

COMPARATIVE CRYSTAL CHEMISTRY OF GEMINITE $\text{Cu}[\text{AsO}_3\text{OH}]\text{H}_2\text{O}$ AND RELATED MINERALS

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Geminite, $\text{Cu}[\text{AsO}_3\text{OH}]\text{H}_2\text{O}$, was discovered in 1990 in a sample of a quartz vein in the mine of Cap Garonne (Var, France) in association with tennantite, covellite, chalcantite, and some other minerals [12]. In the summer of 1995 a microscopic patch of this mineral was given to the Moscow University for a structural investigation. However, after three unsuccessful attempts to obtain the necessary experimental material by means of single-crystal diffractometers provided by three organizations (Departments of Geology and Chemistry of the Moscow University and also by the Institute of Crystallography of the Russian Academy of Sciences), the sample was sent to G. Ferraris, the Head of Department of Mineralogy and Petrology of the Turin University (Italy), in whose laboratory there is a diffractometer with a more powerful (3 kW) X-ray tube. The work on the deciphering of the structure of geminite was near to completion when at the end of 1995 we received No. 5 of the journal *Canadian Mineralogist* with an article devoted to the structure of this mineral [4]. Although the authors were obviously disappointed, they nevertheless decided to continue their work, with emphasis on the comparison of the structure of geminite with chemically closely related Zn, Co, Mn, and Ca arsenates, which was missing in the publication of M. A. Cooper and F. C. Hawthorne [4]. The results of this work are presented in the present paper.

The structural study was carried out on a single crystal of geminite collected at the Salsigne mine (Carrassonne, Aude, France), where it was identified in association with arsenopyrite, chalcopyrite, tellurium, pushcharovskite and other minerals. The crystals are of a rhomboid form (Fig. 1) flattened along a given edge (~ 15.7 Å) of the unit cell. The results of a chemical microprobe analysis (in mass percent) are as follows: CuO, 33.80; As_2O_3 , 53.88; Al_2O_3 , 0.10; H_2O , 12.2 (by difference) and the optical constants $\alpha = 1.660$, $\beta = 1.690$, $\gamma = 1.765$, $2V \approx 70^\circ\text{C}$ as a whole differ insignificantly from the data published earlier for the sample from Cap Garonne.

The parameters of the triclinic unit cell refined on a single-crystal diffractometer ("Italstructures") are as follows: $a = 6.4333(1)$, $b = 8.093(2)$, $c = 15.764(3)$ Å, $\alpha = 86.65(3)$, $\beta = 84.35(3)$, $\gamma = 84.47(3)^\circ$ are related to the parameters of the c -unit cell of geminite ($a = 9.841$, $b = 10.818$, $c = 15.744$ Å, $\alpha = 95.71$, $\beta = 90.94$, $\gamma = 103.11^\circ$) reported by M. Cooper and F. Hawthorne [4], by the transition matrix $\{1-10; 110; 00-1\}$. Both unit cells are different from the unit cell found on the basis of a powder X-ray photograph ($a = 6.395$, $b = 8.110$, $c = 15.732$ Å, $\alpha = 92.01$, $\beta = 93.87$, $\gamma = 95.02^\circ$) and reported by H. Sarp and P. Perroud [12]. The factor responsible for the differences in the values of the parameters obtained by means of single-crystal and powder techniques, according to studies carried by G. Ferraris and M. Prencipe, is that the indexing of the powder X-ray diffraction pattern made with the aid of quadratic formulas is possible on the basis of a knowledge of the axial parameters a , b , c and the moduli of the angle cosines between them. Using these values, one can obtain a complete set of d_{hkl} , though actually the indices h , k , and l are determined for each reflection to within the sign, which, accordingly, allows for 8 different combinations: $\pm(hkl)$, $\pm(-hkl)$, $\pm(h-kl)$, $\pm(hk-l)$. The sets d_{hkl} obtained do not depend on the sign of the angle cosines between the axial parameters. For the same reason, there arises an uncertainty in the determination of the unit-cell type.

The experimental data that characterize the procedure of refinement of the structure are given in Table 1. The final coordinates of basal atoms, their isotropic and anisotropic mean square displacements associated with thermal vibrations, and also interatomic distances are listed in Tables 2, 3, and 4, respectively. Comparison of experimental (Guinier-Hägg chamber, $\text{CuK}_{\alpha 1}$ -radiation) and theoretical [16] powder X-ray diffraction patterns revealed their good agreement. Below are given the values of d_{exp} , d_{cal} , I_{exp} , and I_{cal} for five strongest reflections: (1) 7.83, 7.834, 100, 100; (2) 3.850, 3.851, 30, 8; (3) 3.260, 3.266, 70, 21; (4) 3.070, 3.068, 70, 21; (5) 2.611, 2.617, 50, 10.

