The TAV and TQE indices are 7.84 and 1.002, 17.16 and 1.004, and 39.77 and 1.010, respectively, for the As1, As2, and As3 tetrahedra. All As–O and As–OH bond lengths fall in the ranges observed in other Ca arsenate minerals and compounds (Ferraris & Chiari 1970, Ferraris & Abbona 1972, Ferraris *et al.* 1971, 1972a, 1972b, Catti & Ferraris 1974, Catti *et al.* 1980, Catti & Ivaldi 1983, Mihajlović *et al.* 2004, Kolitsch & Bartu 2004, Đorđević & Karanović 2008, 2010, Lee *et al.* 2009), but with both the shortest (As–O11) and the longest (As–O12H) bonds within the As3 tetrahedra.

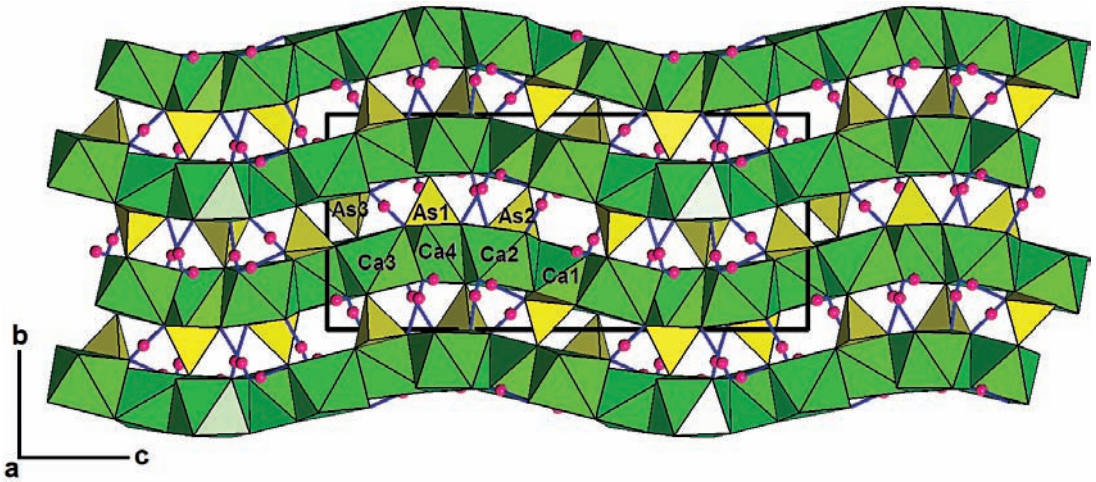

FIG. 1. The crystal structure of vladimirite. Yellow tetrahedra: AsO_4 and AsO_3OH groups, green polyhedra: CaO_7 and CaO_8 groups, and purple spheres: H atoms.

