

# Description and crystal structure of maghrebite, $\text{MgAl}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , from Aghbar, Anti-Atlas, Morocco: first arsenate in the laueite mineral group

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**Abstract:** Maghrebite,  $\text{MgAl}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , is a new mineral occurring at the Aghbar open pit mine, Bou Azzer district, Anti-Atlas, Morocco. Maghrebite is associated with quartz, erythrite, arseniosiderite, wendwilsonite and cabalzarite, and results from the weathering of a Variscan hydrothermal Co-Ni-As-(Cu-U-Mo) vein. Maghrebite forms lozenge-shaped prismatic crystals up to 0.2 mm in length. It is colorless, translucent with vitreous luster.  $D_{\text{meas}}$  is 2.60 (1) g/cm<sup>3</sup>,  $D_{\text{calc}}$  (crystal structure) 2.46 g/cm<sup>3</sup>. The new mineral is biaxial negative without pleochroism. Measured 2V angle is 87 (3)°; the refractive indices measured at 589 nm are:  $\alpha = 1.562$  (2),  $\beta = 1.574$  (2),  $\gamma = 1.586$  (2) with the following orientation  $\alpha \parallel b$ ;  $\beta \wedge c = 28.8^\circ$  and  $\gamma \wedge a = 25.5^\circ$ . The empirical chemical formula is  $(\text{Mg}_{0.96}\text{Co}_{0.01}\text{Ca}_{0.01})_{\Sigma=0.98}(\text{Al}_{1.94}\text{Fe}_{0.06}^{3+})_{\Sigma=2.00}(\text{As}_{2.01}\text{Si}_{0.01})_{\Sigma=2.02}\text{H}_{18.0}\text{O}_{18.02}$ . Maghrebite is triclinic,  $P\bar{1}$ ,  $Z = 1$ , with  $a = 5.436$  (2) Å,  $b = 10.500$  (3) Å,  $c = 7.075$  (2) Å,  $\alpha = 97.701$  (7)°,  $\beta = 110.295$  (5)°,  $\gamma = 102.021$  (6)° and  $V = 361.0$  (2) Å<sup>3</sup>. The six strongest lines in the X-ray powder diffraction pattern are [ $d$  in Å ( $I$ )( $hkl$ )]: 9.9 (100) (010), 6.4 (90) (001), 4.90 (80) ( $\bar{1}01$ ), 3.198 (60) (002), 2.885 (60) ( $\bar{1}31$ ) and 2.622 (60) (13 $\bar{1}$ ). The structure was solved by direct methods and refined to  $R_1 = 0.045$  on the basis of 1064 unique observed reflections. The structure is based upon  $[\text{Al}(\text{AsO}_4)(\text{OH})(\text{H}_2\text{O})_3]^-$  layers parallel to (010) and interlinked by  $[\text{Mg}(\text{H}_2\text{O})_6]^+$  octahedra. In addition, there is one H<sub>2</sub>O molecule in the structure that is not bonded to any cation but is held in between the layers by hydrogen bonds only. The topology of the Al arsenate octahedral-tetrahedral layer is that of the laueite type and belongs to the laueite isomer of the laueite-stewartite-pseudolaueite-metavauxite group of structural and geometrical isomers. Maghrebite is an arsenate analogue of gordonite and is the first natural member of the laueite group to contain arsenate as the major anion group.

**Key-words:** maghrebite, new mineral, crystal structure determination, laueite group, arsenic, Aghbar, Anti-Atlas, Morocco.

## 1. Introduction

The oxidation of polymetallic deposits results in the formation of a great diversity of secondary minerals; deposits like Tsumeb (Namibia) and Broken Hill (Australia) truly are among the mineralogical rainforests of the planet (Pring, 1995). The study of the mineralogy of these deposits contributes to our understanding of heavy-metal mobility in the near-surface environment, with direct applications to using soil sampling from geochemical prospecting, and as analogue for heavy-metal mobility around waste deposits (Williams, 1990).

The vein-type deposits of the Bou Azzer Co-As-(Au) district in Morocco are the only economic deposits where

Co is the primary economic metal (EnNaciri *et al.*, 1997; Liu *et al.*, 2011). The province includes from West to East the mines of Méchoui, Khder, Taghouni, Bou Azzer *sensu stricto*, Aghbar, Bouismass, Oumlil, Tamdrost, Ighem (also spelled Irthem), and Ait Ahmane. The province is famous for its mineralogical diversity, with more than 220 minerals reported so far (Favreau *et al.*, 2007), including six new secondary arsenates: arhbarite,  $\text{Cu}_2\text{Mg}(\text{AsO}_4)(\text{OH})_3$ , Arhbar mine (Schmetzer *et al.*, 1982; Krause *et al.*, 2003); bouazzerite,  $\text{Bi}_6(\text{Mg}, \text{Co})_{11}\text{Fe}_{14}^{3+}(\text{AsO}_4)_{18}(\text{OH})_4\text{O}_{12} \cdot 86\text{H}_2\text{O}$ , Bou Azzer mines (Brugger *et al.*, 2007), irthemite,  $\text{Ca}_4\text{MgH}_2(\text{AsO}_4)_4 \cdot 4\text{H}_2\text{O}$ , Ighem and Bou Azzer mines (Pierrot & Schubnel, 1972); nickelaustinite,  $\text{Ca}(\text{Ni}, \text{Zn})\text{AsO}_4(\text{OH})$ , Bou Azzer district (Cesbron *et al.*, 1987);

