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Guanacoite, $Cu_2Mg_2(Mg_{0.5}Cu_{0.5})(OH)_4(H_2O)_4(AsO_4)_2$, a new arsenate mineral species from the El Guanaco Mine, near Taltal, Chile: Description and crystal structure

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Abstract: Guanacoite, ideally $Cu_2Mg_2(Mg_{0.5}Cu_{0.5})(OH)_4(H_2O)_4(AsO_4)_2$, is a new arsenate mineral from the El Guanaco Mine, around 93 km east of Taltal and 230 km southeast of Antofagasta, 2nd Region, Northern Chile. The mineral occurs as blue to pale blue prismatic to acicular crystals up to 0.7 mm in length, in association with arhbarite, conichalcite, olivenite, chrysocolla, brochantite, quartz and enargite. The crystals are brittle, have a vitreous luster and are transparent. The streak is white to pale blue, the Mohs hardness is 3. Electron microprobe analysis gave (wt. %) CuO 29.67, MgO 17.12, As_2O_5 35.67, H_2O 18 (from thermal analysis), total 100.46. The empirical formula is $Cu_{2.32}Mg_{2.64}(OH)_{4.13}(H_2O)_{4.15}(AsO_4)_{1.93}$, simplified to $Cu_2Mg_2(Mg_{0.5}Cu_{0.5})(OH)_4(H_2O)_4(AsO_4)_2$. Guanacoite is monoclinic, space group $P2_1/c$, with $a = 5.482(4)$, $b = 16.84(1)$, $c = 6.911(5)$ Å, $\beta = 99.98(7)°$, $V = 628.5(5)$ Å^3 from X-ray powder data, and $a = 5.475(1)$, $b = 16.865(3)$, $c = 6.915(1)$ Å, $\beta = 99.80(3)°$, $V = 629.2(2)$ Å^3 from single-crystal data. The measured density is 3.31 g/cm^3, the calculated density ($Z = 2$) is 3.36 g/cm^3 for the ideal composition and 3.30 g/cm^3 for the average Cu/Mg ratio measured by microprobe. Guanacoite is optically biaxial negative with α 1.664(1), β 1.691(1), γ 1.695(1), 2V(meas.) 31(1)°, 2V(calc.) 42° at 589 nm; pleochroism was not observed, dispersion is r > v weak, and the orientation is X ~ *c*, Y ^ a 10° (in obtuse β), Z = *b*. The mineral is isotypic with akrochordite, $(Mn,Mg)_5(OH)_4(H_2O)_4(AsO_4)_2$. Dominating elements of the crystal structure are edge-sharing, distorted (Cu,Mg)-, Cu- and MgO_6 octahedra which form ribbons extending along the *a*-axis, topologically very similar to those in amphiboles. These ribbons are linked to adjacent, parallel ribbons *via* AsO_4 tetrahedra, thus forming heteropolyhedral slabs parallel to (010). The slabs are linked to each other only by very strong hydrogen bonds crossing the (010) plane.

Guanacoite has also been found at Taghouni (Tarouni), Bou Azzer district, Morocco, in association with quartz, dolomite, chalcopyrite, chromite, cuprite, malachite and agardite-(Ce). Cation contents (normalized to 5): Cu 2.33, Mg 2.57, Co 0.10; unit-cell parameters: $a = 5.477(1)$, $b = 16.873(3)$, $c = 6.898(1)$, Å, $\beta = 99.86(3)°$, $V = 628.1(2)$ Å^3; measured density: 3.29(2) g/cm^3; optical properties: α 1.663(1), β 1.691(1), γ 1.693(1) (589 nm), $2V$(meas.) = 31(1)°, dispersion r > v (strong), pleochroism Z greenish blue >> X pale greenish blue > Y nearly colorless, orientation is Z = *b* and Y ^ *a* = 17° (in obtuse β).

Key-words: Guanacoite, new mineral, crystal structure, akrochordite, El Guanaco Mine, Chile, Taghouni, Morocco.

Introduction

In 1997 and 1998, several samples from the El Guanaco Mine, near Taltal, Chile, were submitted for analysis by G. Färber (Samswegen, Germany) and G. Backmann (Dresden, Germany) to one of the authors (T.W.). Semi-quantitative EDX analyses and X-ray powder diffraction studies showed that the material is different from any known mineral or synthetic compound. Subsequent investigations, which included a crystal-structure determination, confirmed that the mineral is a new species. The mineral

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Table 1. Chemical analyses of guanacoite.

Constituent	El Guanaco, Chile 1)		Taghouni, Morocco 2)		wt.% (calc.) 3)
	wt.% (meas.)	Range	wt.% (meas.)	Range	
CuO	29.67	27.60 – 30.65	27.86	27.04 – 28.92	31.19
MgO	17.12	16.49 – 18.03	15.55	14.69 – 16.75	15.80
CoO	–	–	1.16	0.94 – 1.49	
As_2O_5	35.67	35.13 – 36.17	32.86	31.90 – 33.59	36.05
H_2O	18				16.96
total	100.46		(77.43)		100.00

1) Measured wt.%: average of 11 analyses, H_2O from thermal analysis. 2) Measured wt.%: average of 5 analyses. 3) Calculated wt.% for the simplified formula with Mg:Cu = 1:1.

has been named guanacoite after the locality. Both mineral and name have been approved by the IMA Commission on New Minerals and Mineral Names prior to publication (vote 2003-021). Type material is deposited in the Mineralogical Collection of the Bergakademie Freiberg, Germany, as No. 79704.

Independent investigations by one of the authors (ARK) had revealed that a mineral identical to guanacoite also occurs at Taghouni (Tarouni), Bou Azzer district, Morocco. It was decided to combine both datasets into the present description. The specimens of guanacoite from Taghouni studied are preserved in the collection of the Mineral Sciences Department of the Natural History Museum of Los Angeles County as nos. 55435, 55436 and 55437.

