

## Compositional variability and crystal structural features of guanacoite

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### ABSTRACT

Guanacoite with high Mg content from the type locality (El Guanaco mine, Chile) was investigated to elucidate the crystal-chemical characteristics of this arsenate mineral. In this study, WDS X-ray intensity maps revealed that guanacoite single crystals from the investigated specimen show distinct and characteristic compositional zoning, which varies cyclically along [100], which is in the direction of the elongation of the prismatic crystals (Witzke et al. 2006); the boundaries separating different compositional regions lie perpendicular to the prism faces. The crystal structure of a selected fragment [ $a = 5.459(2)$ ,  $b = 16.808(9)$ ,  $c = 6.917(3)$  Å,  $\beta = 100.44(1)^\circ$ ,  $V = 624.1(5)$  Å<sup>3</sup>,  $P2_1/c$ , and  $Z = 2$ ], was solved using direct methods and refined to an  $R$  index of 3.09% for 1385 observed [ $I_o > 4\sigma(I_o)$ ] reflections measured at 103 K using MoK $\alpha$  X-radiation. The chemical formula based on the refinement is  $(\text{Cu}_{0.85}\text{Mg}_{0.15})_2\text{Mg}_2(\text{Mg}_{0.83}\text{Cu}_{0.17})(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2$ . The structure model obtained is in good agreement with the previous structure determination, although the occupancies of the three M sites (M = Mg or Cu) are distinctly different, i.e., the sites are considerably richer in Mg, especially M1 and M3. These structural results suggest that guanacoite's chemical formula should be enlarged from the Cu-rich composition  $\text{Cu}_2\text{Mg}_2(\text{Mg},\text{Cu})(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2$  to  $(\text{Cu},\text{Mg})_2\text{Mg}_2(\text{Mg},\text{Cu})(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2$  to include the Mg-rich members (Mg up to 3.395 apfu). It appears that the chemical variability of guanacoite is mainly due to Mg-Cu substitution on the M1 and M2 sites.

**Keywords:** Guanacoite, copper magnesium arsenate hydrate, crystal structure, chemical analysis, Jahn-Teller distortion

### INTRODUCTION

Guanacoite, a new secondary hydrated Cu-Mg arsenate, was recently discovered in a mine dump at the El Guanaco mine, 93 km east of Taltal, 230 km southeast of Antofagasta, in northern Chile (Witzke et al. 2006). Kolitsch et al. (2000) introduced the unknown Cu-Mg arsenate mineral for the first time; subsequently, the mineral name guanacoite was approved by the IMA Commission on New Minerals and Mineral Names (no. 2003-021). Recently, its description, including chemical composition, optics, morphology, crystal structure, and vibrational spectroscopy, has been documented in detail by Witzke et al. (2006) who also report a further occurrence of guanacoite at Taghouni, Bou Azzer district, Morocco, and provide results from quantitative chemical analyses and a crystal-structure refinement of this material. Guanacoite from the El Guanaco mine occurs as blue to pale blue, prismatic to needle-like crystals elongated along [100], usually as a subparallel intergrowth or radiating sprays, and is accompanied by copper arsenate minerals, arhbarite  $\text{Cu}_2\text{Mg}(\text{AsO}_4)(\text{OH})_3$ , conichalcite  $\text{CaCu}(\text{AsO}_4)(\text{OH})$ , and olivenite  $\text{Cu}_2\text{AsO}_4(\text{OH})$ . At the type locality, the component metals are derived from weathering of enargite  $\text{Cu}_3\text{AsS}_4$  and an apparently dolomitic country rock (Witzke et al. 2006). The ideal chemical formula of guanacoite has been expressed as  $\text{Cu}_2\text{Mg}_2(\text{Mg}_{0.5}\text{Cu}_{0.5})(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2$

according to single-crystal structure refinement analysis (Witzke et al. 2006); the empirical formula derived from the chemical analysis of the type material is slightly richer in Mg,  $\text{Cu}_{2.32}\text{Mg}_{2.64}(\text{OH})_{4.13}(\text{H}_2\text{O})_{4.15}(\text{AsO}_4)_{1.93}$ .

This paper presents the crystal-chemical characteristics of a new guanacoite sample from the type locality, which has a considerably higher Mg content, significantly exceeding the small range reported previously for the guanacoite type material (Witzke et al. 2006). The chemical compositions inferred from the Mg-rich guanacoite are apparently beyond the range of the recently reported chemical formula of guanacoite. The finding suggests that it may be appropriate to define the Mg-rich guanacoite as separate species.