nickeltalmessite  $\text{Ca}_2\text{Ni}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ , Ait Ahmane (Chukanov *et al.*, 2009), smolianinovite,  $(\text{Co}, \text{Ni}, \text{Ca}, \text{Mg})_3(\text{Fe}, \text{Al})_2(\text{AsO}_4)_4 \cdot 11\text{H}_2\text{O}$ , Bou Azzer district (Yakhontova *et al.*, 1973); and wendwilsonite,  $\text{Ca}_2(\text{Mg}, \text{Co})(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ , Bou Azzer district (Dunn *et al.*, 1987). The district is also the second world locality for species such as cobaltarthurite, cobaltlotharmeyerite, nickellotharmeyerite, guanacoite, and is one of the multiple localities included in the description of bendadaite (Favreau *et al.*, 2007). The district provided the World's best specimens for several mineral species, including erythrite (Jacob & Schubnel, 1972), roselite, roselite- $\beta$ , skutterudite and gersdorffite, and more recently cobaltaustinite, cobaltlotharmeyerite, karibibite and vladimirite.

In this paper we describe the new mineral “maghrebite” from the Aghbar Open Pit in the Bou Azzer District. The word *maghreb* is derived from the Arabic *al-maghrib*, meaning “region where the sun sets”, and originally signified the region lying between the high ranges of the Atlas Mountains in the south, and the Mediterranean Sea. Today the term is generally used to refer collectively to the African countries of Morocco, Algeria, Tunisia, Libya, and Mauritania. The new mineral and its name have been accepted by the International Mineralogical Association (IMA 2005–044). The type specimens of maghrebite are deposited at the Musée Géologique Cantonal, Lausanne, Switzerland (sample MGL #79792 is the holotype; samples MGL #79793 and #79794 are co-types).

## 2. Occurrence and origin

Maghrebite was found during recent mining activity in the Aghbar mine in the Bou Azzer As-Co-Ni-Cr-Ag-Au district in the Anti-Atlas Mountains, Morocco. All the studied samples of maghrebite were collected in May 2000, from an open cut quarry recently opened east of the Aghbar main shaft. Maghrebite was found in a poorly mineralized host rock neighboring a rich lens of cobalt ore; other minerals include erythrite, talmessite/roselite- $\beta$ , wendwilsonite, arseniosiderite, pharmacalumite and cabalzarite (Meisser & Brugger, 2006). Aghbar is the second occurrence of cabalzarite, after the type locality in the metamorphosed Mn deposit of Falotta, Swiss Alps (Brugger *et al.*, 2000).

The Bou Azzer Co-As-Ni-Cr-Ag-Au deposit (1,350,000 t ore extracted between 1933 and 1995 from “Filon 7 and 5”) formed by hydrothermal remobilization of Ni, Co, Cu, As, and Au from a Proterozoic ophiolite complex during the Variscan Orogeny (Leblanc & Billaud, 1982; Favreau & Dietrich, 2001). In the Aghbar deposit, at least two separate oxidation episodes affected the primary cobalt and nickel arsenides, creating a rich suite of secondary arsenates. During the first phase of oxidation, probably under epithermal conditions, relatively large crystals of roselite-wendwilsonite and talmessite were deposited within dolomite in quartzitic cavities. The second phase of oxidation resulted in deposition of micro- to cryptocrystalline arsenates, including earthy arseniosiderite,

cabalzarite and erythrite, over the earlier secondary minerals and in small cracks in the rock. Maghrebite formed during this second phase.

## 3. Appearance, physical and optical properties of maghrebite

Maghrebite occurs as glassy, colorless, pointed tabular crystals to 0.2 mm (Fig. 1). Commonly these occur in



Fig. 1. Morphology of maghrebite. (a) SEM picture of a maghrebite crystals spray. Note the perfect {010} cleavage. Picture width: 250  $\mu\text{m}$ . (b) Optical microphotograph of isolated maghrebite crystal on Co-bearing talmessite. Picture width: 1 mm.

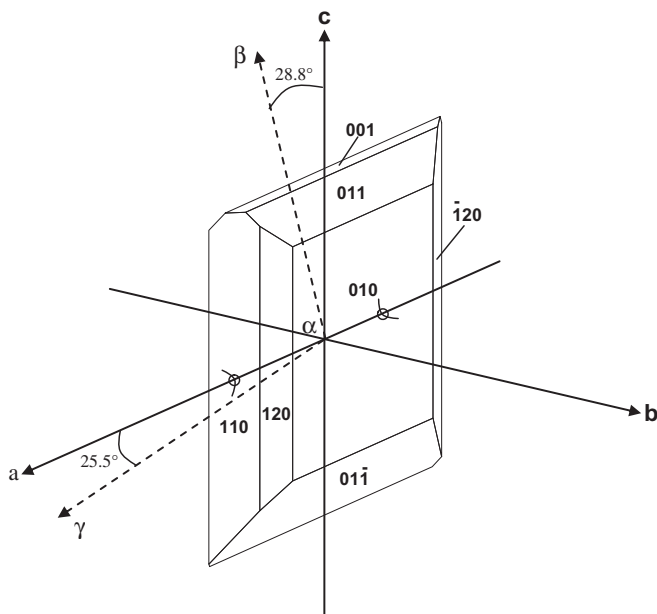


Fig. 2. Morphology and optical orientation for platy habit maghrebite crystal.

fan-shaped aggregates covering surfaces measuring up to several square millimeters in narrow fissures. Single crystals display a typically triclinic morphology; they resemble gypsum crystals but are more brittle and distinctly harder. The crystals may be prismatic, elongated along [001]; or platy, flattened on [010]. The most prominent forms are {010}, {001} and {110}; {120} and {011} are subordinate (Fig. 2).