Occurrence and paragenesis

The type locality of guanacoite is the El Guanaco mine (or Guanaco mine), 93 km east of Taltal, approximately 230 km southeast of Antofagasta, 2nd Region (Antofagasta), Northern Chile. The El Guanaco mine consist of several pits and underground workings. All guanacoite samples were found on a mine dump, so the exact position of the occurrence within the mining field is not known.

The El Guanaco deposit is a high sulphidation-style, Au-rich epithermal deposit hosted by felsic rocks belonging to a Paleocene to early Eocene volcanic belt. Acid alteration and weathering processes (mainly alteration of enargite) have led to formation of a variety of supergene minerals, including arhbarite, bismoclite, brochantite, chenevixite, clinoclase, conichalcite, iodargyrite, lammerite, lavendulan, lemanskiite (Ondruš *et al.*, 2006), malachite, olivenite and scorodite. The El Guanaco mine has been worked for gold, silver and copper, and, although mining operations ceased in 1997, recovery of metal from the leach pads continued and exploration led to the discovery of further mineralizations. At present, the mine is owned by the Diamon Rose company and specimen collecting is restricted (A. Molina, pers. comm., 2004).

Guanacoite is associated with dark blue, dense crusts of arhbarite, $Cu_2Mg(AsO_4)(OH)_3$ (Färber *et al.*, 1998, Krause *et al.*, 2003), conichalcite, olivenite and chrysocolla. On other specimens, brochantite, quartz and enargite were observed. The enargite forms black crystals covered by a relatively thick crust of arhbarite which in turn forms the base of guanacoite sprays. Small, supergene quartz prisms are perched on the arbharite.

At Taghouni, Bou Azzer district, Morocco, guanacoite occurs in cavities in quartz and pink cobaltoan dolomite. Crystals of chalcopyrite and chromite are found imbedded in the quartz and crystals of cuprite occur in the dolomite. Other secondary minerals closely associated with guanacoite include malachite and agardite-(Ce). The material containing guanacoite was originally collected by one of the authors (GF) on mine dumps.

It appears that the formation of guanacoite is restricted to arid and Mg-rich rich environments. At the type locality, the component metals are derived from the weathering of enargite (Cu, As) and an apparently dolomitic country rock (Mg). The Mg-Cu-arsenate arbharite seems to be a characteristic mineral accompanying guanacoite.

Appearance and physical properties

Guanacoite from the type locality occurs as blue to pale blue, prismatic to needle-like crystals up to 0.7 mm in length, usually in subparallel intergrowths or radiating sprays. The crystals are elongated along [100]. They show {031} as the dominant form and are terminated by {120}. Rarely, the forms $\{\bar{1}11\}$ and $\{\bar{1}21\}$ were observed. The Taghouni material is elongated on [100], shows dominant prisms {021} and is terminated by {100}.

The streak of the mineral is white to pale blue. The crystals have a vitreous luster and are transparent. The Mohs hardness of guanacoite is 3. The mineral is brittle and its fracture is uneven to conchoidal. It shows a cleavage parallel to {010}. The cleavage plane was derived from effects of preferred orientation in the X-ray powder diffraction pattern recorded in reflection geometry. The isotypic arsenate mineral akrochordite (see Discussion) has an identical cleavage. Guanacoite shows no fluorescence when irradiated with ultraviolet light, independent of the excitation frequency. The density, measured by the flotation method in a mixture of diiodomethane and tetrabromoethane, is 3.31(2) g/cm^3. The calculated density for Z = 2 is 3.36 g/cm^3 for the ideal composition and 3.30 g/cm^3 for the average Cu/Mg ratio measured by electron microprobe (calculated according to Mandarino, 1981a). For the material from Taghouni a density of 3.29(2) g/cm^3 was measured by the flotation method in Clerici solution.

Table 2. X-ray powder diffraction data for guanacoite from El Guanaco.

$I_{meas.}$	$I_{calc.}$	$d_{meas.}$(Å)	$d_{calc.}$(Å)	*h*	*k*	*l*
100	100	8.420	8.421	0	2	0
	3		6.310	0	1	1
5	38	5.384	5.399	1	0	0
4	17	5.128	5.141	1	1	0
2	8	4.535	4.545	1	2	0
4	17	4.463	4.473	1	1	–1
21	38	4.322	4.331	0	3	1
64	24	4.210	4.211	0	4	0
	1		4.063	1	2	–1
3	14	3.888	3.892	1	3	0
	2		3.811	1	1	1
9	14	3.577	3.581	0	4	1
	2	3.577	3.576	1	3	–1
3	15	3.549	3.548	1	2	1
6	21	3.402	3.403	0	0	2
3	10	3.330	3.336	0	1	2
4	14	3.320	3.320	1	4	0
2	9	3.211	3.210	1	3	1
2	1	3.148	3.135	1	0	–2
3	10	3.119	3.118	1	4	–1
3	28	3.078	3.081	1	1	–2
12	18	3.016	3.019	0	5	1
2	14	2.941	2.938	1	2	–2
10	35	2.907	2.910	0	3	2
1	5	2.870	2.866	1	4	1
1	3	2.854	2.858	1	5	0
7	3	2.809	2.807	0	6	0
	35	2.727	2.737	1	3	–2
5	10	2.727 *b*	2.726	1	5	–1
	13	2.727	2.700	2	0	0
	25	2.669	2.677	1	0	2
5	19	2.669	2.666	2	1	0
	2		2.644	1	1	2
	2		2.640	2	1	–1
5	10	2.599	2.595	0	6	1
2	6	2.564	2.571	2	2	0
2	6	2.552	2.553	1	5	1
	1	2.552	2.551	1	2	2
1	1	2.544	2.548	2	2	–1
	5		2.514	1	4	–2
4	12	2.492	2.491	1	6	0
	4		2.433	2	3	0
	1		2.416	1	3	2
	5		2.414	2	3	–1
	2		2.401	1	6	–1
1	1	2.398	2.394	0	5	2
2	7	2.342	2.349	2	1	1
1	4	2.293	2.298	2	1	–2
	3		2.284	2	2	1
5	23	2.281	2.281	1	6	1
	2		2.268	0	7	1
2	4	2.257	2.259	1	4	2
	6	2.257	2.257	2	4	–1
1	1	2.238	2.237	2	2	–2
2	18	2.217	2.215	1	1	–3
1	1	2.202	2.198	1	7	0
	3		2.185	2	3	1
1	1	2.164	2.166	0	6	2
	1		2.160	1	2	–3
	6		2.144	2	3	–2
	2		1.136	1	7	–1
8	2	2.106	2.105	0	8	0
	3	2.106	2.104	0	3	3
	3		2.094	2	5	–1
	3		2.076	1	3	–3
2	7	2.065	2.067	2	4	1
	1		2.049	1	7	1
	1		2.032	2	4	–2
1	2	2.011	2.011	0	8	1
	1		1.997	0	4	3
	2		1.974	1	4	–3
	1		1.964	0	7	2
6	10	1.961	1.962	1	8	0
	2	1.961	1.960	1	1	3
	3		1.956	2	0	2
	4		1.943	2	1	2
	2		1.919	2	5	–2
	2		1.908	1	7	–2
1	1	1.882	1.882	0	5	3
	2		1.861	1	3	3
	6		1.854	2	2	–3
1	1	1.853	1.854	1	8	1