### EXPERIMENTAL METHODS

The sample used in this study is from the type locality, the El Guanaco mine, Chile (Kolitsch et al. 2000; Witzke et al. 2006), commercially available from Dakota Matrix Minerals (South Dakota, U.S.A.). The guanacoite is associated with arhbarite, quartz, and enargite, as mentioned previously (Witzke et al. 2006). The sample's chemical composition was determined using an electron microprobe (EMP) equipped with a fully automated X-ray wave-dispersive spectrometer (JXA8621 Superprobe; JEOL). The electron beam diameter was 10  $\mu\text{m}$  with acceleration voltage of 20 kV and beam current of 10 nA. Raw data were corrected using the conventional ZAF program. Cuprite (CuK $\alpha$ ), MgO (MgK $\alpha$ ), and GaAs (AsK $\alpha$ ) were used as standards. Other elements that were sought (e.g., Pb, Ca, Na, Bi, Fe, Mn, Sn, Zn, Sb, Co, Ni, P, V, and S) were below the detection limits. The paucity of pure uncontaminated material prevented quantitative determination of H<sub>2</sub>O using classical methods. However, its presence was confirmed using infrared spectroscopic analysis; H<sub>2</sub>O was calculated by stoichiometry. In the present study,

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X-ray WDS intensity maps for  $\text{CuK}\alpha$  and  $\text{MgK}\alpha$  lines were recorded to clarify the variations of the distribution between Mg and Cu in single crystals (Fig. 1). Table 1 presents averaged results of EMP analyses (30 different spots on five crystals). The empirical formula, calculated based on 10 anhydrous O atoms (including four OH), can be written as  $\text{Cu}_{1.87(12)}\text{Mg}_{3.13(12)}\text{As}_{2.00(1)}\text{O}_8(\text{OH})_4(\text{H}_2\text{O})_4$ . The variation of Cu vs. Mg contents is shown in Figure 2.

A small crystal with prismatic shape ( $0.40 \times 0.10 \times 0.10$  mm) was selected for single-crystal X-ray diffraction studies. The sample was glued to a 0.1 mm diameter glass fiber and mounted on an image plate diffractometer (Raxis-Rapid; Rigaku Intl. Corp., Japan) using graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069$  Å). The diffractometer was equipped with a liquid nitrogen cryostat, which allowed temperature control of precision better than  $\pm 1$  K throughout the measurement. After cooling the crystal adequately at 103 K for 2 h, intensity data were collected at this temperature according to standard procedures. In all, 44 images were collected in continuous omega-rotation mode in  $5.0^\circ$  steps between  $130$  and  $190^\circ$  ( $\chi = 45^\circ$ ,  $\phi = 0^\circ$ ) and between  $0$  and  $160^\circ$  ( $\chi = 45^\circ$ ,  $\phi = 180^\circ$ ); each image was irradiated for 3 min/deg. Intensity data were corrected for Lorentz and polarization effects. Absorption corrections were made using the ABSCOR program based on Fourier-coefficient fitting to the intensities of symmetry-equivalent reflections (Higashi 1995). The structure was solved in space group  $P2_1/c$  by direct methods using the SIR97 program package (Altomare et al. 1999) and refined using full-matrix least-squares method with the CRYSTALS program (Watkin et al. 1996) and the crystal structure data of Witzke et al. (2006) as a subsequent starting model. The  $R$  index sharply decreased to 3.8% without site occupancy refinement. The measured unit-cell parameters show good agreement with the previous crystal-structure data of Witzke et al. (2006). The low temperature measurement at 103 K has little influence on shrinkage of the cell. Subsequently, the M site occupancies were freely refined and the model converged at an  $R_i$  index of 0.0309 based on 1385 observed unique reflections. According to Sheldrick (1997), it is difficult to locate H atoms accurately using X-ray data because of their low scattering power, and because the corresponding electron density is smeared out, asymmetrical, and is not centered at the position of the nucleus. In addition H atoms tend to have larger librational amplitudes than other atoms. Consequently, H atoms were restrained with O-H bond distances ( $1.00 \pm 0.05$  Å) and H-O-H angles ( $109.0 \pm 1.0^\circ$ ). The site occupancy

factors were refined based on the average chemical composition measured using the electron microprobe analyses described above to investigate a chemical order over the three M sites. Refinement of the structure with 127 parameters based on 1385 observed reflections with  $I_o > 4\sigma(I_o)$  yielded residuals of  $R_1 = 0.0309$ ,  $wR_2 = 0.0818$ , and  $\text{GOF} = 1.036$ . The structural refinement shows high residual electron density, the largest peak ( $2.05 \text{ e}/\text{Å}^3$ ) being at  $1.66$  Å from the As atom. Table 2 shows crystal data and details related to intensity data collection and structural refinement. Tables 3 and 4 list atomic coordinates, M site occupancies, and displacement parameters along with selected bond lengths (including H bonds) and angles. Coordination polyhedron parameters for three M sites calculated using the IVTON program (Balić-Žunić and Vicković 1996) are shown in Table 5.

## RESULTS AND DISCUSSION

### Chemical composition

Compositional zoning is an important characteristic of minerals because it can provide information related to the growth history of individual grains (e.g., variations in growth rates on different crystal faces and episodes of dissolution) (Shore and Fowler 1996). An important feature in the interpretation of zoning patterns is the spatial relationship between regions of different composition and growth surfaces. In this study, the WDS X-ray intensity maps shown in Figure 1 portray that the guanacoite single crystals have distinct and characteristic compositional zoning between Mg and Cu. The structural, chemical, and optical studies performed by Witzke et al. (2006) suggested the Mg:Cu ratio in guanacoite is somewhat variable, even in a single crystal. They described that the MgO content is correlated inversely with the CuO content because of the mutual substitution of  $\text{Mg}^{2+}$  and  $\text{Cu}^{2+}$  cations in the crystal structure. Here, the chemical