Maghrebite displays a perfect cleavage parallel to the {010} prism (Fig. 1). The mineral dehydrates quickly under vacuum; this results in a significant contraction and fracturing along the cleavage directions for crystals observed under the electron scanning microscope or the electron microprobe.

The density measured by immersion in diiodomethane – 1-chloronaphtalene is 2.60 (1) g/cm<sup>3</sup> (average on three crystals). The density calculated from the crystal structure refinement is 2.46 (1) g/cm<sup>3</sup>. The calculated density is from the crystal-structure refinement, using a cell volume of 361.0 (2) Å<sup>3</sup> and the ideal chemical formula; the quoted error reflects the range in metal substitutions from the electron microprobe (EMP) analyses. Discrepancy between the measured and calculated densities may reflect a contamination of maghrebite crystals by inclusions or coatings of cabalzarite and wendwilsonite ( $\rho > 3.5$  g/cm<sup>3</sup>), or possibly partial dehydration of maghrebite in the diiodomethane – 1-monochloronaphtalene medium.

Optically, maghrebite is biaxial negative without pleochroism. The 2V angle measured with Kamb's method is 87 (3)°, within error of the calculated 2V angle of 89.2°. Dispersion is medium, with  $r > v$ . Refractive indices, measured at  $\lambda = 589$  nm (NaD

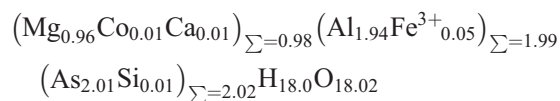
line at 25 °C) using the immersion method, are:  $\alpha = 1.562$  (2),  $\beta = 1.574$  (2),  $\gamma = 1.586$  (2). The optical orientation was determined using a spindle stage and the Buerger precession single-crystal method:  $\alpha \parallel b$ ;  $\beta \wedge c = 28.8^\circ$  and  $\gamma \wedge a = 25.5^\circ$ . Using the ideal chemical formula  $\text{MgAl}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  and the calculated density of 2.46 g/cm<sup>3</sup>, the mean refractive index  $n_{\text{mean}}$  calculated using Gladstone-Dale relationship is 1.562, corresponding to a compatibility index  $(1 - K_P/K_C) = -0.027$  (excellent) (Mandarino, 1976, 1981).

#### 4. Chemical composition

The chemical composition of maghrebite was measured using a Cameca SX-51 electron microprobe (Table 1), under the following analytical conditions: accelerating voltage 15 kV, beam current 25 nA, counting times of 10 s on the peak and 5 s on each side of the peak for background, tightly focused beam scanned over a  $\sim 10 \mu\text{m}^2$  surface. The following elements were quantified using wavelength dispersive spectrometers (WDS) with the following analytical standards: As ( $L\alpha$  X-ray fluorescence line; TAP analyzer crystal), adamite; Ca ( $K\alpha$ , PET), wollastonite; Co ( $K\alpha$ , LiF), Co metal; Mg ( $K\alpha$ , TAP), forsterite; Ni ( $K\alpha$ , LiF), Ni metal; Si ( $K\alpha$ , TAP), Fe ( $K\alpha$ , LiF) and Al ( $K\alpha$ , TAP), almandine garnet. Mn, P, Pb and Cu were also measured but their concentrations were found to be below 0.05 wt%.

Maghrebite dehydrates easily under vacuum. This resulted in relatively high analytical totals and in a strong degradation of the sample polish that accounts for the relatively large standard deviation on the analytical totals. It seems that not only the 2H<sub>2</sub>O per formula unit (pfu) that are not bonded to a metal ( $\text{O}_{\text{W}7}$  on Fig. 3) are released in the vacuum of the electron microprobe, but also 3–4 of the remaining 6 H<sub>2</sub>O pfu. Note that the dehydration did not affect the measurement of the Al:As:Mg ratios via EMP, and that the crystal structure refinement was used to determine the original hydration level in maghrebite, because the size of the crystals and the scarcity of the material precluded a direct analysis of H<sub>2</sub>O content.

The empirical structural formula for maghrebite is (normalization on five cations pfu and water contents from the crystal structure refinement):



Taking into account the crystal structure solution that shows that maghrebite belongs to the paravauxite-laeite mineral group, the ideal formula of maghrebite is:  $\text{MgAl}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ .



Table 1. Electron microprobe analyses of maghrebite from Aghbar, Morocco.

Sample	MGL no 79792					
Number of points	6					
	mean	min.	max.	st.dev.	mean to 100 %	Ideal comp.
Oxides (wt%)						
As <sub>2</sub> O <sub>5</sub>	52.52	50.91	54.10	1.15	42.94	43.02
SiO <sub>2</sub>	0.14	0.07	0.20	0.05	0.11	
Al <sub>2</sub> O <sub>3</sub>	22.51	20.96	24.28	1.22	18.41	19.08
Fe <sub>2</sub> O <sub>3</sub>	0.90	0.34	1.90	0.54	0.74	
MgO	8.83	7.27	9.59	0.83	7.22	7.53
CaO	0.14	0.05	0.40	0.13	0.11	
CoO	0.23	0.05	0.43	0.16	0.19	
NiO	0.08	0.05	0.21	0.08	0.07	
H <sub>2</sub> O <sub>calc</sub> <sup>a</sup>	36.94	35.66	38.67	1.02	30.21	30.37
Sum	122.29			2.55	100.00	100.00
Atoms per formula unit <sup>b</sup>						
As	2.01	1.94	2.10	0.062	2.01	2.00
Si	0.01	0.00	0.01	0.003	0.01	
Sum	2.02			0.062	2.02	2.00
Al	1.94	1.81	2.01	0.083	1.94	2.00
Fe <sup>3+</sup>	0.06	0.03	0.15	0.040	0.06	
Mg	0.96	0.82	1.01	0.072	0.96	1.00
Ca	0.01	0.00	0.03	0.010	0.01	
Co	0.01	0.00	0.02	0.009	0.01	
Ni	0.00	0.00	0.01	0.005	0.00	
Sum	2.98			0.063	2.98	3.00
O	18.02	17.93	18.20	0.096	18.02	18.00