TABLE 3. COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN VLADIMIRITE

Atom	*x*	*y*	*z*	U_{iso}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Vladimirite (R100075) from Morocco										
Ca1	0.67087(6)	0.72601(4)	0.00250(2)	0.00903(8)	0.0088(1)	0.0097(2)	0.0086(2)	-0.0011(2)	0.0013(1)	0.0001(1)
Ca2	0.00525(6)	0.85202(4)	0.14094(2)	0.00875(8)	0.0084(1)	0.0089(2)	0.0091(2)	0.0012(2)	0.0012(1)	0.0005(1)
Ca3	0.88901(6)	0.32115(4)	0.10694(2)	0.01124(8)	0.0120(1)	0.0128(2)	0.0094(2)	0.0024(2)	0.0030(1)	0.0027(1)
Ca4	0.43361(6)	0.36411(4)	0.24537(2)	0.01010(8)	0.0096(1)	0.0096(2)	0.0107(2)	-0.0003(2)	-0.0005(1)	0.0005(1)
As1	0.86851(3)	0.54829(2)	0.21401(1)	0.00704(5)	0.0076(1)	0.0061(1)	0.0073(1)	0.0004(1)	0.0005(1)	0.0006(1)
As2	0.54070(3)	0.00128(2)	0.09702(1)	0.00733(5)	0.0071(1)	0.0067(1)	0.0083(1)	0.0006(1)	0.0013(1)	0.0006(1)
As3	0.23074(3)	0.58486(2)	0.04956(1)	0.00718(5)	0.0070(1)	0.0070(1)	0.0076(1)	0.0001(1)	0.0010(1)	0.0002(1)
O1	0.8563(2)	0.7138(1)	0.21273(6)	0.0096(3)	0.0114(5)	0.0065(7)	0.0112(7)	0.0005(6)	0.0025(5)	0.0003(5)
O2	0.1321(2)	0.4972(1)	0.20166(7)	0.0140(3)	0.0118(6)	0.0141(7)	0.0171(8)	0.0037(6)	0.0056(5)	0.0057(5)
O3	0.6737(2)	0.4811(1)	0.16106(7)	0.0146(3)	0.0180(6)	0.0100(7)	0.0139(8)	-0.0008(6)	-0.0063(6)	0.0002(5)
O4	0.7917(2)	0.4918(1)	0.27804(6)	0.0121(3)	0.0149(6)	0.0117(7)	0.0104(8)	0.0021(6)	0.0044(5)	-0.0008(5)
O5	0.5444(2)	0.1643(1)	0.08188(6)	0.0103(3)	0.0124(6)	0.0071(7)	0.0113(7)	0.0017(6)	0.0006(5)	0.0006(5)
O6	0.2650(2)	0.9502(1)	0.08624(7)	0.0134(3)	0.0079(5)	0.0146(7)	0.0175(8)	0.0041(6)	0.0011(5)	-0.0027(5)
O7	0.6643(2)	0.9778(1)	0.16747(6)	0.0117(3)	0.0137(6)	0.0121(7)	0.0090(7)	0.0031(6)	0.0001(5)	0.0018(5)
O8	0.7147(2)	0.9148(1)	0.05839(6)	0.0120(3)	0.0124(6)	0.0110(7)	0.0130(8)	-0.0039(6)	0.0034(5)	0.0024(5)
O9	0.6999(2)	0.3858(1)	0.01805(6)	0.0128(3)	0.0113(6)	0.0202(8)	0.0071(7)	0.0024(6)	0.0013(5)	0.0003(5)
O10	0.0132(2)	0.6745(1)	0.06959(7)	0.0114(3)	0.0085(5)	0.0122(7)	0.0131(8)	-0.0026(6)	-0.0003(5)	0.0029(5)
O11	0.1964(2)	0.4254(1)	0.06268(7)	0.0111(3)	0.0142(6)	0.0058(8)	0.0140(8)	-0.0008(6)	0.0049(5)	-0.0012(5)
O12H	0.4885(2)	0.6398(1)	0.08884(6)	0.0101(3)	0.0083(5)	0.0114(7)	0.0100(7)	0.0016(6)	-0.0018(5)	-0.0001(5)
OW1	0.0230(2)	0.1537(1)	0.04187(8)	0.0140(3)	0.0117(6)	0.0102(7)	0.0198(9)	0.0015(6)	0.0010(6)	0.0015(5)
OW2	0.2526(2)	0.2276(2)	0.16275(7)	0.0127(3)	0.0149(6)	0.0124(7)	0.0116(8)	0.0003(6)	0.0046(5)	0.0012(6)
OW3	0.7696(2)	0.2283(2)	0.19865(7)	0.0140(3)	0.0158(6)	0.0130(7)	0.0121(8)	0.0002(6)	-0.0028(5)	-0.0014(6)
OW4	0.6579(2)	0.2295(2)	0.31522(7)	0.0119(3)	0.0122(6)	0.0118(7)	0.0122(8)	0.0015(6)	0.0034(5)	0.0008(5)
H1	-0.071(5)	0.138(3)	0.019(1)	0.03						
H2	0.082(5)	0.081(3)	0.054(1)	0.03						
H3	0.231(5)	0.154(3)	0.178(1)	0.03						
H4	0.341(5)	0.219(3)	0.138(1)	0.03						
H5	0.740(5)	0.146(3)	0.191(1)	0.03						
H6	0.869(5)	0.234(3)	0.221(1)	0.03						
H7	0.707(5)	0.158(3)	0.307(1)	0.03						
H8	0.605(5)	0.210(3)	0.342(1)	0.03						
H9	0.567(5)	0.573(3)	0.118(1)	0.03						