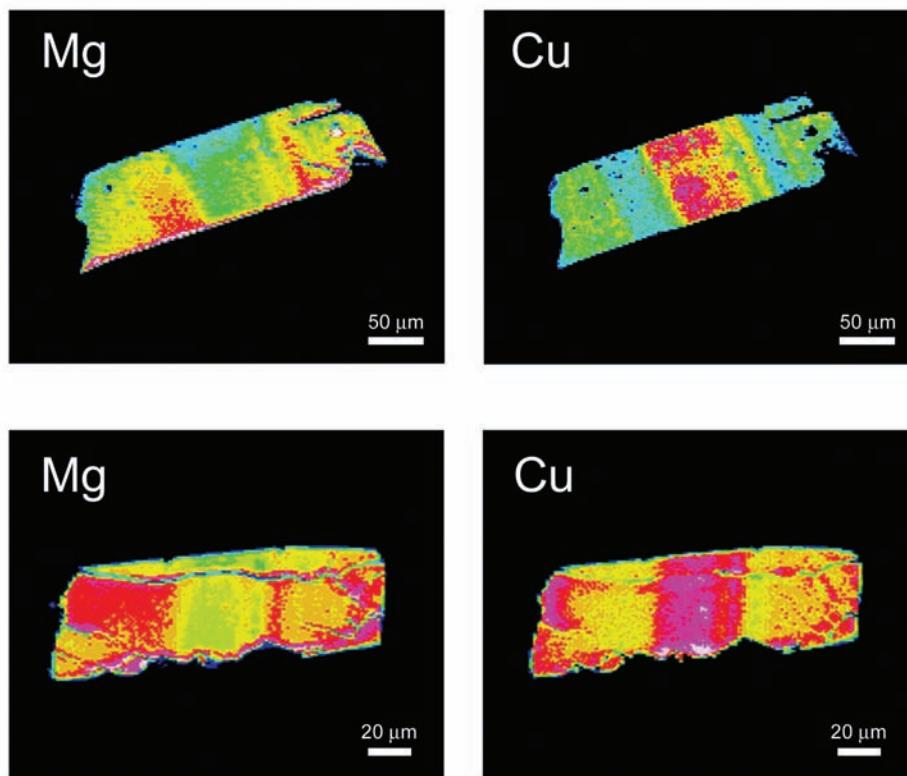
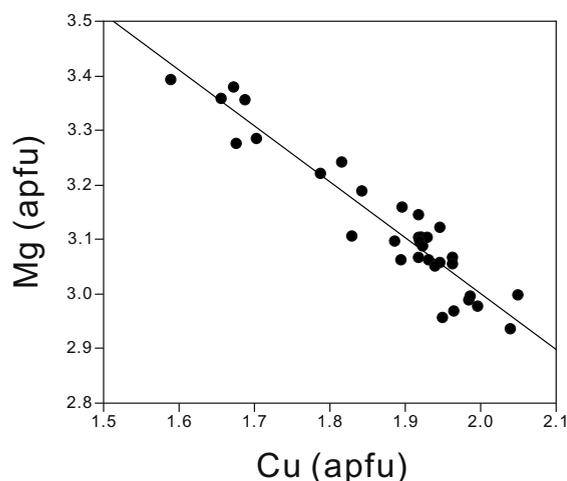


FIGURE 1. Compositional maps for Mg and Cu in a single crystal of Mg-rich guanacoite. The higher concentration zones of the element are shown in red and orange colors, whereas the lower concentration zones are shown in green and blue colors.

**TABLE 1.** Electron-microprobe analyses of Mg-rich guanacoite (in weight percent)

	This study Mg-rich guanacoite		Witzke et al. (2006) guanacoite			
	El Guanaco, Chile		El Guanaco, Chile		Taghouni, Morocco	
	Mean	Range	Mean	Range	Mean	Range
As <sub>2</sub> O <sub>3</sub>	37.50	36.73–38.53	35.67	35.13–36.17	32.86	31.90–33.59
CoO	–	–	–	–	1.16	0.94–1.49
CuO	24.34	21.11–26.29	29.67	27.60–30.65	27.86	27.04–28.92
MgO	20.66	19.11–22.87	17.12	16.49–18.03	15.55	14.69–16.75
H <sub>2</sub> O	17.50*		18.00		22.57*	
Total	100.00		100.46		100.00	
<b>Number of cations on the basis of 10 anhydrous O atoms</b>						
As	1.997	1.972–2.027	1.930		1.682	
Co	–	–	–		0.091	
Cu	1.873	1.588–2.048	2.320		2.061	
Mg	3.135	2.939–3.395	2.641		2.270	
Total	7.005		6.891		6.104	

\*H<sub>2</sub>O not determined; the content was calculated by the difference to 100%.



**FIGURE 2.** Plot of Mg vs. Cu in guanacoite, calculated based on 10 O atoms, derived from electron microprobe data.

composition varies cyclically in the direction of the elongation of the prismatic crystals, which is parallel to [100] as described previously (Witzke et al. 2006); the boundaries separating the different compositional regions are aligned alternatively in widths of approximately 50  $\mu\text{m}$  (Fig. 1). This suggests that the zoning profile may be associated with local variations in secondary fluid composition that are manifested in the reaction kinetics at the crystal-fluid interface (Fig. 1).