Notes: Other analyzed elements: MnO  $\leq$  0.07 wt%; P<sub>2</sub>O<sub>5</sub>  $\leq$  0.06 wt%; PbO  $\leq$  0.08 wt%; CuO  $<$  0.05 wt%. No additional element with atomic number  $\geq$  9 was detected ( $<$ 0.1 wt%).

<sup>a</sup>H<sub>2</sub>O calculated assuming 18 H per formula unit (pfu) from the crystal structure refinement; the high analytical totals reflect partial dehydration under the vacuum of the electron microprobe.

<sup>b</sup>Normalization based on 5 cations pfu (from the crystal structure solution).

## 5. Crystal structure

### 5.1. Data collection and refinement

A crystal of maghrebite was selected and mounted on a Bruker PLATFORM goniometer equipped with a 1K SMART CCD detector with a crystal-to-detector distance of 5 cm. The data were collected using MoK $\alpha$  X-radiation and frame widths of 0.3° in  $\omega$ , with 45 s used to acquire each frame. More than a hemisphere of three-dimensional data was collected. The unit-cell dimensions were refined on the basis of 619 reflections using least-squares techniques (Table 2). The data were reduced and corrected for Lorentz, polarization, absorption and background effects using the Bruker programs SAINT and XPREP. A semi-empirical absorption-correction based upon the intensities of equivalent reflections was done by modeling the crystal as an ellipsoid.

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from International Tables for X-Ray Crystallography, Vol. IV (Ibers & Hamilton, 1974). The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the structures. The structures were solved by

direct methods, which gave the positions of the As, Mg and Al atoms. Oxygen atoms were located in difference-Fourier maps calculated following least-squares refinements of the partial-structure models. The structures were refined on the basis of  $F^2$  for all unique data. The final refinement included the atomic positional parameters of all atoms, with an allowance for anisotropic displacement of all atoms, and included a weighting scheme of the structure factors. H atoms were localized from the inspection of electron density difference Fourier maps; in the final refinement, the O-H bonds were restrained to be within the 0.97–0.99 Å distance limits. The final atom coordinates and displacement parameters are listed in Tables 3 and 4, respectively. Selected cation-anion bond lengths and parameters of hydrogen bonding system are given in Table 5.

### 5.2. Structure description

The structure contains As<sup>5+</sup> in tetrahedral coordination with 4 oxygen atoms, Mg<sup>2+</sup> in octahedral coordination with 2 oxygen atoms and 4 H<sub>2</sub>O groups, and two octahedral Al<sup>3+</sup> sites, with Al1 coordinated by 2 OH<sup>−</sup> groups, 2 H<sub>2</sub>O groups and 2 oxygen atoms, and Al2 coordinated by 2 OH<sup>−</sup> groups and 4 oxygen atoms. The two Al<sup>3+</sup> sites form

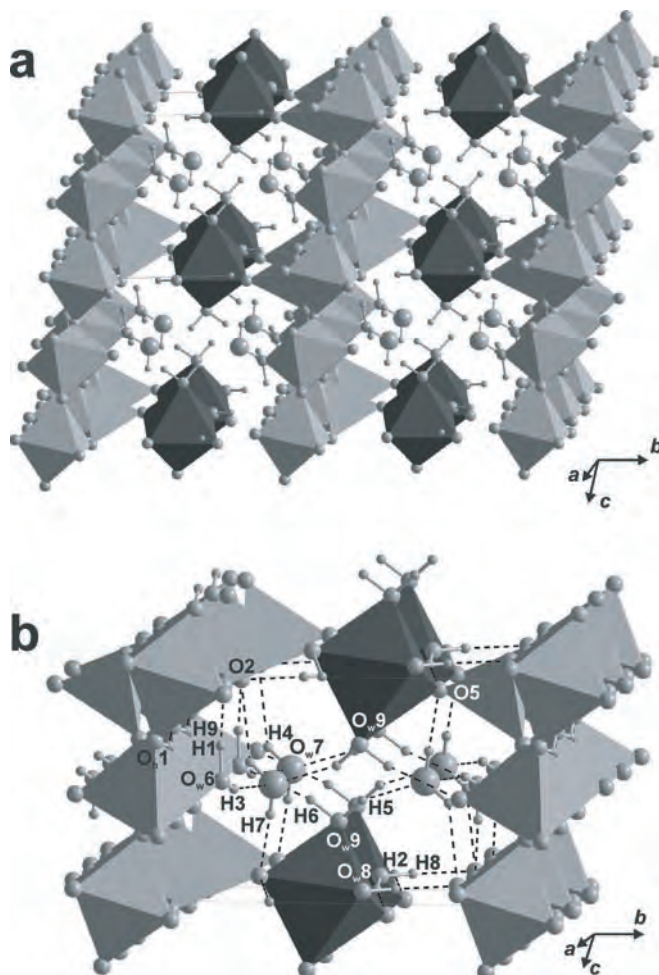


Fig. 3. The crystal structure of maghrebite (a) and portion of the structure showing the hydrogen bonding scheme (b). Light gray octahedra: Al; light grey tetrahedra: As; dark grey octahedra: Mg; large and small grey spheres are oxygen atoms of  $\text{H}_2\text{O}$  groups and H atoms, respectively.