Both structural decipherings made with a high degree of accuracy allow us to regard mixed (001) sheets formed by Cu-octahedra and As-tetrahedra as the basis of the structure of geminite (Fig. 2). These layers, which are united into a three-dimensional framework by H bonds, show zig-zag columns parallel to $[110]$ and formed by Cu-octahedra. The

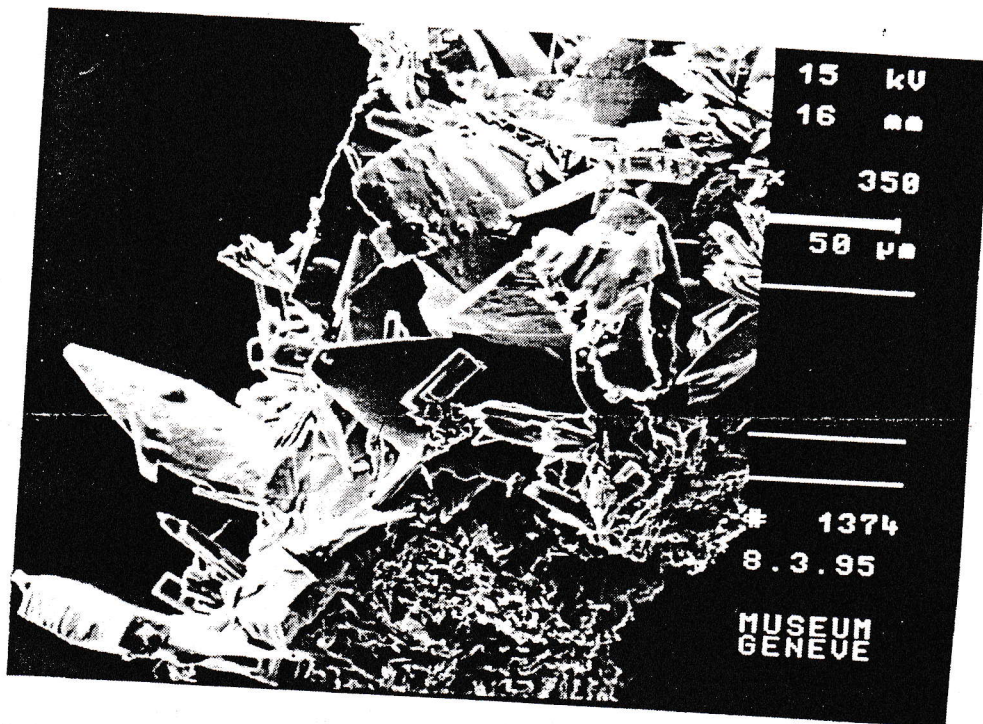


Fig. 1

Photograph of the geminite microdruse taken in an electron scanning microscope ($\times 350$).

Table 1

Experimental Data Characterizing the Procedure of Refinement of the Structure of Geminite

Formula	$\text{Cu}[\text{AsO}_3\text{OH}]\text{H}_2\text{O}$
Molecular weight	218.47
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal size	0.11 \times 0.07 \times 0.04 mm
Crystal system	Triclinic
Space group	P-1
Unit cell parameters	$a = 6.433(1) \text{ Å}; \alpha = 86.65(3)^\circ$ $b = 8.093(2) \text{ Å}; \beta = 84.35(3)^\circ$ $c = 15.764(3) \text{ Å}; \gamma = 84.47(3)^\circ$
Volume, Z	811.9(3) Å ³ , 8
Density (calculated)	3.574 mg/m ³
Absorption coefficient	13.4 mm ⁻¹
F (000)	820
Theta range for data collection	2.53-20.00°
Limiting indices	$-6 \leq h \leq 6, -7 \leq k \leq 7, -15 \leq c \leq 15$
Total number of reflexions	3019
Number of independent reflexions	1477 [$R_{\text{int}} = 0.0138$]

Table 1
(continued)

Method of refinement	Full-matrix, least-squares on F^2
Weight	$1/[\sigma(F)]^2$
Number of reflexions/parameters	1477/253
Goodness of fit on F^2	1.065
R indices [$F > 3 \sigma(F)$]	$R1 = 0.032, wR2 = 0.057$
Largest diffraction peak and hole on a difference Fourier map	0.500 and $-0.475 e/\text{\AA}^3$
Correction for absorption	ψ -scanning [11] according to DIFABS program [15]