As reported by Witzke et al. (2006), guanacoite with the chemical formula  $\text{Cu}_2\text{Mg}_2(\text{Mg,Cu})(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2$  is isotypic with the Mn-Mg arsenate mineral, akrochordite  $(\text{Mn,Mg})_5(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2$  (Moore et al. 1989). The present electron microprobe analyses of Mg-rich guanacoite showed that the number of As atoms and (Mg + Cu) atoms, respectively, closely approximate 2.00 and 5.00 apfu (Table 1). A distinct linear negative correlation exists between Mg and Cu cation contents (Fig. 2), confirming results of Witzke et al. (2006). The linear regression obtained is  $\langle \text{Mg}(\text{apfu}) \rangle = 5.048 - 1.023 \times \langle \text{Cu}(\text{apfu}) \rangle$  ( $R^2 = 0.949$ ). However, the Mg contents are markedly higher than those of the previous report (Witzke et al. 2006). The microprobe analyses of the studied guanacoite samples give the empirical formula  $\text{Cu}_{1.87(12)}\text{Mg}_{3.13(12)}\text{As}_{2.00(1)}\text{O}_8(\text{OH})_4(\text{H}_2\text{O})_4$  in

**TABLE 2.** Summary of the crystallographic data of Mg-rich guanacoite

Diffractometer	Rigaku RAXIS-RAPID
X-ray radiation	MoK $\alpha$ ( $\lambda = 0.71075 \text{ \AA}$ )
X-ray power	50 kV, 40 mA
Temperature (K)	103(1)
Empirical formula	$\text{Cu}_{1.87}\text{Mg}_{3.13}\text{As}_{2.00}\text{O}_8(\text{OH})_4(\text{H}_2\text{O})_4$
Crystal size (mm)	$0.40 \times 0.10 \times 0.10$
Formula Weight	612.28
Crystal system	Monoclinic
Space group	$P2_1/c$
$a$ ( $\text{\AA}$ )	5.459(2)
$b$ ( $\text{\AA}$ )	16.808(9)
$c$ ( $\text{\AA}$ )	6.917(3)
$\beta$ ( $^\circ$ )	100.44(1)
$V$ ( $\text{\AA}^3$ )	624.1(5)
$Z$	2
$D_{\text{calc}}$ ( $\text{g/cm}^3$ )	3.261
Absorption coefficient ( $\text{mm}^{-1}$ )	8.709
$F(000)$	595.58
Reflection collected	6571
Independent reflections	1675
$R_{\text{int}}$	0.030
Observed reflections	1385
Refined parameters	127
GOE	1.036
$R_1$ [ $I_o > 4\sigma(I_o)$ ]	0.0309
$wR_2$ [ $I_o > 4\sigma(I_o)$ ]	0.0818
Peak and hole ( $\text{e}/\text{\AA}^3$ )	2.05/–0.93

this study (Table 1). Ranges are 2.939–3.395 apfu for Mg and 1.588–2.048 apfu for Cu (Fig. 2). Variations for M-site cations clearly exceed the solid solution range reported previously for guanacoite, about 2.5 to 2.8 apfu for Mg and about 2.1 to 2.4 apfu for Cu (Witzke et al. 2006).

### Crystal structure of Mg-rich guanacoite

The present discussion emphasizes the considerably high Mg content in guanacoite and its relationship to the crystal structure. The crystal structure of guanacoite contains one crystallographically distinct, tetrahedrally coordinated As site. In addition, three non-equivalent M sites are occupied by  $\text{Mg}^{2+}$  and  $\text{Cu}^{2+}$  cations coordinated by six O atoms in more or less distorted octahedral arrangements (Witzke et al. 2006). The structural determination was carried out initially based on the average chemical composition of the Mg-rich guanacoite  $\text{Cu}_{1.873}\text{Mg}_{3.135}\text{As}_{1.997}\text{O}_8(\text{OH})_4(\text{H}_2\text{O})_4$ . The unrestrained refinement of the Cu/Mg occupancy ratios yielded a chemical composition deviating only slightly from the average chemical composition determined by EPMA. This result suggests that the average chemical composition of