b = broad

Optically, guanacoite is biaxial negative with α 1.664(1), β 1.691(1), γ 1.695(1) (wavelength 589 nm), and 2V(meas.) = 31(1)°, 2V(calc.) = 42°. Optic angle dispersion is weak, r > v. The orientation is X ~ *c*, Y ^ *a* 10° (in obtuse β), and Z = *b*. A pleochroism was not observed. Crystals lying on {031} show an oblique extinction of ~ 10° with respect to their elongation. For the material from Taghouni α 1.663(1), β 1.691(1), γ 1.693(1) (589 nm), 2*V*(meas.) = 31(1)°, a strong dispersion r > v and a pleochroism Z greenish blue >> X pale greenish blue > Y nearly colorless was observed. The orientation is Z = *b* and Y ^ *a* = 17° (in obtuse β).

Chemical composition

Chemical analyses of guanacoite were performed by means of both energy-dispersive (EDX) and wavelength-dispersive (WDX) X-ray spectrometry. An EDX spectrum revealed Cu, Mg, As (note that the latter two overlap completely), and O as the only elements present with atomic number > 7. Quantitative analyses were conducted with a Jeol JXA-8900R electron microprobe operated at an acceleration voltage of 20 kV and a beam current of 23 nA with $CuFeS_2$ (Cu), $MgAl_2O_4$ (Mg), and NiAs (As) as standards. The CAMECA program PAP was used for data reduction.

The crystal was analyzed at 11 different points. The average analysis (wt.% and standard deviation) is given in Table 1. The MgO content is inversely correlated with the CuO content due to the mutual substitution of Mg^{2+} and Cu^{2+} cations in the crystal structure (see below). For that reason also increased standard deviations for CuO and MgO were obtained. The water content was determined by thermal analysis. The mineral shows a weight loss in two broad steps around 200°C and 500°C. The total weight loss measured, 18 wt.%, is considered only approximate because of the very small amount of material available for the analysis. Nonetheless, the H_2O content calculated from

Table 3. Crystal data, data collection information and refinement details for type guanacoite.

Crystal data	
Formula	$Cu_2(Cu_{0.50}Mg_{0.50})(Mg_{0.96},Cu_{0.04})_2$ $Mg_2(OH)_4(H_2O)_4(AsO_4)_2$
Formula weight	320.35
Space group	$P2_1/c$
a, b, c (Å)	5.475(1), 16.865(3), 6.915(1)
β (°)	99.80(3)
V (Å^3), Z	629.19(18), 2
F(000), ρ_{calc} (g·cm^{-3})	620, 3.382
μ (mm^{-1})	9.769
Absorption correction	multi-scan*
Crystal dimensions (mm)	0.04 × 0.07 × 0.07
Data collection and refinement	
Diffractometer	Nonius KappaCCD system
λ (Mo-$K\alpha$) (Å), T (K)	0.71073, 293
Detector distance (mm)	34
Rotat. axis; rot. width (ϒ)	φ, ω; 1
Total no. of frames	1025
Collect. time/degree (s)	230
Collect. mode, $2\theta_{max}$ (ϒ)	sphere, 62.50
h, k, l ranges	$-8 \rightarrow 8$, $-25 \rightarrow 25$, $-10 \rightarrow 10$
Total refls. measured	4429
Unique reflections	2249 (R_{int} 1.26 %)
$R1(F)$, $wR2_{all}(F^2)$**	2.10 %, 4.59 %
'Observed' refls.	2052 [$F_o > 4s(F_o)$]
Extinct. coefficient	0.0029(3)
No. of refined parameters	135
GooF	1.198
$(\Delta/\sigma)_{max}$	0.0001
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e/Å^3)	-0.52, 0.57

Note: Unit-cell parameters were refined from 3543 recorded reflections. Scattering factors for neutral atoms were employed in the refinement.

* Otwinowski & Minor (1997); Otwinowski *et al.* (2003).

** $w = 1/[\sigma^2(F_o^2) + (0.003P)^2 + 1.26P]$; $P = ([\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$.

the weight loss is in satisfacory agreement with the content of the ideal formula.

The empirical formula, calculated on the basis of 16 O atoms, is $Cu_{2.32}Mg_{2.64}(OH)_{4.13}(H_2O)_{4.15}(AsO_4)_{1.93}$. The simplified formula is $Cu_2Mg_2(Mg,Cu)(OH)_4(H_2O)_4(AsO_4)_2$ or, taking into account the mixed Cu/Mg site according to the single-crystal structure analysis, $Cu_2Mg_2(Mg_{0.5}Cu_{0.5})(OH)_4(H_2O)_4(AsO_4)_2$.