Table 2

The Coordinates of Atoms ($\times 10^4$) and Their Equivalent Isotropic Displacements ($\text{\AA}^2 \times 10^3$)*

Atom	x	y	z	U(eq)
As(1)	4095(2)	4401(1)	3974(1)	11(1)
As(2)	3617(2)	3611(1)	885(1)	11(1)
As(3)	1097(1)	1495(1)	5923(1)	11(1)
As(4)	1453(1)	294(1)	8957(1)	9(1)
Cu(1)	1357(2)	6379(1)	9589(1)	13(1)
Cu(2)	3876(2)	8537(1)	4533(1)	14(1)
Cu(3)	-1134(2)	4060(1)	4398(1)	14(1)
Cu(4)	6425(2)	888(1)	-656(1)	11(1)
O(1)	4753(1)	6215(7)	3549(4)	20(2)
O(2)	5936(9)	-6560(6)	4552(4)	14(2)
O(3)	1748(9)	4463(7)	4553(4)	18(2)
O(4)	3988(9)	4782(7)	1681(4)	16(2)
O(5)	5783(9)	3255(6)	218(3)	12(1)
O(6)	1565(9)	4292(7)	323(4)	14(2)
O(7)	-858(9)	1825(7)	5311(4)	13(2)
O(8)	3333(9)	871(7)	5359(4)	19(2)
O(9)	516(9)	186(7)	6767(4)	18(2)
O(10)	1023(9)	-1689(6)	8770(4)	11(1)
O(11)	-721(9)	1399(6)	9383(4)	14(2)
O(12)	3447(9)	458(6)	9543(3)	8(1)
OH1	4021(20)	3126(7)	3140(4)	18(2)
OH2	2928(9)	-1764(6)	1377(4)	16(2)
OH3	8507(9)	-3349(6)	3630(4)	13(2)
OH4	2218(10)	1245(7)	7998(4)	19(2)
H ₂ O(1)	1806(10)	4945(8)	8169(4)	27(2)
H ₂ O(2)	3708(9)	9795(7)	3388(4)	16(2)
H ₂ O(3)	-630(10)	3149(7)	3247(4)	20(4)
H ₂ O(4)	6411(9)	1949(7)	-1788(4)	16(2)

* The numbering of atoms is according to [4].

similarity in the unit-cell parameters and also in the chemical formulas indicates that geminite may be looked upon as a mineral belonging to a sufficiently large isotopic series with the general formula $R^{2+}[\text{AsO}_3\text{OH}]\text{H}_2\text{O}$, where there is observed the correspondence to formulas with $R^{2+} = \text{Cu}$ (geminite), $R^{2+} = \text{Zn}$ (koritnigit) [10], $R^{2+} = \text{Mn}$ (krautite) [8], $R^{2+} = \text{Co}$ (synthetic crystal) [17], and $R^{2+} = \text{Ca}$ (Haidingerite) [6]. The unit-cell parameters of geminite (our setup) and

koritnigit and also the coordinates of atoms are coupled by the matrix {001; -100; 010}. At the same time, there is an obvious difference between the two structures: in the case of geminite the Cu-octahedra show a considerable distortion associated with the Jan-Teller effect, whereas the Zn-octahedra in the structure of koritnigit are characterized by a more regular form: practically all Zn-O bonds are within 2.045-2.169 and only for one Zn-OH bond in two out of the four Zn-polyhedra is there an increase up to 2.487 and 2.495. In all four Cu-octahedra of geminite four Cu-O distances are shortened (1.987) and two are lengthened (2.402).

Table 3

Parameters of Anisotropic Atom Displacements ($\text{\AA} \times 10^3$) Included in the
Formula $T = \exp - 2\pi^2 [h^2 - a^2 U_{11} + \dots + 2hka^* b^* U_{12} \dots]$,
Where T is the Temperature Coefficient