Vladimirite (R080001) from Chile

Ca1	0.67085(10)	0.72608(4)	0.00248(2)	0.0090(1)	0.0066(3)	0.0106(2)	0.0096(2)	-0.0012(1)	0.0011(2)	-0.0000(2)
Ca2	0.00530(10)	0.85201(4)	0.14095(2)	0.0089(1)	0.0069(3)	0.0097(2)	0.0100(2)	0.0010(1)	0.0008(2)	0.0006(2)
Ca3	0.88891(11)	0.32106(4)	0.10693(2)	0.0112(1)	0.0098(4)	0.0141(2)	0.0102(2)	0.0027(1)	0.0025(2)	0.0028(2)
Ca4	0.43350(10)	0.36410(4)	0.24541(2)	0.0101(1)	0.0071(3)	0.0110(2)	0.0118(2)	-0.0000(1)	-0.0007(2)	0.0006(2)
As1	0.86861(5)	0.54833(2)	0.21400(1)	0.0073(1)	0.0062(2)	0.0073(1)	0.0083(1)	0.0004(1)	0.0001(1)	0.0004(1)
As2	0.54074(5)	0.00134(2)	0.09702(1)	0.0075(1)	0.0057(2)	0.0076(1)	0.0091(1)	0.0007(1)	0.0010(1)	0.0007(1)
As3	0.23069(5)	0.58485(2)	0.04961(1)	0.0072(1)	0.0051(2)	0.0079(1)	0.0083(1)	0.0000(1)	0.0005(1)	0.0001(1)
O1	0.8569(4)	0.7141(1)	0.21263(7)	0.0102(4)	0.010(1)	0.0078(6)	0.0136(7)	0.0013(5)	0.0024(7)	0.0008(7)
O2	0.1328(4)	0.4972(2)	0.20183(8)	0.0138(4)	0.007(1)	0.0152(7)	0.0202(8)	0.0039(6)	0.0047(8)	0.0055(7)
O3	0.6746(4)	0.4809(2)	0.16103(7)	0.0143(4)	0.013(1)	0.0109(6)	0.0166(8)	-0.0015(5)	-0.0079(8)	0.0008(7)
O4	0.7922(4)	0.4919(1)	0.27806(7)	0.0113(4)	0.010(1)	0.0131(7)	0.0114(7)	0.0023(5)	0.0046(7)	-0.0011(7)
O5	0.5436(4)	0.1645(1)	0.08186(7)	0.0096(4)	0.007(1)	0.0075(6)	0.0139(7)	0.0019(5)	0.0008(7)	0.0005(6)
O6	0.2656(4)	0.9504(2)	0.08639(7)	0.0125(4)	0.002(1)	0.0161(7)	0.0186(8)	0.0032(6)	-0.0004(8)	-0.0021(7)
O7	0.6648(4)	0.9779(2)	0.16753(7)	0.0116(4)	0.010(1)	0.0144(7)	0.0105(7)	0.0018(5)	-0.0011(7)	0.0014(7)
O8	0.7146(4)	0.9149(2)	0.05848(7)	0.0119(4)	0.008(1)	0.0136(7)	0.0142(7)	-0.0039(5)	0.00250(7)	0.0037(7)
O9	0.6999(4)	0.3859(2)	0.01794(7)	0.0127(4)	0.010(1)	0.0202(7)	0.0080(7)	0.0022(6)	0.0010(7)	0.0000(7)
O10	0.0131(4)	0.6746(2)	0.06964(7)	0.0117(4)	0.008(1)	0.0130(7)	0.0142(7)	-0.0031(6)	0.0020(7)	0.0032(7)
O11	0.1970(4)	0.4255(1)	0.06269(7)	0.0120(4)	0.014(1)	0.0063(6)	0.0169(7)	0.0002(5)	0.0056(8)	-0.0012(7)
O12H	0.4880(4)	0.6396(2)	0.08876(7)	0.0092(4)	0.002(1)	0.0125(6)	0.0119(7)	0.0008(5)	-0.0029(7)	-0.0019(7)
OW1	0.0227(4)	0.1531(2)	0.04194(8)	0.0136(4)	0.009(1)	0.0134(7)	0.0173(8)	0.0005(6)	-0.0005(8)	0.0008(7)
OW2	0.2525(4)	0.2277(2)	0.16279(8)	0.0131(4)	0.014(1)	0.0126(7)	0.0132(8)	-0.0005(6)	0.0050(8)	0.0006(8)
OW3	0.7694(4)	0.2285(2)	0.19865(8)	0.0142(4)	0.015(1)	0.0121(7)	0.0139(8)	0.0009(6)	-0.0029(8)	-0.0004(8)
OW4	0.6570(4)	0.2295(2)	0.31533(7)	0.0124(4)	0.012(1)	0.0133(7)	0.0124(7)	0.0016(6)	0.0033(8)	0.0008(7)
H1	-0.067(8)	0.150(3)	0.018(2)	0.03						
H2	0.083(7)	0.084(3)	0.056(1)	0.03						
H3	0.220(7)	0.154(3)	0.176(1)	0.03						
H4	0.338(7)	0.220(3)	0.141(1)	0.03						
H5	0.747(7)	0.149(3)	0.190(1)	0.03						
H6	0.889(7)	0.240(3)	0.223(2)	0.03						
H7	0.711(7)	0.168(3)	0.307(1)	0.03						
H8	0.585(7)	0.212(3)	0.344(1)	0.03						
H9	0.579(7)	0.556(3)	0.124(1)	0.03						