corner-sharing chains of octahedra extending along [001], the shared corner being occupied by an  $\text{OH}^-$  group. The  $\text{Al}^{3+}$  chains are linked together by  $\text{AsO}_4$  groups, forming infinite sheets parallel to (010) (Fig. 3a). These sheets are in turn connected by isolated  $\text{MgO}_2(\text{H}_2\text{O})_4$  octahedra, linking the apices of arsenate tetrahedra across the layers (Fig. 4a). An additional  $\text{H}_2\text{O}$  group is located in tunnels extending along [100] and is hydrogen-bonded only. The scheme of hydrogen bonding system is shown in Fig. 4b; the respective geometrical parameters are provided in Table 5.

## 6. X-ray powder diffraction study

The X-ray powder-diffraction pattern of maghrebite (Table 6) was measured with a 114.6 mm diameter Gandolfi camera using Ni-filtered  $\text{CuK}\alpha$  radiation (40 kV, 30 mA; 50 h exposure time). The intensities were

Table 2. Crystallographic data and refinement parameters for maghrebite.

$a$ (Å)	5.4363 (17)
$b$ (Å)	10.500 (3)
$c$ (Å)	7.075 (2)
$\alpha$ (°)	97.701 (7)
$\beta$ (°)	110.295 (5)
$\gamma$ (°)	102.021 (6)
$V$ (Å <sup>3</sup> )	361.0 (2)
Space group	$P\bar{1}$
$F_{000}$	266
$m$ (cm <sup>-1</sup> )	4.892
$Z$	1
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	2.46 (1)
Crystal size (mm <sup>3</sup> )	$0.08 \times 0.06 \times 0.12$
Temperature (K)	293
Radiation $\text{MoK}\alpha$	0.71073
$2\theta_{\text{max}}$	55.28
Data completeness	0.895
Total Ref.	2052
Unique Ref.	1506
Unique $ F_o  \geq 4s_F$	1064
$h_{\text{min}}, h_{\text{max}}$	-4, 7
$k_{\text{min}}, k_{\text{max}}$	-9, 8
$l_{\text{min}}, l_{\text{max}}$	-13, 12
$R_{\text{int}}$	0.051
$R_1$	0.045
$wR_2$	0.095
$S$	0.903
$\rho_{\text{min}}, \rho_{\text{max}}$ (e <sup>-</sup> Å <sup>-3</sup> )	-1.324, 1.161

Notes:  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ ;  $w = 1/[s^2(F_o^2)]$ ;  $S = \{ \sum [w(F_o^2 - F_c^2)] / (n - p) \}^{1/2}$  where  $n$  is the number of reflections and  $p$  is the number of refined parameters.

visually estimated. The calculated intensities are for the crystal structure model. The six strongest lines in the X-ray powder diffraction pattern are [ $d$  in Å ( $I$ )( $hkl$ )]: 9.9 (100) (010), 6.4 (90) (001), 4.90 (80) ( $-101$ ), 3.198 (60) (002), 2.885 (60) ( $-131$ ) and 2.622 (60) (13-1). Least-squares refinement of the powder diffraction data using the program UnitCell (Holland & Redfern, 1997) and 17 unambiguously indexed lines leads to  $a = 5.408$  (5) Å,  $b = 10.433$  (8) Å,  $c = 7.020$  (6) Å,  $\alpha = 97.83$  (7)°,  $\beta = 110.52$  (8)°,  $\gamma = 102.00$  (6)° and  $V = 353.3$  (4) Å<sup>3</sup>. The calculated  $d$ -spacings and intensities listed in Table 6 were obtained for the formula  $\text{MgAl}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  with the program CrystalDiffract of D.C. Palmer (www.crystallmaker.com). The powder pattern is consistent with the results of crystal-structure analysis (Table 2).

## 7. Discussion

### 7.1. Relations to other species

According to the Chemical Structural Mineral Classification System of Strunz & Nickel (2001),

Table 3. Atomic fractional coordinates, displacement parameters ( $\text{\AA}^2$ ), and bond-valence sums (BVS, valence units) for the structure of maghrebite.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	BVS <sup>a</sup>
Al1	0	0	1/2	0.0108 (6)	2.85
Al2	0	0	0	0.0113 (6)	2.86
Mg	1/2	1/2	0	0.0133 (7)	2.03
As	−0.51690 (14)	−0.16695 (7)	−0.92788 (11)	0.0130 (2)	4.85
O <sub>H</sub> 1	−0.1279 (9)	0.0075 (4)	−0.2847 (7)	0.0148 (10)	1.04
O2	−0.3119 (8)	−0.1497 (4)	−1.0633 (6)	0.0146 (10)	1.66
O3	−0.3702 (8)	−0.0666 (4)	−0.6885 (7)	0.0158 (10)	1.75
O4	−0.8092 (8)	−0.1268 (4)	−1.0603 (6)	0.0162 (10)	1.62
O5	−0.6033 (9)	−0.3275 (4)	−0.9118 (7)	0.0193 (11)	1.59
O <sub>w</sub> 6	−0.0222 (9)	0.1851 (5)	−0.5307 (7)	0.0198 (11)	0.38
O <sub>w</sub> 7	−0.5981 (10)	−0.3076 (5)	−0.5051 (8)	0.0283 (12)	0.00
O <sub>w</sub> 8	−0.1690 (10)	−0.3876 (5)	−0.0435 (9)	0.0334 (14)	0.35
O <sub>w</sub> 9	−0.2589 (10)	−0.4878 (5)	−0.6870 (8)	0.0319 (13)	0.32
H1	−0.110 (15)	0.160 (7)	−0.681 (2)	0.05 (3)	
H2	0.025 (6)	−0.384 (11)	0.004 (18)	0.13 (5)	
H3	−0.166 (16)	0.210 (11)	−0.495 (17)	0.12 (5)	
H4	−0.453 (12)	−0.228 (5)	−0.416 (10)	0.05 (3)	
H5	−0.305 (18)	−0.536 (8)	−0.589 (10)	0.07 (3)	
H6	−0.210 (16)	−0.400 (3)	−0.596 (9)	0.04 (2)	
H7	−0.580 (16)	−0.316 (7)	−0.639 (6)	0.04 (2)	
H8	−0.237 (19)	−0.309 (6)	−0.050 (15)	0.08 (3)	
H9	−0.320 (7)	0.000 (12)	−0.361 (15)	0.12 (5)	