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
As(1)	11(1)	10(1)	11(1)	-2(1)	-1(1)	0(1)
As(2)	11(1)	11(1)	10(1)	-1(1)	-1(1)	0(1)
As(3)	11(1)	12(1)	10(1)	-2(1)	-2(1)	0(1)
As(4)	10(1)	8(1)	10(1)	-2(1)	-1(1)	0(1)
Cu(1)	12(1)	11(1)	16(1)	1(1)	-2(1)	-1(1)
Cu(2)	13(1)	14(1)	15(1)	0(1)	-2(1)	-2(1)
Cu(3)	14(1)	13(1)	14(1)	-3(1)	-1(1)	-1(1)
Cu(4)	11(1)	11(1)	12(1)	-1(1)	-2(1)	-1(1)
O(1)	21(4)	16(4)	23(4)	3(3)	-1(3)	-4(3)
O(2)	19(4)	13(3)	12(4)	0(3)	-5(3)	-1(3)
O(3)	18(4)	13(3)	21(4)	-5(3)	-4(3)	1(3)
O(4)	19(4)	17(4)	14(4)	-5(3)	-6(3)	3(3)
O(5)	12(4)	12(3)	13(4)	0(3)	4(3)	-5(3)
O(6)	13(4)	18(4)	10(4)	0(3)	-1(3)	1(3)
O(7)	17(4)	13(3)	10(3)	-2(3)	-4(3)	-1(3)
O(8)	16(4)	15(3)	25(4)	-5(3)	-6(3)	3(3)
O(9)	16(4)	11(3)	27(4)	-1(3)	-1(3)	-4(3)
O(10)	10(4)	8(3)	14(4)	-2(3)	2(3)	-2(3)
O(11)	13(4)	14(3)	14(4)	-5(3)	3(3)	1(3)
O(12)	11(3)	3(3)	10(3)	0(2)	-1(3)	3(3)
OH1	23(4)	21(4)	12(4)	-8(3)	-3(3)	1(3)
OH2	22(4)	4(3)	21(4)	-1(3)	-3(3)	1(3)
OH3	15(4)	6(3)	19(4)	-4(3)	-1(3)	1(3)
OH4	19(4)	19(4)	18(4)	0(3)	1(3)	-6(3)
H ₂ O(1)	29(4)	27(4)	25(4)	-2(3)	1(3)	1(3)
H ₂ O(2)	20(4)	14(3)	13(4)	-2(3)	2(3)	-1(3)
H ₂ O(3)	26(4)	22(4)	13(4)	-6(3)	-2(3)	0(3)
H ₂ O(4)	17(4)	15(3)	18(4)	-4(3)	1(3)	-5(3)

In all four [AsO₃OH] tetrahedra one As-OH bond is noticeably lengthened relative to the other three bonds. The average lengths of these bonds (1.717) is close to that established on the basis of a statistical analysis of 36 bonds (As-OH = 1.731), which is characteristic for As-tetrahedra with one OH group [5]. According to Ferraris and Ivaldi [5], such a differentiation of bonds in tetrahedral oxoanions containing hydroxyl groups is interpreted within the framework of the concept of the valence force balance. In the case of As-tetrahedra the valence force from the central As³⁺ cation is equal to 5/4. The lengthening of the As-OH bond prevents the oversaturation of the OH group with valence forces and, conversely, determines a certain approach of the other unprotonated anions O²⁻ to the central As

atom. As a result, the average cation-anion distances in tetrahedral oxoanions are very stable and depend little on the number of OH groups that participate in the tetrahedron. In this respect the structure of geminite with an average As-O, OH distance of 1.685 only confirms this regularity (for comparison, the average As-O distance in [AsO₄] tetrahedra of olivenite, Cu₂[AsO₄]OH, is equal to 1.681 [14]).

Table 4

Interatomic Distances (Å), Angles (deg), and Volumes of Polyhedra (Å)³
in the Structure of Geminite*