**TABLE 3.** Atomic coordinates and displacement parameters ( $\text{\AA}^2$ ) of Mg-rich guanacoite

Atom	x	y	z	B <sub>eq</sub>	Occ.	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
					Cu/Mg						
M1	0.0000	0.0000	0.0000	0.62(2)	0.168(1)/0.832(1)	0.0071(6)	0.0069(6)	0.0096(6)	0.0002(5)	0.0015(5)	0.0014(5)
M2	0.48881(3)	0.06213(3)	0.81095(3)	0.197(8)	0.851(1)/0.149(1)	0.0013(2)	0.0009(2)	0.0050(2)	0.0004(1)	-0.0000(1)	0.0000(1)
M3	-0.03802(8)	0.12874(8)	0.65934(8)	0.38(2)	0.000(1)/1.000(1)	0.0040(5)	0.0039(5)	0.0064(5)	0.0000(4)	0.0010(4)	0.0004(4)
As	0.37842(8)	0.11681(2)	0.33403(6)	0.418(6)		0.0055(1)	0.0042(1)	0.0061(1)	0.0002(1)	0.0009(1)	-0.0002(1)
O1	0.3393(5)	0.0421(1)	0.1656(4)	0.67(5)		0.011(1)	0.005(1)	0.009(1)	0.001(1)	-0.000(1)	-0.0021(9)
O2	0.6132(5)	0.0955(1)	0.5184(4)	0.67(5)		0.007(1)	0.009(1)	0.008(1)	0.001(1)	0.001(1)	0.001(1)
O3	0.1097(5)	0.1343(1)	0.4122(4)	0.73(5)		0.008(1)	0.011(1)	0.010(1)	-0.000(1)	0.004(1)	0.002(1)
O4	0.4346(5)	0.1985(1)	0.2044(4)	0.67(4)		0.009(1)	0.007(1)	0.010(1)	-0.001(1)	0.002(1)	0.001(1)
O5	0.1522(5)	0.0220(1)	0.7471(4)	0.56(4)		0.006(1)	0.005(1)	0.011(1)	-0.0017(9)	0.002(1)	-0.0011(9)
O6	0.8201(5)	0.1040(1)	0.9153(4)	0.60(4)		0.007(1)	0.008(1)	0.008(1)	0.0003(9)	0.0004(9)	-0.0008(9)
O7	0.3134(5)	0.1671(1)	0.8332(4)	0.60(4)		0.008(1)	0.005(1)	0.009(1)	0.0010(9)	-0.001(1)	0.0022(9)
O8	0.1253(5)	-0.2494(1)	0.3338(4)	0.75(5)		0.009(1)	0.009(1)	0.011(1)	0.001(1)	0.002(1)	0.001(1)
H1	-0.002(3)	0.006(1)	0.707(9)	1.500							
H2	0.884(1)	0.146(2)	0.003(8)	1.500							
H3	0.338(12)	0.177(3)	0.972(3)	1.500							
H4	0.359(12)	0.214(2)	0.768(6)	1.500							
H5	0.993(2)	0.2910(9)	0.198(7)	1.500							
H6	0.713(3)	0.2702(6)	0.170(8)	1.500							

the single crystal corresponds approximately with that of several single crystals measured in this study. The total M-site content provided by the refined occupancy factors is  $(\text{Cu}_{1.87}\text{Mg}_{3.13})_{\Sigma 5.00}$ ; the refined occupancies are  $\text{M1} = \text{Cu}_{0.168(1)}\text{Mg}_{0.832(1)}$ ,  $\text{M2} = \text{Cu}_{0.851(1)}\text{Mg}_{0.149(1)}$ ,  $\text{M3} = \text{Cu}_{0.000(1)}\text{Mg}_{1.000(1)}$  (Tables 3 and 5). Compared to the crystal-chemical features of the type guanacoite [the empirical formula is  $\text{Cu}_{2.32}\text{Mg}_{2.64}(\text{OH})_{4.13}(\text{H}_2\text{O})_{4.15}(\text{AsO}_4)_{1.93}$ ; Witzke et al. 2006], the site occupancies in the presently studied sample reflect a distinctly higher Mg content of all three M sites (Table 5); the M1 site has the occupancy  $\text{Cu}_{0.17}\text{Mg}_{0.83}$  (vs.  $\text{Cu}_{0.5}\text{Mg}_{0.5}$  in the type material), the M2 site has  $\text{Cu}_{0.85}\text{Mg}_{0.15}$  (vs.  $\text{Cu}_{1.00}\text{Mg}_{0.00}$ ), and the M3 site has  $\text{Cu}_{0.00}\text{Mg}_{1.00}$  (vs.  $\text{Cu}_{0.04}\text{Mg}_{0.96}$ ). Therefore, it appears that the site occupancies of the M1 and M2 sites are variable in the crystal structure of guanacoite, whereas the M3 site can incorporate only traces of Cu.

The guanacoite structure consists of edge-sharing octahedra running parallel to [100] (Fig. 3a). The edge-sharing octahedral bands are held together by O1, O2, and O3 of  $\text{AsO}_4$  tetrahedra to form a strip-like modular unit that is parallel to [001] (Fig. 3b). Guanacoite is isotypic with akrochordite,  $(\text{Mn,Mg})_3(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2$ , which belongs to the general family of basic manganous arsenate minerals,  $\text{Mn}_{2-z}^{2+}(\text{OH})_{2n-3z}(\text{H}_2\text{O})_n(\text{AsO}_4)_z^-$  (Moore et al. 1989; Witzke et al. 2006). The average As-O bond distance is 1.688 Å, and the deviations from the average are slight. The As-O bond distances of Mg-rich guanacoite are similar to those of guanacoite (1.684 Å) and akrochordite (1.686 Å) (Moore et al. 1989; Witzke et al. 2006). The tetrahedral angles range from 104.3 to 112.9° and are very close to those of the type guanacoite (Witzke et al. 2006). The M1 site environment is coordinated by  $\text{O6} \times 2$ ,  $\text{O5} \times 2$ , and  $\text{O1} \times 2$  atoms with M1-O bond distances ranging from 2.037 to 2.116 Å, whereas those of the M2 and M3 sites are coordinated irregularly by six O atoms with M2-O bond distances of 1.938–2.742 Å and M3-O bond distances of 2.021–2.166 Å, respectively (Table 4). The average M-O bond distances of the Mg-rich guanacoite are practically identical to those of guanacoite (Witzke et al. 2006): mean M1-O = 2.084 Å (vs. 2.090 Å in the type guanacoite), mean M2-O = 2.159 Å (vs. 2.154 Å), mean the M3-O = 2.088 Å (vs. 2.092 Å). In the present study, the M1 site is dominantly occupied by Mg, whereas it is occupied by an equal amount of Cu and Mg in the type specimen. The small differences of the