Note: <sup>a</sup>Bond-valences calculated using parameters taken from Brown & Altermatt (1985) without taking into account contributions from hydrogen bonds.

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2$ ) of non-hydrogen atoms in the structure of maghrebite.

Atom	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>
Al1	0.0074 (14)	0.0146 (14)	0.0131 (14)	0.0059 (11)	0.0043 (12)	0.0060 (11)
Al2	0.0072 (13)	0.0160 (15)	0.0142 (14)	0.0071 (12)	0.0045 (12)	0.0074 (11)
Mg	0.0093 (16)	0.0119 (16)	0.0235 (18)	0.0082 (13)	0.0079 (14)	0.0074 (13)
As1	0.0077 (3)	0.0174 (4)	0.0178 (4)	0.0083 (3)	0.0054 (3)	0.0081 (3)
O <sub>H</sub> 1	0.010 (2)	0.023 (3)	0.015 (2)	0.009 (2)	0.004 (2)	0.009 (2)
O2	0.011 (2)	0.018 (2)	0.019 (2)	0.0056 (19)	0.008 (2)	0.0075 (19)
O3	0.006 (2)	0.019 (2)	0.023 (3)	0.007 (2)	0.004 (2)	0.0061 (19)
O4	0.008 (2)	0.028 (3)	0.018 (2)	0.011 (2)	0.004 (2)	0.013 (2)
O5	0.013 (2)	0.018 (3)	0.029 (3)	0.008 (2)	0.009 (2)	0.006 (2)
O <sub>w</sub> 6	0.018 (3)	0.024 (3)	0.021 (3)	0.006 (2)	0.008 (2)	0.011 (2)
O <sub>w</sub> 7	0.024 (3)	0.036 (3)	0.032 (3)	0.014 (3)	0.015 (3)	0.013 (3)
O <sub>w</sub> 8	0.015 (3)	0.030 (3)	0.063 (4)	0.021 (3)	0.017 (3)	0.011 (2)
O <sub>w</sub> 9	0.028 (3)	0.031 (3)	0.033 (3)	0.009 (3)	0.006 (3)	0.010 (3)

maghrebite can be classified in group 8.DC.30, as a hydrated arsenate with additional anion and with only medium-sized cations:  $(\text{Me}^{2+} + \text{Me}^{3+} + \text{OH}):\text{AsO}_4 < 2:1$ .

Maghrebite is a hydrated Mg-Al arsenate, isostructural with laueite and is the arsenate analogue of the phosphate gordonite. In general, maghrebite belongs to the large group of minerals and inorganic compounds containing laueite-type layers, *i.e.* layers consisting of chains of trans-corner-sharing octahedra interlinked by  $\text{TO}_4$  tetrahedra ( $T = \text{P}, \text{As}, \text{S}$ ). The crystal chemistry of these compounds was investigated by Moore (1975) and recently reconsidered by Krivovichev (2004, 2008). The group is

characterized by structural and geometrical isomerism with four basic isomers first recognized by Moore (1975): laueite, stewartite, pseudolaueite and metavauxite. The structural isomerism is the result of topological variations of interchain tetrahedral linkage, while the geometrical isomerism is the result of different orientations (up or down) of tetrahedra relative to the plane of the layer. Laueite and stewartite share the same topology of polyhedral linkage but are different geometrical isomers. Analogously, pseudolaueite and metavauxite are geometrical isomers but have a different topology from that of laueite and stewartite (see Krivovichev (2004, 2008) for more details). The Al-arsenate layer in maghrebite has the

Table 5. Selected cation-anion bond lengths (Å) and parameters of hydrogen bond system (Å, deg) for maghrebite.