As1-O3	1.685	O1-As1-O3	114.9	2.814			
As1-O1	1.654	OH1-As1-O3	108.0	2.759			
As1-OH1	1.724	O2-As1-O3	109.6	2.742			
As1-O2	1.671	OH1-As1-O1	107.0	2.715			
(1.684)		O2-As1-O1	112.3	2.761			
V = 2.44		O2-As-OH1	104.4	2.684			
As2-O5	1.673	O6-As2-O5	109.8	2.752			
As2-O6	1.692	O4-As2-O5	112.7	2.778			
As2-O4	1.664	OH2-As2-O5	109.5	2.771			
As2-OH2	1.720	O4-As2-O6	115.3	2.835			
(1.687)		OH2-As2-O6	104.3	2.694			
V = 2.44		OH2-As2-O4	104.8	2.682			
As3-O8	1.666	O9-As3-O8	112.5	2.788			
As3-O9	1.686	OH3-As3-O8	107.0	2.741			
As3-OH3	1.744	O7-As3-O8	111.2	2.738			
As3-O7	1.652	OH3-As3-O9	104.7	2.716			
(1.687)		O7-As3-O9	111.6	2.762			
V = 2.46		O7-As3-OH3	109.4	2.772			
As4-O10	1.702	O11-As4-O10	112.8	2.824			
As4-O11	1.689	O12-As4-O10	114.8	2.843			
As4-O12	1.673	O12-As4-O11	109.6	2.747			
As4-OH4	1.708	OH4-As4-O10	107.3	2.746			
(1.693)		OH4-As4-O11	107.9	2.746			
V = 2.47		OH4-As4-O12	103.8	2.661			
Cu1-O6'	1.997	Cu2-O7	1.980	Cu3-O7	2.249	Cu4-OH2	2.246
-O5	1.948	-O8'	1.931	-H ₂ O (3)	1.983	-H ₂ O(4)	1.984
-O10	1.977	-O1	2.491	-O3'	2.079	-O12'	1.972
-H ₂ O(1)	2.522	-H ₂ O (2)	2.025	-OH3	2.362	-O11	1.929
-O6"	1.992	-O2	2.092	-O2	1.985	-O12"	2.014
-O11	2.467	-O8"	2.334	-O3"	1.954	-O5	2.403
(2.151)		(2.141)		(2.102)		(2.120)	
V = 12.47		V = 12.56		V = 11.94		V = 12.20	

* Standard deviations are 0.006 Å in calculations of the distances and 0.3° in calculations of the angles.