The Gladstone-Dale compatibility index is -0.022, indicating 'excellent' agreement between the chemical and physical data (Mandarino, 1981b).

Chemical analyses of guanacoite from Taghouni were conducted using a Cameca SX50 electron microprobe operated at 15 kV and 15 nA with Cu metal (Cu), diopside glass (Mg) and $CoAs_2$ (Co) as standards. Five analyses, each on separate grains, gave the results presented in Table 1. No water analysis was performed on the Taghouni material.

Guanacoite is slowly dissolved in cold and rapidly dissolved in warm dilute mineral acids, such as HCl, H_2SO_4 and HNO_3.

X-ray powder diffraction

The X-ray powder diffraction pattern (Table 2) was recorded using a Siemens D500 diffractometer with Cu$K\alpha_1$ radiation (λ = 1.5406 Å) and a secondary graphite monochromator. The reflections were indexed based on the results of the single-crystal study. Refinement of the powder diffraction data gave the unit-cell parameters a = 5.482(4), b = 16.84(1), c = 6.911(5) Å, β = 99.98(7)°, V = 628.57(5) Å^3.

The X-ray powder diffraction pattern for guanacoite from Taghouni was obtained using a using a 114.6 mm diameter Gandolfi camera and Ni-filtered Cu$K\alpha$ radiation. It was in good agreement with the powder data of the type material.

Table 4. Fractional atomic coordinates and displacement parameters (in Å^2) for guanacoite.

Atom	x	y	z	U_{eq}/U_{iso}	Occupancy
Cu(1)	0.0	0.0	0.0	0.00995(15)	$Cu_{0.504(3)}Mg_{0.496(3)}$
Cu(2)	0.48613(5)	0.061215(16)	0.81351(4)	0.01084(7)	Cu
Mg(3)	–0.03662(13)	0.12866(4)	0.66179(10)	0.0108(2)	$Mg_{0.961(2)}Cu_{0.039(2)}$
As	0.38336(4)	0.117186(13)	0.33611(3)	0.00885(6)	
O(1)	0.3498(3)	0.04317(9)	0.1671(2)	0.0138(3)	
O(2)	0.6149(3)	0.09660(10)	0.5199(2)	0.0150(3)	
O(3)	0.1144(3)	0.13312(11)	0.4139(2)	0.0156(3)	
O(4)	0.4383(3)	0.19887(9)	0.2077(2)	0.0139(3)	
Oh(5)	0.1484(3)	0.02198(10)	0.7504(2)	0.0114(3)	
Oh(6)	0.8180(3)	0.10178(10)	0.9159(3)	0.0116(3)	
Ow(1)	0.3132(3)	0.16615(10)	0.8361(3)	0.0118(3)	
Ow(2)	0.8780(3)	0.25109(11)	0.1683(3)	0.0165(3)	
H(1)	0.137(7)	–0.007(2)	0.693(5)	0.029(11)	
H(2)	0.817(7)	0.129(2)	0.971(5)	0.025(10)	
H(3)	0.354(6)	0.203(2)	0.789(5)	0.029(9)	
H(4)	0.340(6)	0.177(2)	0.963(5)	0.032(9)	
H(5)	0.968(7)	0.224(2)	0.235(6)	0.033(10)	
H(6)	0.735(7)	0.241(2)	0.178(5)	0.033(10)	

Note: Oxygens of hydroxyl groups are designated as Oh, those of water molecules as Ow.

Table 5. Anisotropic displacement parameters for guanacoite.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	0.0083(2)	0.0107(3)	0.0109(3)	0.00220(19)	0.00163(18)	0.00063(18)
Cu(2)	0.00813(12)	0.00980(13)	0.01437(13)	0.00045(9)	0.00132(9)	0.00096(9)
Mg(3)	0.0095(3)	0.0127(4)	0.0105(4)	–0.0010(2)	0.0024(2)	–0.0001(2)
As	0.00849(10)	0.00944(10)	0.00868(10)	–0.00005(7)	0.00163(7)	–0.00036(7)
O(1)	0.0188(8)	0.0095(7)	0.0125(7)	–0.0023(6)	0.0007(6)	0.0021(6)
O(2)	0.0103(7)	0.0210(8)	0.0123(7)	0.0028(6)	–0.0018(6)	0.0001(6)
O(3)	0.0098(7)	0.0246(9)	0.0133(7)	0.0021(6)	0.0047(6)	0.0036(6)
O(4)	0.0169(8)	0.0101(7)	0.0155(8)	0.0019(6)	0.0047(6)	–0.0008(6)
Oh(5)	0.0111(7)	0.0106(7)	0.0124(7)	–0.0026(6)	0.0017(6)	–0.0003(6)
Oh(6)	0.0110(7)	0.0115(8)	0.0122(7)	–0.0019(6)	0.0021(6)	0.0002(6)
Ow(1)	0.0130(7)	0.0090(7)	0.0134(7)	0.0015(6)	0.0024(6)	–0.0006(6)
Ow(2)	0.0118(8)	0.0141(8)	0.0228(9)	0.0036(7)	0.0010(7)	–0.0016(6)

Crystal structure

Structure determination

The crystal structure of guanacoite has been solved from single-crystal intensity data collected with a Nonius KappaCCD four-circle diffractometer (Mo*K*α radiation, CCD area detector, 293 K). A full sphere of reciprocal space up to 2θ = 65° was measured from a suitably sized fragment (see Table 3 for details). The measured intensity data were processed with the Nonius program suite DENZO-SMN and corrected for Lorentz, polarization, background and absorption effects. Extinction conditions and intensity statistics unambiguously indicated the space group $P2_1/c$. The structure was then solved in space group $P2_1/c$ by direct methods (SHELXS-97, Sheldrick, 1997a) and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-squares refinements on F^2 (SHELXL-97, Sheldrick, 1997b). All hydrogen atoms could be located. Because the structure-solution showed guanacoite to be isotypic with akrochordite, $(Mn,Mg)_5(OH)_4(H_2O)_4(AsO_4)_2$ (Moore *et al.*, 1989), the atom site designations of akrochordite were subsequently adopted. The final refinement step yielded $R1(F) = 2.10$ % and for 2052 'observed' reflections with $F_o > 4\ \sigma(F_o)$ [$wR2_{all}(F^2) = 4.59$ %]. The final positional and displacement parameters are given in Tables 4 and 5. Selected bond distances, bond angles and the hydrogen bonds are presented in Table 4. A bond-valence analysis is given in Table 7. A list of observed and calculated structure factors can be obtained from one of the authors (U.K.) or through the E.J.M. Editorial Office – Paris.