Al1-OH1	1.880 (4) 2×	Mg-O <sub>w</sub> 8	2.079 (5) 2×
Al1-O3	1.903 (4) 2×	Mg-O5	2.086 (4) 2×
Al1-O <sub>w</sub> 6	2.008 (5) 2×	Mg-O <sub>w</sub> 9	2.116 (5) 2×
<Al1-O>	1.930	<Mg-O>	2.094
Al2O <sub>H</sub> 1	1.908 (4) 2×	As-O5	1.683 (4)
Al2O2	1.929 (4) 2×	As-O3	1.688 (4)
Al2O4	1.940 (4) 2×	As-O2	1.702 (4)
<Al2-O>	1.925	As-O4	1.712 (4)
		<As-O>	1.696

Hydrogen bonding system					
D-H	d(D-H), Å	A	d(H...A), Å	<DHA, deg	d(D...A), Å
O <sub>w</sub> 6-H1	0.973	O4	1.692	167.40	2.653
O <sub>w</sub> 6-H3	0.974	O <sub>w</sub> 7	1.797	154.74	2.713
O <sub>w</sub> 7-H4	0.977	O2	2.316	127.92	3.017
O <sub>w</sub> 7-H7	0.979	O5	1.877	170.42	2.847
O <sub>w</sub> 8-H2	0.980	O5	1.835	163.58	2.788
O <sub>w</sub> 8-H8	0.977	O2	1.803	170.78	2.772
O <sub>w</sub> 9-H5	0.976	O <sub>w</sub> 7	1.900	153.45	2.808
O <sub>w</sub> 9-H6	0.977	O <sub>w</sub> 6	2.231	153.69	3.137
O <sub>H</sub> 1-H9	0.977	O3	2.066	138.45	2.871

Note: **D** = donor; **A** = acceptor.

same topology and geometrical structure as the Al-phosphate layer in laueite (Fig. 4). The black-and-white graph shown in Fig. 4b represents the topology of polyhedral linkage with black and white nodes symbolizing Al and As polyhedra, respectively. Figure 4c provides the same graph with the symbols of orientation of tetrahedra indicated near the white nodes (**u** = “up”; **d** = “down”; empty squares represent vacancies in the layer relative to the parent graph (Krivovichev, 2004).

Maghrebite is the first known natural representative of the paravauxite-laeite group with arsenate as the dominant anion; the other natural representatives of the group are phosphates. The only known arsenate compound with layers of the same topology is (enH<sub>2</sub>)[Fe<sup>3+</sup>Fe<sup>2+</sup>F<sub>2</sub>(HAsO<sub>4</sub>)(AsO<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>] (en = ethylenediamine, NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>), reported by Ekabaram & Sevov (2000).

Maghrebite resulted from the alteration of Co arsenides in an arid environment. Arsenate minerals with a layered structure are common in these environments: for example, tsumcorite-group minerals (AB<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O,OH)<sub>2</sub>) are topologically similar to maghrebite, the main difference consisting in the connection of the octahedral chains via the edges in the tsumcorite group (Krause *et al.*, 1998a; Brugger *et al.*, 2002). Minerals of the tsumcorite group are arsenates, except for the phosphate phosphogartrellite (Krause *et al.*, 1998b); they occur most commonly as alteration of polymetallic deposits, but part of the diversity of the tsumcorite group (18 named minerals) can be related to occurrence in different geochemical environments: for example cabalzarite and manganlotharmeyerite were discovered in metamorphosed exhalative Mn deposits (Brugger *et al.*, 2000, 2002), and the vanadates of the

group were discovered in V-rich deposits: mounanaïte in a sandstone-hosted U-V deposit (Cesbron & Fritsche, 1969) and krettnichite in a hydrothermal Mn-V vein (Brugger *et al.*, 2001).

In contrast, all the minerals from the paravauxite-laeite group described to date were phosphates, resulting mainly

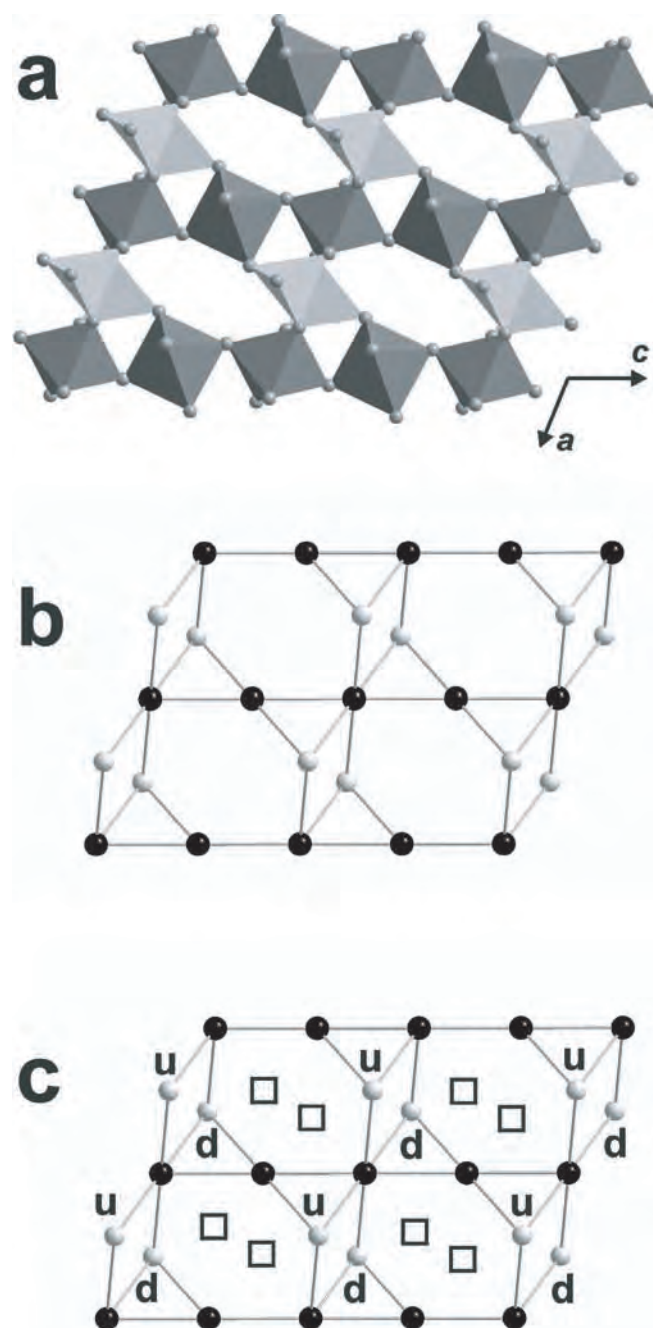


Fig. 4. Al arsenate octahedral-tetrahedral layer in maghrebite (a: dark octahedra = Al; light grey tetrahedra = As), its black-and-white graph (b: black and white nodes symbolize Al and As polyhedra, respectively), and black-and-white graph with symbols of tetrahedra orientation (**u** = up and **d** = down, relative to the plane of the layer) and vacancies (c). See text for details.