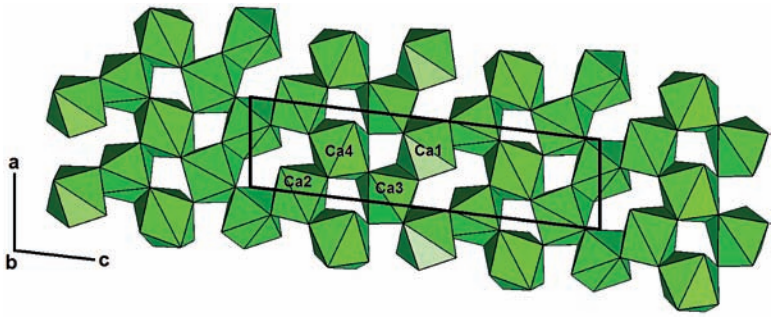

FIG. 2. A layer of Ca polyhedra in vladimirite.

The bond-valence sums of three As^{5+} cations, calculated using the parameters from Brese & O'Keeffe (1991), are 4.96, 4.96, and 4.95 *vu* for As1, As2, and As3, respectively (Table 5).

All four Ca polyhedra in vladimirite are quite irregular, with each of the Ca1 and Ca2 polyhedra having one H_2O group in its coordination and each of the Ca3 and Ca4 polyhedra having three H_2O groups in its coordination. Whereas each of the four Ca polyhedra shares three edges with other Ca polyhedra to form the undulating layers, the Ca3 and Ca4 polyhedra also share a vertex (Ow2) with each other (Fig. 2). The calculated bond-valence sums for Ca1, Ca2, Ca3, and Ca4 are 2.09, 1.99, 1.91, and 1.91 *vu*, respectively (Table 5). The corrugation of the layers of Ca polyhedra in vladimirite is presumably caused by the mismatches in size among four nonequivalent Ca polyhedra (Table 4), due to different numbers of H_2O groups coordinated to

each Ca^{2+} cation, which give rise to different hydrogen-bonding environments (see below). The hydrogen bonds are proposed to be responsible for the corrugation of the layers of $CoO_4(H_2O)_2$ octahedra in the synthetic compound $Co_{2.39}Cu_{0.61}(PO_4)_2 \bullet H_2O$ (Assani *et al.* 2010).

Table 6 shows the hydrogen-bonding scheme in vladimirite. Except for H1...O6, which has a distance of 2.69 Å, all other distances between H atoms and acceptors are shorter than 2.08 Å. In fact, the H1...O6 distance may be too long to be regarded as a hydrogen bond, suggesting that the H1 atom from the OW1 could be dangling in the structure. Whereas none of four H_2O groups is the H-acceptor, all four O atoms in the As1 tetrahedron, three (O5, O6, and O7) in the As2 tetrahedron, and one (O12H) in the As3 tetrahedron are H-acceptors. However, four oxygen atoms (O8, O9, O10, and O11) are not engaged in any hydrogen-bonding, as also indicated by the calculated bond-valence sums (Table 5). Only O12H from the AsO_3OH group acts as both H-donor (H9 to O3) and H-acceptor (H8 from OW4). Remarkably, the distance between O12H–H...O3 in vladimirite is only 2.47 Å, which is the shortest donor–acceptor distance (d_{D-A}) of all Ca arsenate minerals (Ferraris & Ivaldi 1984) and belongs to the shortest known examples, in which the donor and acceptor atoms are symmetrically distinct (Mihajlović & Effenberger 2006, Đorđević & Karanović 2008, 2010). Nonetheless, such a short d_{D-A} value has been observed in several synthetic compounds containing the AsO_3OH groups, such as $Sr_5(As_2O_7)_2(AsO_3OH)$ with d_{D-A} = 2.49 Å (Mihajlović *et al.* 2004), $Mg_7(AsO_4)_2(AsO_3OH)_4$ with d_{D-A} = 2.47 Å (Kolitsch & Bartu 2004), $Sr_4Cu_3(AsO_4)_2(AsO_3OH)_4 \bullet 3H_2O$ with d_{D-A} = 2.48 Å (Đorđević & Karanović 2008), and $Ba(AsO_3OH)$ with d_{D-A} = 2.46 Å (Đorđević & Karanović 2010). It should be pointed out that Ferraris & Chiari (1970) and Ferraris *et al.* (1972b), respectively, also observed the very short hydrogen-bond distances in weilite (O7...O7 = 2.397 Å) and in švenekite (O5...O5 = 2.436 Å and O8...O8 = 2.444 Å); those hydrogen bonds are symmetrical, rather than asymmetrical, as we observe in vladimirite.