**TABLE 4.** Bond distances (Å) for Mg-rich guanacoite

	This study	Witzke et al. (2006)
	Mg-rich guanacoite	guanacoite
M1-O6 × 2	2.037(3)	2.0198(17)
M1-O5 × 2	2.098(3)	2.0626(17)
M1-O1 × 2	2.116(3)	2.1862(18)
Mean	2.084	2.0895
M2-O5	1.938(3)	1.9426(17)
M2-O6	1.952(3)	1.9579(18)
M2-O1	1.980(3)	1.9705(16)
M2-O7	2.025(3)	2.0225(17)
M2-O2	2.318(3)	2.3373(17)
M2-O1	2.742(3)	2.6922(17)
Mean	2.159	2.1538
M3-O3	2.021(3)	2.0272(18)
M3-O2	2.056(3)	2.0636(18)
M3-O8	2.081(3)	2.0834(19)
M3-O6	2.099(3)	2.0983(18)
M3-O5	2.107(3)	2.1040(18)
M3-O7	2.166(3)	2.1760(19)
Mean	2.088	2.0921
As-O2	1.675(3)	1.6714(17)
As-O3	1.679(3)	1.6733(16)
As-O4	1.698(3)	1.6934(16)
As-O1	1.700(3)	1.6987(16)
Mean	1.688	1.6842
	<b>Hydrogen bonds</b>	
O5-H1	0.95(2)	0.62(4)
O6-H2	0.95(4)	0.60(3)
O7-H3	0.96(2)	0.75(4)
O7-H4	0.96(4)	0.88(4)
O8-H5	0.95(2)	0.76(4)
O8-H6	0.96(2)	0.82(4)
H1...O3	3.11(4)	3.106(3)
H1...O2	2.83(3)	3.162(3)
H2...O8	2.90(4)	3.050(3)
H3...O4	2.91(4)	2.578(2)
H4...O4	2.98(4)	2.604(2)
H5...O3	3.03(3)	2.787(3)
H6...O4	2.00(2)	2.621(2)

bond distances result from the similarity of the effective ionic radii of  $\text{Cu}^{2+}$  (0.73 Å) and  $\text{Mg}^{2+}$  (0.72 Å) (Shannon 1976).

The polyhedral volumes are  $\text{M1O}_6 = 11.67$ ,  $\text{M2O}_6 = 12.65$ , and  $\text{M3O}_6 = 11.80 \text{ \AA}^3$  in the study. The cation eccentricity values are 0.000 Å for M1, 0.24 Å for M2, and 0.07 Å for M3. The eccentricity of a coordination polyhedron is defined as the distance between the central atom and the centroid divided by the fitted-