We note that in our previous, preliminary account of the crystal structure (Kolitsch *et al.*, 2000), which was based on a measurement of a distinctly smaller, Mg-richer crystal fragment with the dimensions 50 × 50 × 30 µm (resulting in poor intensity statistics), we had assumed that the structure is possibly triclinic (space group $P\overline{1}$), albeit strongly pseudo-monoclinic (pseudo-$P2_1/c$). However, the *R*-values and standard uncertainties for both models ($R1(F)$ for $P\overline{1}$ = 3.7 % for 3166 'observed' reflections; $R1(F)$ for $P2_1/c$ ~ 3.9 %) did not allow a definite statement on the correct space group, and not all H atoms were detectable. The present data, obtained from a bigger crystal fragment measured up to 65° 2θ, do not indicate any deviation from monoclinic symmetry. The triclinic cell, $a = 5.476(1)$, $b = 6.915(1)$, $c = 16.865(3)$ Å, $\alpha = 89.98(3)$, $\beta = 89.98(3)$, $\gamma = 80.21(3)$, $V = 629.3(2)$ Å^3, is metrically monoclinic within error limits; the refined parameters of the monoclinic cell, $a = 5.475(1)$, $b = 16.865(3)$, $c = 6.915(1)$ Å, $\beta = 99.80(3)°$, $V = 629.2(2)$ Å^3 (Table 3), are very close to those refined from the X-ray powder diffraction data (see previous section). Furthermore, the values for R_{int} and standard uncertainties are all better for the monoclinic model, and a search for higher symmetry in the triclinic model with PLATON (Spek, 2003) clearly indicates space group $P2_1/c$.

Intensity data for a guanacoite crystal from Taghouni were collected with a Bruker 1K SMART Platform CCD diffractometer and Mo*K*α radiation. The refinement.yielded $R1(F) = 5.23$ % for 1115 'observed' reflections with $F_o > 4\ \sigma(F_o)$ [$wR2_{all}(F^2) = 8.09$ %]. The results are in good agreement with the model refined for type guanacoite. The site occupancies refined as follows: Cu(1) $Mg_{0.529}Cu_{0.471}$, Cu(2) $Cu_{0.981}Mg_{0.019}$, Mg(3) $Mg_{0.929}Cu_{0.071}$. The unit cell obtained for guanacoite from Taghouni is $a = 5.477(1)$, $b = 16.873(3)$, $c = 6.898(1)$ Å, $\beta = 99.86(3)°$, $V = 628.1(2)$ Å^3. Atomic coordinates and other details can be obtained from one of the authors (ARK).

Description of the crystal structure

The asymmetric unit of guanacoite contains one Cu(1) site which is occupied by a mixture of Cu and Mg [refined occupancy ratio 0.504(3):0.496(3)], one Cu(2) site, one Mg(3) site containing a very small amount of Cu [refined occupancy ratio 0.961(2):0.039(2)], one As site, eight O sites and 16 H atoms (all detected and refined without restraints) (Table 4). The Cu(2) site has a distorted [4+1+1]-coordination (Table 6); the sixth O neighbour of the Cu atom is at 2.6922(17) Å, and, although it may be too remote to be counted as a ligand, its inclusion facilitates the topological description. The Cu(1) site forms a slightly distorted $(Cu,Mg)O_6$ octahedron (range of (Cu,Mg)-O bond lengths: 2.0198(17) to 2.1862(18) Å), whereas the Mg(3) site forms a similarly distorted MgO_6 octahedron with Mg-O bond lengths ranging from 2.0272(18) to

Table 6. Selected bond distances (Å) and angles (°) for the coordination polyhedra in guanacoite.

Cu(1)*	–Oh(6) x2	2.0198(17)	Cu(2)	–Oh(5)	1.9426(17)
	–Oh(5) x2	2.0626(17)		–Oh(6)	1.9579(18)
	–O(1) x2	2.1862(18)		–O(1)	1.9705(16)
<Cu(1)–O>		2.090		–Ow(1)	2.0255(17)
				–O(2)	2.3373(17)
				–O(1)	2.6922(17)
			<Cu(2)–O>		[4+1] 2.047
					[6] 2.154
Mg(3)	–O(3)	2.0272(18)	As	–O(2)	1.6714(17)
	–O(2)	2.0636(18)		–O(3)	1.6733(16)
	–Ow(2)	2.0834(19)		–O(4)	1.6934(16)
	–Oh(6)	2.0983(18)		–O(1)	1.6987(16)
	–Oh(5)	2.1040(18)	<As–O>		1.684
	–Ow(1)	2.1760(19)			
<Mg(3)–O>		2.092			
			O(2)–As–O(3)		112.58(8)
			O(2)–As–O(4)		112.85(8)
			O(3)–As–O(4)		106.41(8)
			O(2)–As–O(1)		110.47(8)
			O(3)–As–O(1)		109.96(9)
			O(4)–As–O(1)		104.18(8)
			<O–As–O>		109.41

* Occupancy of Cu(1): (Cu$_{0.50}$,Mg$_{0.50}$)

			Hydrogen bonds		
Oh(5)	–H(1)	0.62(4)	Oh(5) –H(1)···O(3)	3.106(3)	144(4)*
			Oh(5) –H(1)···O(2)	3.162(2)	143(4)*
Oh(6)	–H(2)	0.60(3)	Oh(6) –H(2)···Ow(2)	3.050(3)	169(4)
Ow(1)	–H(3)	0.75(4)	Ow(1)–H(3)···O(4)	2.578(2)	170(4)
	–H(4)	0.88(4)	Ow(1)–H(4)···O(4)	2.604(2)	172(3)
Ow(2)	–H(5)	0.76(4)	Ow(2)–H(5)···O(3)	2.787(3)	163(4)
	–H(6)	0.82(4)	Ow(2)–H(6)···O(4)	2.621(2)	169(4)

* Part of a bifurcated hydrogen bond.