TABLE 4. SELECTED BOND-LENGTHS (Å) IN VLADIMIRITE

		R100075	R080001			R100075	R080001
Ca1	-O8	2.306(2)	2.307(2)	As1	-O2	1.678(1)	1.678(2)
	-O11	2.341(1)	2.339(2)		-O4	1.685(1)	1.683(1)
	-O10	2.424(1)	2.423(2)		-O1	1.687(1)	1.688(1)
	-O9	2.437(1)	2.436(2)		-O3	1.701(2)	1.700(2)
	-O5	2.442(2)	2.438(2)	Avg.		1.688	1.687
	-OW1	2.480(2)	2.482(2)				
	-O12H	2.513(1)	2.512(2)	As2	-O8	1.674(1)	1.670(2)
Avg.		2.421	2.421		-O6	1.678(1)	1.673(2)
					-O5	1.696(1)	1.696(1)
Ca2	-O6	2.306(1)	2.305(2)		-O7	1.702(2)	1.703(2)
	-O1	2.404(1)	2.397(2)	Avg.		1.688	1.685
	-O10	2.440(2)	2.438(2)				
	-OW4	2.437(2)	2.439(2)	As3	-O11	1.668(1)	1.664(1)
	-O8	2.465(2)	2.463(2)		-O10	1.671(1)	1.670(2)
	-O7	2.500(1)	2.496(2)		-O9	1.673(1)	1.671(2)
	-O4	2.517(2)	2.515(2)		-O12H	1.747(1)	1.742(2)
Avg.		2.438	2.436	Avg.		1.690	1.688
Ca3	-O9	2.291(2)	2.292(2)				
	-O11	2.408(1)	2.410(2)				
	-OW1	2.453(2)	2.453(2)				
	-O3	2.477(2)	2.472(2)				
	-OW3	2.478(2)	2.475(2)				
	-OW2	2.525(2)	2.523(2)				
	-O5	2.576(1)	2.575(2)				
Avg.		2.458	2.458				
Ca4	-O2	2.345(1)	2.340(2)				
	-OW4	2.374(2)	2.373(2)				
	-O7	2.433(1)	2.431(2)				
	-OW2	2.478(2)	2.476(2)				
	-O4	2.496(1)	2.497(2)				
	-O1	2.551(1)	2.549(2)				
	-OW3	2.719(2)	2.716(2)				
	-O3	2.785(2)	2.785(2)				
Avg.		2.523	2.520				