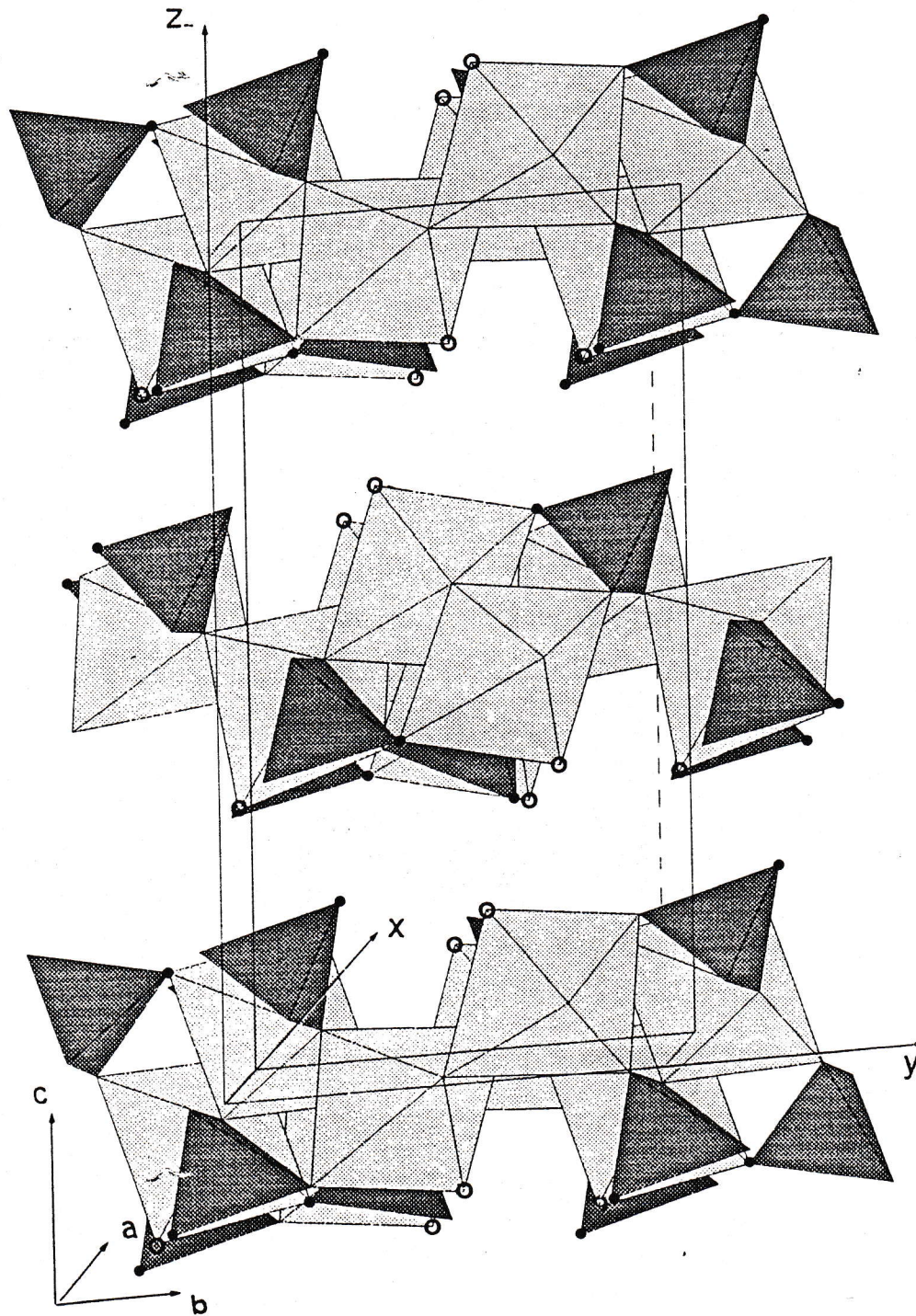


Fig. 2

The structure of geminite containing mixed sheets of Cu-octahedra and As-tetrahedra parallel to (001). Empty and filled circles represent oxygen atoms in water molecules and hydroxyl groups, respectively.

The totally octahedral (albeit distorted) copper coordination in the structure of geminite distinguishes it from olivenite [14], where part of Cu atoms, located in compacted pseudotrigonal bipyramids, is characterized by a (2 + 3) coordination, and also from other minerals of this family with the general formula $R_2[TO_4]X$, where R and T correspond to the pairs Cu + As (olivenite), Cu + P (libethenite), Zn + As (adamine), Mg + P (wagnerite) and Al + Si (andalusite), and $X = O, OH$. The relationship between composition and structure manifests itself, when these minerals are compared, in that the relative increase of the number of R cations and the absence of water molecules in the case of olivenite and isotopic compounds evidently determines the formation of a framework of R polyhedra [14], whereas in geminite and its analogs the polyhedra of nontetrahedral cations are united into columns. The mineral that fill the spacing between the two groups may be legrandite $Zn_2[AsO_4]OH \cdot H_2O$ [1], in the structure of which the Zn-polyhedra form corrugated walls. Thus, on the basis of the comparisons made there is revealed the morphological series $R[TO_3OH]H_2O - R_2[TO_4]OH \cdot H_2O - R_2[TO_4]OH$ with a subsequent increase in the degree of condensation of the cationic polyhedra and with the distinctly cationic role of the amphoteric R-cations, this being shown by the edge linkages between their polyhedra.

Table 5

Regularities in Variation of Density and Refractive Indices as a Function of Water Content (+OH) and Stoichiometric Ratios O/Cu in Aqueous Copper Arsenates Chemically Related to Geminite

Mineral, author	O/Cu	nH_2O (+OH)	Density	Average refractive index
Geminite [12] $CuAsO_3(OH)H_2O$	5	1 (2)	3.57	1.706
Euchroite [7] $Cu_2AsO_4OH \cdot 3H_2O$	4	3 (4)	3.46	1.709
Strashimerite $Cu_2AsO_4(OH)H_2O$	3	1 (2)	3.81	1.736
Olivenite [14] Cu_2AsO_4OH	2.5	- (1)	4.45	1.815
Cornwallite $Cu_5(AsO_4)_2(OH)_4$	2.4	- (4)	4.04	1.85
Cornubite [13] $Cu_5(AsO_4)_2(OH)_4$	2.4	- (4)	4.85	1.8-1.9
Clinoclase [9] $Cu_3AsO_4(OH)_3$	2.3	- (3)	4.42	1.842

As a result of the study of sufficiently large series of aqueous calcium arsenates $CaHAsO_4 \cdot nH_2O$ [2] and aqueous sodium phosphates $NaH_2PO_4 \cdot nH_2O$ [3], it has been concluded that the increase of structural density is accompanied by a loss of water by the corresponding compounds and correlates with a decrease of the stoichiometric O/(Ca, Na) ratios. The data collected in Table 5, which refer to the family of hydrated copper arsenates chemically related to geminite confirm this conclusion. The arrangement of these compounds in accordance with the decrease of the values of the O/Cu ratio makes possible the manifestation of the "antibonding" structural function of OH group and water molecules, which is responsible for a decrease in the density of some compounds of this series. In this case, the refractive indices, on the contrary, increase with increasing degree of hydration in compounds that have close O/Cu ratios, which may be accounted for by the greater polarizability of O^{2-} anions which are in contact with the protons.

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