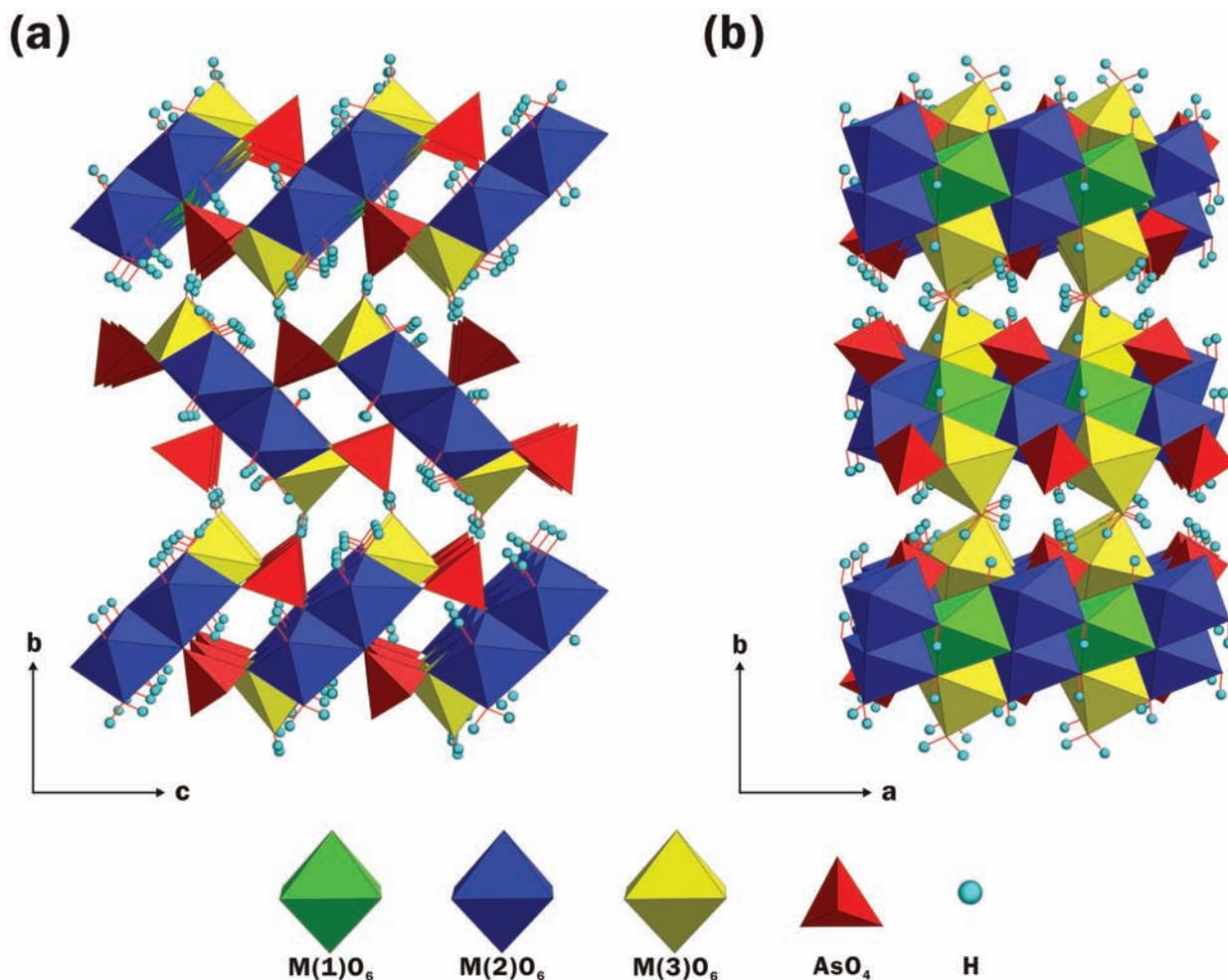


FIGURE 3. Polyhedral crystal structure representations projected along (a) [100] and (b) [001] in guanacoite.

TABLE 5. Comparison for polyhedral parameters of Mg-rich guanacoite, guanacoite, and akrochordite

	Guanacoite		Akrochordite	
	This study	Witzke et al. (2006)	Moore et al. (1989)	
	El Guanaco mine	El Guanaco mine	Taghouni	
<b>Site occupancy</b>				
M1	Cu <sub>0.17</sub> Mg <sub>0.83</sub>	Cu <sub>0.50</sub> Mg <sub>0.50</sub>	Cu <sub>0.47</sub> Mg <sub>0.53</sub>	–
M2	Cu <sub>0.85</sub> Mg <sub>0.15</sub>	Cu <sub>1.00</sub> Mg <sub>0.00</sub>	Cu <sub>0.98</sub> Mg <sub>0.02</sub>	–
M3	Cu <sub>0.00</sub> Mg <sub>1.00</sub>	Cu <sub>0.04</sub> Mg <sub>0.96</sub>	Cu <sub>0.07</sub> Mg <sub>0.93</sub>	–
<b>Polyhedral volume</b>				
V <sub>M1</sub>	11.67	11.60	–	13.21
V <sub>M2</sub>	12.65	12.52	–	14.23
V <sub>M3</sub>	11.80	11.83	–	13.35
<b>Cation eccentricity</b>				
d <sub>M1</sub>	0.00	0.00	–	0.00
d <sub>M2</sub>	0.24	0.18	–	0.24
d <sub>M3</sub>	0.07	0.07	–	0.05

Note:  $V$  = polyhedral volume ( $\text{\AA}^3$ );  $d$  = distance between the centroid and central atom of the octahedron (cation eccentricity) ( $\text{\AA}$ ). These parameters are calculated with the IVTON program (Balić-Žunić and Vicković 1996).

sphere radius (Balić-Žunić and Makovický 1996). The polyhedral parameters calculated from the type guanacoite (Witzke et al. 2006) and akrochordite (Moore et al. 1989) are also presented in Table 5. There is a marked geometrical similarity for the

three  $\text{MO}_6$  polyhedra in these minerals. For both guanacoite and akrochordite, the values of cation eccentricity increase in order of the polyhedral volume. Furthermore, no correlation exists between polyhedral volumes and incorporated cations because the polyhedral volume of the M3 site occupied by the smaller Mg cation is larger than that of the M1 site, which incorporates the larger Cu cation. Taking into consideration the small difference in the ionic radii, the basic structural feature remains unchanged even though chemical substitutions occur widely among the octahedral cations. This may be a main structural characteristic of guanacoite and isotypic arsenate minerals.

The Cu atom environment is usually a tetragonal dipyrmaid ( $4 + 2$  coordination) (Deeth and Hitchman 1986). Octahedrally coordinated  $\text{Cu}^{2+}$  spontaneously induces a local distortion caused by the Jahn-Teller effect. In particular, the M2 site, with high Cu content, shows an extremely distorted octahedral coordination with four short bonds (mean  $\text{M2-O} = 1.974 \text{ \AA}$ ) and two longer ones ( $\text{M2-O}_2 = 2.318$  and  $\text{M2-O}_1 = 2.742 \text{ \AA}$ ), reflecting the strong influence of the Jahn-Teller effect (cf. Fig. 4b). Consequently, this M2 site environment, among the three M sites in the guanacoite structure, is the most suitable for structural