Raman spectra

There have been numerous studies on a variety of arsenate minerals and compounds, especially those containing the AsO_3OH groups, by means of infrared and Raman spectroscopic techniques (*e.g.,* Mihajlović *et al.* 2004, Đorđević & Karanović 2008, 2010, Sejkora *et al.* 2010, Frost *et al.* 2010, 2011a, 2011b, Čejka *et al.* 2011). We present our Raman spectroscopic measurements of vladimirite in Figure 3. Based on previous studies on various hydrous arsenates, we made a tentative assignment of major Raman bands for vladimirite (Table 7). However, because of the presence of three symmetrically nonequivalent AsO_4 groups, of which one is protonated, and four H_2O groups in vladimirite, it is difficult to unambiguously assign some Raman bands to specific modes. Figure 3b shows the Raman bands originating mainly from the OH stretching vibrations between 2700 and 3800 cm^{-1}, and H_2O bending vibrations between 1500 and 1750 cm^{-1}. The O–H...O hydrogen-bond lengths inferred from the measured spectrum are in the range 2.60–2.85 Å (Libowitzky 1999), which compare well with those determined from our X-ray structural analysis (2.61–2.80 Å), except for the very short O12H–H9...O3 distance, 2.47 Å. According to Libowitzky (1999), the short O12H–H9...O3 hydrogen bond may be responsible for the band at 1475 cm^{-1}. Yet, it should be noted that the Raman bands in the region of 1400–1800 cm^{-1} may also result from the H_2O bending vibrations, although Raman spectroscopy is not very sensitive for the detection of the H–O–H bending mode. The sharp, relatively strong peak at 2253 cm^{-1} may be ascribed to the stretching vibration of the strongly hydrogen-bonded OH in the AsO_3OH unit (Frost *et al.* 2011b). Vibrations of the arsenate AsO_4 and AsO_3OH groups are responsible for the bands between 700 and 1000 cm^{-1}, and weak ones between 300 and 550 cm^{-1}. The bands below 300 cm^{-1} are attributed to lattice vibrational modes and Ca–O interactions.

TABLE 5. BOND-VALENCE SUMS (*vu*) FOR VLADIMIRITE FROM MOROCCO (R100075)

	Ca1	Ca2	Ca3	Ca4	As1	As2	As3	Sum	H-bonding
O1		0.307		0.206	1.241			1.754	H6
O2				0.360	1.272			1.632	H7
O3			0.252	0.110	1.195			1.557	H9
O4		0.226		0.239	1.248			1.713	H3
O5	0.277		0.193			1.212		1.682	H4
O6		0.400				1.272		1.672	H2, H1(?)
O7		0.237		0.284		1.192		1.713	H5
O8	0.400	0.260				1.286		1.946	
O9	0.280		0.417				1.289	1.986	
O10	0.291	0.278					1.296	1.865	
O11	0.364		0.304				1.307	1.975	
O12H	0.229						1.056	1.285	H8
OW1	0.250		0.269					0.519	
OW2			0.221	0.251				0.472	
OW3			0.251	0.131				0.382	
OW4		0.281		0.333				0.614	
Sum	2.091	1.989	1.907	1.914	4.956	4.962	4.948		

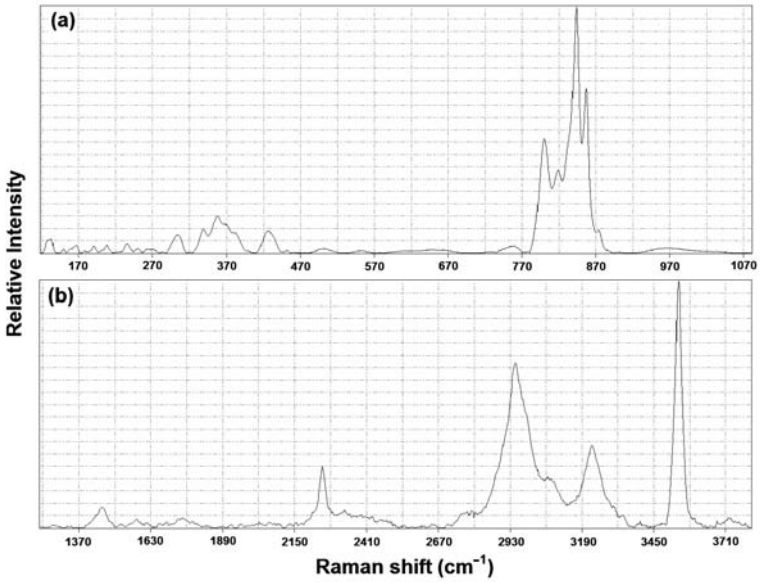

FIG. 3. Raman spectra of vladimirite: (a) between 120 and 1080 cm^{-1} and (b) between 1230 and 3800 cm^{-1}.