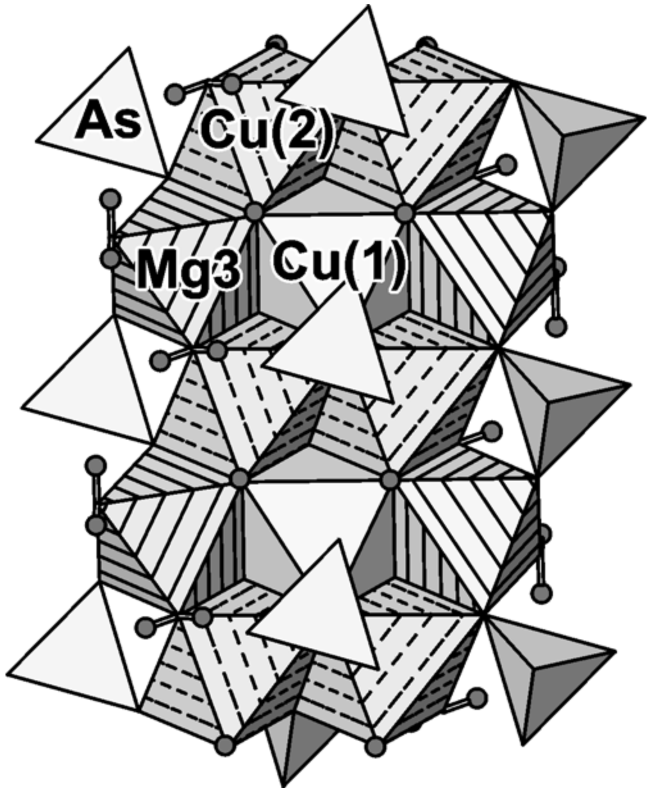

Fig. 1. The dominant element in the crystal structure of guanacoite: a ribbon of edge-sharing metal-oxygen octahedra (see text). Cu(1) is occupied by a mixture of Cu and Mg in approximately equal amounts, Cu(2) is occupied by Cu only, and Mg(3) is occupied by Mg and a very small amount of Cu. Also shown are the O-H bonds and the AsO$_4$ tetrahedra connecting the ribbons *via* common corners.

2.1760(19) Å (Table 6). The AsO$_4$ tetrahedron is fairly regular, with As-O distances ranging between 1.6714(17) and 1.6987(16) Å, and maximum angular distortions from ideal tetrahedral angles are less than 5.3° (Table 6).

The dominating elements of the structure are edge-sharing, distorted Cu(1)-, Cu(2)- and Mg(3)O$_6$ octahedra which form a ribbon extending along the *a*-axis (Fig. 1,2). The octahedral ribbon represents a portion of brucite [Mg(OH)$_2$]-type layers, not rarely encountered in transition metal oxysalt structures. The topology of the ribbons is very similar to those in amphiboles (*e.g.*, the ribbon in tremolite, which, according to amphibole nomenclature, consists of *M*(1)-, *M*(2)- and *M*(3)O$_6$- octahedra where *M* = Mg). Comparable octahedral ribbons also exist in Na$_4$K$_2$REE$_2$Si$_{16}$O$_{38}$·10H$_2$O, REE = Eu, Tb (Ananias *et al.*, 2001), where they are composed of NaO$_6$ and REEO$_6$ octahedra; unlike in tremolite, adjacent ribbons are edge-linked *via* additional REEO$_6$ octahedra. The octahedral ribbons in guanacoite are linked to adjacent, parallel ribbons *via* corners of AsO$_4$ tetrahedra (Fig. 2,3). Thus, heteropolyhedral slabs parallel to (010) are formed (Fig. 3). As in isotypic akrochordite, the slabs are linked to each other only by very strong hydrogen bonds crossing the (010) plane at y ~0.25 and ~0.75 at oblique angles (Tables 6, 7; Fig. 3). The very strong hydrogen bond Ow(1)–H(4)···O(4), directed approximately along the *a*-axis (Fig. 3), provides an internal stabilisation of the slab. The calculated bond-valence sum of O(4) is noteworthy. Although its value, 1.22 valence units (Table 7), seems very low and, at first sight, would suggest that O(4) represents an OH group, this is not the case. Whereas AsO$_3$OH groups characteristically have one long As-OH bond and three short ('normal') As-O bonds (*e.g.*, Ferraris, 1970; Ferraris & Ivaldi, 1984), the As-O(4) bond length in guanacoite, 1.6934(16) Å, is not significantly different from the other three As-O bond lengths (Table 6). Furthermore, O(4) receives considerable bond-valence contributions from the H atoms bonded to *three* Ow atoms. As in akrochordite, these three hydrogen bonds are very strong: Ow···O(4) with distances of 2.578(2), 2.604(2) and 2.621(2) Å (Table 6). O(3) is also distinctly underbonded (1.69 v.u.) but receives considerable bond-valence contributions from the H atoms bonded to Ow(2) and Oh(5).