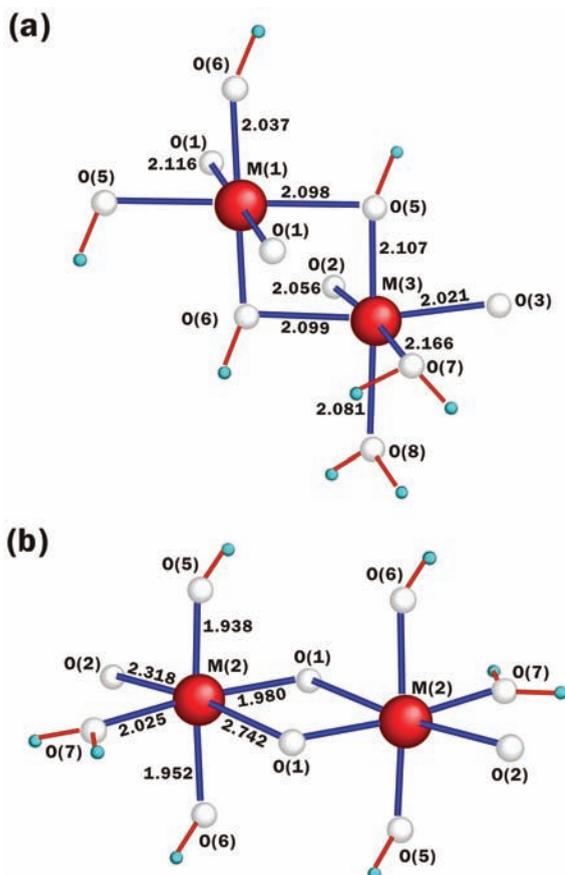


FIGURE 4. Configurations of the M sites surrounded by six O atoms. The edge-sharing octahedral coordinations between (a) the M1 and the M3 site, and (b) the M2 sites.

occupation by the  $\text{Cu}^{2+}$  cation with the Jahn-Teller effect. The elongated octahedral configuration of the M2 site is visible in the type guanacoite reported as well (Witzke et al. 2006), but the M2 site configuration in akrochordite presents an extremely distorted environment without the Jahn-Teller effect (Moore et al. 1989). The metal site environment, with one extremely long bond, is observed not only among guanacoite but also among many basic  $\text{Mn}^{2+}$  arsenate minerals containing sheet-like arrangement of  $\text{MO}_6$  polyhedra in the structure (Moore et al. 1989). That is, the presence of an elongated tetragonal dipyramid configuration is a common structural feature of the manganese arsenate minerals.

In akrochordite, according to the crystal-structure determination by Moore et al. (1989), it is likely that Mg substitutes at the M1, then at the M3 site, although refinements of the Mn:Mg ratio have not been carried out by these authors. Results of the crystal structural analyses in the present study indicate that the M3 site in akrochordite should be occupied solely (or at least preferably) by  $\text{Mg}^{2+}$ .

The degree of polyhedral distortion can be quantified according to the method of Baur (1974), in which the distortion index associated with the M-O distances is defined as

$$\frac{\sum_{i=1}^6 |d(\text{M-O})_i - d(\text{M-O})_m|}{\sum_{i=1}^6 d(\text{M-O})_i}$$

where the subscript  $i$  denotes an individual M-O distance and the subscript  $m$  signifies the mean values within the  $\text{MO}_6$  octahedron. With the definition, the length distortions about M1 and M3 are  $1.49 \times 10^{-2}$  and  $1.71 \times 10^{-2}$ , respectively. Cation eccentricity values of M1 and M3 site were found to be 0.00 and 0.07, respectively (Table 5). These values suggest that arrangement of O atoms around the M3 position is more distorted. However, the polyhedral volume of the M3 site is  $11.80 \text{ \AA}^3$ , which is slightly larger than that of the M1 site (Table 5). It is noteworthy that the larger  $\text{Cu}^{2+}$  cation cannot be incorporated into the larger M3 site, but occupies the smaller and slightly less distorted M1 site. However, the M1 site displays symmetric (4 + 2) octahedron coordination, an environment more appropriate for incorporation of  $\text{Cu}^{2+}$ . For this geometrical constraint,  $\text{Cu}^{2+}$  cation is distributed to the M2 and the M1 sites, exhibiting a tetragonal dipyramidal coordination. Consequently, the M3 site can be occupied dominantly by  $\text{Mg}^{2+}$  cation because the environmental configuration is unsuitable for  $\text{Cu}^{2+}$  cation, which prefers the tetragonal dipyramid coordination.

Witzke et al. (2006) documented that the chemical variation in guanacoite occurs mainly in the M1 site, which engenders the small solid-solution range of Cu and Mg. In the present study of Mg-rich guanacoite, the compositional variability is restricted to the M1 and M2 sites because there was not enough Cu in the crystal-forming solutions to allow its additional incorporation into the M3 site. This finding suggests that the chemical formula of guanacoite should be enlarged from  $\text{Cu}_2\text{Mg}_2(\text{Mg,Cu})(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2$ , as determined previously (Witzke et al. 2006), to  $(\text{Cu,Mg})_2\text{Mg}_2(\text{Mg,Cu})(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2$ . According to the IMA Commission on New Minerals and Mineral Names (Nickel and Grice 1998), a general guideline for compositional criteria in a solid solution series is that the compositional range of the species is taken to apply from that of the end-member to 50 mol% of the series; this is generally known as the “50% rule.” If the composition of one of the end-members exceeds 50 mol% by a small amount, then that part of the series exceeding the 50% mark could be regarded as a separate species. In multiple solid-solution series, the 50% rule is interpreted to mean predominant occupancy of a particular structural site. Therefore, the finding of Mg dominating the M1 site suggests that the Mg-rich guanacoite in the present study could be defined as a separate species.

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