By dehydration of ferrarisite, $Ca_5(AsO_3OH)_2(AsO_4)_2•9H_2O$, at 60 °C for an hour, Catti & Ivaldi (1981) obtained a new triclinic phase of composition $Ca_5(AsO_3OH)_2(AsO_4)_2•5H_2O$ (Z = 1), with unit-cell parameters *a* 8.286(4), *b* 6.673(3), *c* 9.743(4) Å, α 86.58(3), β 111.10(3), γ 99.74(3)°, and claimed that this new phase is a polymorph of monoclinic vladimirite, on the basis of the chemical formula $Ca_5(AsO_3OH)_2(AsO_4)_2•5H_2O$ proposed for vladimirite in the literature. By analogy to this dehydration reaction, they further suggested that dehydration of guérinite ($P2_1/n$), the monoclinic polymorph of ferrarisite, should preferentially lead to the formation of vladimirite, provided that the reaction is carried out sufficiently slowly. However, with the revision of the chemical formula of vladimirite, it is evident

that this mineral does not belong to the group of minerals and inorganic salts with the general formula $M_5(XO_4)_2(XO_3OH)_2 \bullet nH_2O$, where X = As, P and M = Ca, Mg, Mn, Zn (Catti & Ivaldi 1981), and, as a consequence, it cannot be obtained simply by dehydration of other compounds in this group, unless a decomposition process is involved to achieve the proper M:X ratio of 4:3 for vladimirite. Nonetheless, given the monoclinic symmetry and the M:X ratio of 5:4, it seems that sainfeldite (*C*2/*c*), $Ca_5(AsO_4)_2(AsO_3OH)_2 \bullet 4H_2O$ (Ferraris & Abbona 1972) might be energetically more favorable to form through dehydration of guérinite.

TABLE 6. HYDROGEN BONDS IN VLADIMIRITE

D–H	*d*(D–H) (Å)	*d*(H···A) (Å)	<DHA (°)	*d*(D···A) (Å)	A
Vladimirite from Morocco (R100075)					
OW1-H1	0.73(3)	2.69(3)	156(3)	3.369(2)	O6
OW1-H2	0.84(3)	1.81(3)	166(3)	2.639(2)	O6
OW2-H3	0.84(3)	1.95(3)	173(3)	2.784(2)	O4
OW2-H4	0.81(3)	1.94(3)	169(3)	2.738(2)	O5
OW3-H5	0.87(3)	1.83(3)	175(3)	2.699(2)	O7
OW3-H6	0.73(3)	2.07(3)	169(3)	2.797(2)	O1
OW4-H7	0.81(3)	1.91(3)	170(3)	2.713(2)	O2
OW4-H8	0.75(3)	1.88(3)	170(3)	2.615(2)	O12H
O12H-H9	1.03(3)	1.44(3)	178(3)	2.465(2)	O3
Vladimirite from Chile (R080001)					
OW1-H1	0.71(4)	2.72(4)	154(4)	3.371(3)	O6
OW1-H2	0.89(3)	1.77(4)	164(4)	2.633(3)	O6
OW2-H3	0.82(3)	1.97(3)	167(4)	2.782(2)	O4
OW2-H4	0.68(4)	2.06(4)	167(4)	2.735(3)	O5
OW3-H5	0.81(3)	1.89(3)	174(4)	2.698(2)	O7
OW3-H6	0.79(4)	2.02(4)	169(3)	2.798(3)	O1
OW4-H7	0.73(4)	2.00(4)	168(4)	2.712(2)	O2
OW4-H8	0.78(3)	1.86(3)	163(4)	2.612(2)	O12H
O12H-H9	1.19(3)	1.28(3)	173(3)	2.465(2)	O3

Note: D: donor, A: acceptor.

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TABLE 7. TENTATIVE ASSIGNMENT OF RAMAN BANDS FOR VLADIMIRITE

Bands (cm^{-1})	Intensity	Assignment
2953, 3071, 3235	relatively strong to strong	$v_1 + v_3$ symmetric and antisymmetric
3542, 3736	relatively sharp to sharp	stretching vibrations of hydrogen-bonded H_2O
2253	relatively strong, sharp	typical O-H stretching vibrations of hydrogen-bonded OH in the (AsO_3OH) unit
1584, 1750	weak, broad	v_2 (δ) H_2O bending vibrations
1457	weak, sharp	strong O-H···O hydrogen bond
760, 800, 819, 843, 857, 875, 966	weak to strong and broad to sharp bands	$v_1 + v_3$ (AsO_4 and AsO_3OH) symmetric and antisymmetric stretching
620-680	very weak and broad bands	H_2O librational mode
304, 338, 360, 371, 383, 427, 435, 502	weak, relatively sharp bands	$v_2 + v_4$ (AsO_4 and AsO_3OH) symmetric and antisymmetric stretching
<300	weak and broad	lattice vibrational modes and Ca–O interactions

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