In the structure of the previously studied fragment (Kolitsch *et al.*, 2000), the mixed-cation site Cu(1) is char-

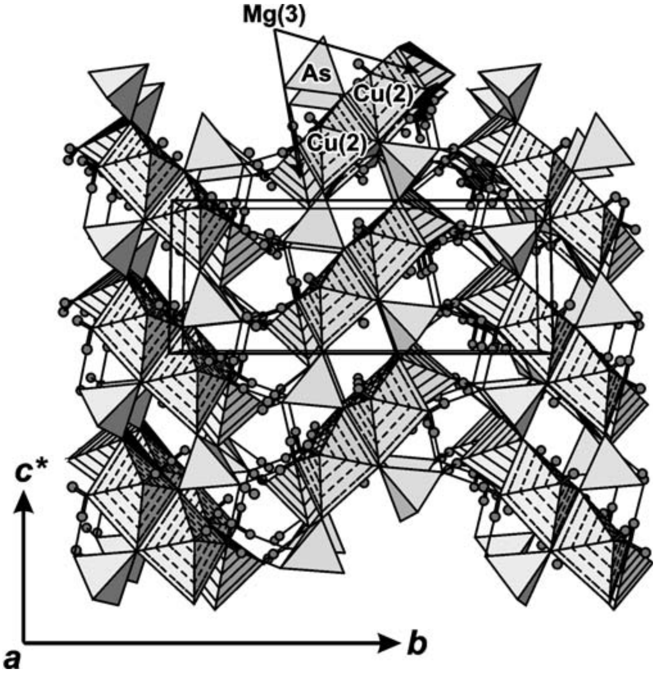

Fig. 2. The crystal structure of guanacoite in a perspective view along [100], showing the octahedral-tetrahedral slabs parallel to the (010) plane which are linked to adjacent slabs only by strong hydrogen bonds across (010) (thin lines; weak hydrogen bonds are not shown). The distorted $Cu(1)O_6$ octahedra in the centre of the ribbons can not be readily seen in this view. Legend as in Fig. 2.

acterised by a higher Cu:Mg ratio: the refined occupancy is $Cu_{0.525(3)}Mg_{0.475(3)}$. Thus, structural, chemical and optical data demonstrate that the Cu:Mg ratio in guanacoite is somewhat variable, even in single crystals. The formula obtained from the chemical analysis, $Cu_{2.32}Mg_{2.64}(OH)_{4.13}(H_2O)_{4.15}(AsO_4)_{1.93}$, has a slightly higher Mg:Cu ratio (1.14) than that obtained from the present structure refinement, $Cu_2(Mg_{0.96}Cu_{0.04})_2(Cu_{0.50}Mg_{0.50})(OH)_4(H_2O)_4(AsO_4)_2$ (ratio 0.94). Thus, it would not seem useful to establish two different end-members based on the occupancy of the mixed Cu(1) site, but rather to accept guanacoite as a species with a certain homogeneity range ranging from the hypothetical composition $Cu_3Mg_2(OH)_4(H_2O)_4(AsO_4)_2$ with only Cu on Cu(1) to $Cu_2Mg_3(OH)_4(H_2O)_4(AsO_4)_2$ with only Mg on Cu(1).

Relationships to other minerals

As already mentioned briefly above, guanacoite is isotypic with akrochordite, $(Mn,Mg)_5(OH)_4(H_2O)_4(AsO_4)_2$, a rare arsenate originally described from Långban (Flink, 1922; Moore *et al.*, 1989). Table 8 gives a brief comparison of relevant data of the two species. The comparison shows that the unit-cell volume of akrochordite is larger by about 7 % (expected from the larger size of the Mn^{2+} cation), although the cell parameter *c* is larger in guanacoite. The latter increase might be explained by the distorted coordination environment of the Cu(2) site [a referee pointed out that especially the Cu(1) and As sites show a stronger bond-angle distortion than the equivalent sites in akrochordite, and that these distortions and the concomitant shear within the unit cell allow O(4) to form the strong hydrogen bonds connecting the slabs]. The packing efficiency V_E of the atomic arrangement of guanacoite, which is obtained by dividing the unit cell volume by the total number of anions in a given cell, amounts to $V_E = 19.7$ Å^3, *i.e.*, smaller than that of akrochordite ($V_E = 21.1$ Å^3).

Table 7. Bond-valence analysis of guanacoite.

	Cu(1) (Cu/Mg)	Cu(2)	Mg(3)	As	Sum
O(1)	0.259 ↓x2	0.454 0.064		1.202	1.98
O(2)		0.169	0.367	1.296	1.83
O(3)			0.405	1.288	1.69
O(4)				1.219	1.22*
Oh(5)	0.361 ↓x2	0.490	0.369		1.22
Oh(6)	0.406 ↓x2	0.470	0.334		1.21
Ow(1)		0.391	0.271		0.66
Ow(2)			0.348		0.35
Sum	2.05	2.04	2.05	5.01	

Note: Bond-valence parameters used are from Brese & O'Keeffe (1991); sum values were calculated taking into account the refined occupancy of the mixed Cu(1) ($Cu_{0.50}Mg_{0.50}$) site. Bond-valence contributions of H atoms are not listed.
* See text for explanation.

In akrochordite, all three cation sites in the octahedral ribbon are strongly dominated by Mn. For unknown reasons, Moore *et al.* (1989) did not refine the Mn:Mg ratios on these three sites, although they state that «It is likely that Mg substitutes at Mn(1) followed by Mn(3).» Thus, the preference of Mg for one of the three sites seems different in akrochordite. Mg in akrochordite does not seem to have a stabilising role: akrochordite from Sterling Hill, New Jersey, is nearly Mg-free (Dunn, 1981), unlike the magnesian samples from Långban.

Atomic arrangements very similar to that in guanacoite, but involving *triple* chains (ribbons) of $^{[4+2]}CuO_6$ octahedra corner-linked by XO_4^{2-} tetrahedra, are found in three closely related Cu oxysalts: antlerite $[Cu_3(SO_4)(OH)_4]$, synthetic $Cu_3(SeO_4)(OH)_4$ and szenicsite $[Cu_3(MoO_4)(OH)_4]$. Heteropolyhedral slabs only connected by

Table 8. Comparison of guanacoite and akrochordite.

Mineral	Guanacoite	Akrochordite
Formula	$Cu_2Mg_2(Mg,Cu)(OH)_4(H_2O)_4(AsO_4)_2$	$(Mn,Mg)_5(OH)_4(H_2O)_4(AsO_4)_2$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	5.475	5.682
b (Å)	16.865	17.627
c (Å)	6.915	6.832
β (°)	99.80	99.49
V (Å^3)	629.2	674.9
Z	2	2
$D_{calc.}$ (g/cm^3)	3.36	3.26
Reference	this work	Moore *et al.* (1989)

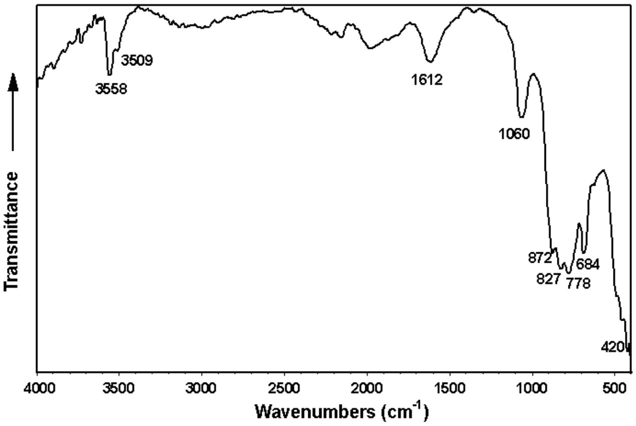

Fig. 3. FTIR spectrum of guanacoite. See text for band positions

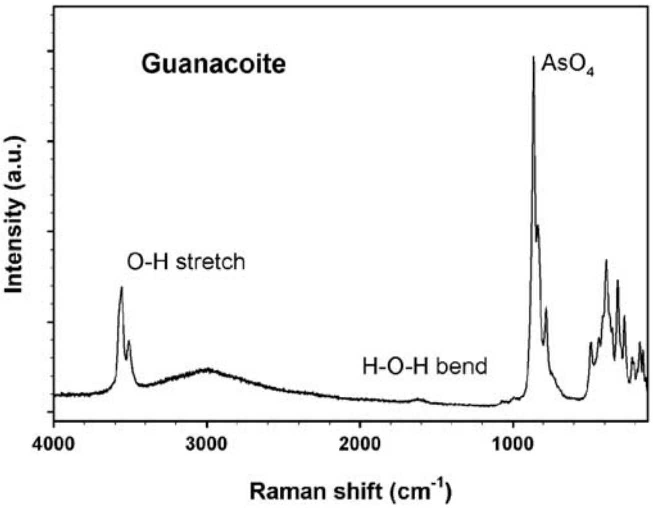

Fig. 4. Single-crystal laser-Raman spectrum of guanacoite. See text for band positions.

hydrogen bonding are also present in the chemically related nissonite [$Cu_2Mg_2(PO_4)_2(OH)_2 \cdot 5H_2O$] (Groat & Hawthorne, 1990); however, these slabs are completely different from those in guanacoite, and the hydrogen bonding is effected by a water molecule located in the space between adjacent slabs.

Guanacoite represents only the second known natural Cu-Mg-arsenate, the first one being arhbarite ($Cu_2Mg(AsO_4)(OH)_3$, Krause *et al.*, 2003). The only known Cu-Mg-phosphate mineral is nissonite ($Cu_2Mg_2(PO_4)_2(OH)_2 \cdot 5H_2O$, Groat & Hawthorne, 1990) which is structurally unrelated to guanacoite or arhbarite.

Vibrational spectroscopy

An FTIR spectrum of a powder sample (Fig. 3) was recorded with a Nicolet 5PC FTIR using a diamond microcell (resolution ± 2 cm^{-1}). The spectrum shows strong absorption bands at 3554 and 3509 cm^{-1} due to hydroxyl groups (O-H stretching vibrations). There is a significant indication of molecular water (H-O-H bending mode) at 1614 cm^{-1}. Strong to very strong absorption bands are due to vibrations of the arsenate group at 1063, 872, 827, 827, 777, 685, 489, 452 and 420 cm^{-1}.

Laser-Raman spectra of single-crystal fragments of guanacoite (Fig. 4) were recorded in the range from 4000 to 100 cm^{-1} with a Renishaw M1000 MicroRaman Imaging System using a laser wavelength of 633 nm and excitation through a Leica DMLM optical microscope (spectral resolution ± 2 cm^{-1}, minimum lateral resolution ~2 μm, unpolarised laser light, random sample orientation). The spectrum shows two slightly broadened bands due to O-H stretching vibrations at 3561 (medium strong) and 3510 cm^{-1} (weak), in agreement with the presence of at least two different OH molecules in the structure. Using the correlation established by Libowitzky (1999), O–H···O distances between roughly 2.9 and 3.0 Å can be calculated from the measured O-H band positions; these distances would correspond to the hydrogen bonds provided by Oh(5) and Oh(6) (Table 6). A very broad and weak bump at ~2996 cm^{-1} is attributed to O-H vibrations involved in the strong hydrogen bonding scheme; the band position would correspond to an O–H···O distance of roughly 2.63 Å, *i.e.*, in good agreement with the three strong hydrogen bonds donated by Ow(1) and Ow(2) (Table 5). A very weak, broad peak at 1619 cm^{-1} could indicate the presence of molecular water (H-O-H bending mode), although it must be pointed out that Raman spectroscopy is not very sensitive for the detection of water bending modes. The triplet of very strong to weak reflections at 865, 837 and 738 cm^{-1}, including the shoulders at ~740 and ~685 cm^{-1}, are characteristic of vibrational modes of an AsO_4 tetrahedron in a low-symmetry environment. The very weak features at ~1069 and 996 cm^{-1} may also belong to these modes. Most of the strong to weak, partly overlapping peaks below 500 cm^{-1} (490, 439, 411, 390, ~367, 352, 315, ~295, 271, 221, 212, 188, 171, 149 and 131 cm^{-1}) are assignable to lattice modes including vibrations of the bonds in the Cu- and Mg-O polyhedra. The low symmetry of guanacoite and the low site symmetries of almost all its atom positions allow a large number of modes to be Raman active, making exact band assigments difficult.

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