Table 6. X-ray powder data for maghrebite.

$I_{\text{meas}}$	$d_{\text{meas}}(\text{\AA})$	$D_{\text{calc}}(\text{\AA})$	$I_{\text{calc}}$	$h$	$k$	$l$
<b>100</b>	<b>9.9</b>	9.9	100	0	1	0
<b>90</b>	<b>6.4</b>	6.4	60	0	0	1
20	5.08	4.97	2	0	2	0
		4.90	7	0	1	1
<b>80</b>	<b>4.90</b>	4.90	27	-1	0	1
		4.87	12	1	0	0
20	4.59	4.59	8	-1	1	1
20	4.44	4.45	4	0	-2	1
50	4.08	4.08	9	1	1	0
20	3.97	3.96	3	1	1	0
10	3.69	3.68	3	-1	2	1
10	3.55	3.56	<1	0	2	1
		3.325	5	1	2	-1
40	3.314	3.313	3	0	3	0
		3.307	8	1	0	1
20	3.249	3.261	11	0	3	-1
		3.244	4	1	-2	1
<b>60</b>	<b>3.198</b>	3.206	22	0	0	2
		3.214	7	1	1	-2
40	3.181	3.172	16	1	-3	0
10	3.121	3.119	4	-1	1	2
10	3.100	3.082	5	1	2	0
30	3.028	3.026	4	0	2	-2
		2.887	8	1	1	1
<b>60</b>	<b>2.885</b>	2.884	12	-1	3	1
		2.866	3	0	1	2
10	2.840	2.837	5	1	2	-2
20	2.805	2.804	5	1	-3	1
20	2.702	2.703	3	0	3	1
		2.693	2	-2	1	1
<b>60</b>	<b>2.622</b>	2.624	14	1	3	-1
10	2.550	2.558	3	-2	2	1
		2.530	4	-2	1	0
20	2.529	2.518	5	0	4	-1
30	2.471	2.469	6	2	-2	0
40	2.442	2.445	2	1	3	0
		2.438	4	-2	1	2
		2.434	1	1	2	1
		2.434	4	2	0	0
10	2.401	2.398	4	1	-1	2

Following lines not indexed because of many overlapping lines

<10	2.321
<10	2.301
20 broad	2.206
<10	2.161
10	2.117
10	2.083
20	2.047
<10	2.014
20 broad	1.996
20 broad	1.890
10 broad	1.833
20 broad	1.792
10	1.757
10	1.740
20	1.700
10	1.670
40	1.656
20	1.626
10	1.601
10	1.586
20 broad	1.566
20 broad	1.530
20 broad	1.521
10	1.468
20	1.445
10	1.435
30	1.414
10	1.400

Notes: X-ray diffraction powder pattern of maghrebite measured with a Gandolfi camera, 114.6 mm in diameter; Ni-filtered CuK/X-ray radiation; elemental Si as external standard; generator operated at 40 kV, 30 mA; 50 h exposure time. Intensities were visually estimated. The calculated intensities are for the crystal structure model. The six strongest lines are in bold

Table 7. Relation between the members of the laueite group.

Name	Formula	Space group	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	$V$ (Å <sup>3</sup> )	Reference
Maghrebite	MgAl <sub>2</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub> •8H <sub>2</sub> O	$P\bar{1}$	5.436	10.500	7.075	97.701	110.295	102.021	361.0	This study
Gordonite	MgAl <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub> •8H <sub>2</sub> O	$P\bar{1}^a$	5.246	10.532	6.975	107.51	111.03	72.21	334.5	Leavens & Rheingold (1988)
Kastnigite	(Mn <sup>2+</sup> Fe <sup>2+</sup> )Al <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub> •8H <sub>2</sub> O	$P\bar{1}$	7.010	10.205	10.504	71.82	89.62	69.90	670.44	Adiwidjaja <i>et al.</i> (1999)
Laueite	Mn <sup>2+</sup> (Fe <sup>3+</sup> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub> •8H <sub>2</sub> O	$P\bar{1}$	5.28	10.66	7.14	107.92	110.98	71.12	346.6	Moore (1965)
Mangangordonite	(Mn,Fe,Mg)Al <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub> •8H <sub>2</sub> O	$P\bar{1}$	5.257	10.363	7.040	105.44	113.07	78.69	338.3	Leavens <i>et al.</i> (1991)
Paravauxite	Fe <sup>2+</sup> Al <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub> •8H <sub>2</sub> O	$P\bar{1}$	5.233	10.541	6.96	106.9	110.8	72.1	334.3	Baur (1969b)
Pseudolaueite	Mn <sup>2+</sup> (Fe <sup>3+</sup> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub> •7H <sub>2</sub> O	$P2_1/a$	9.647	7.428	10.194	90.00	104.63	90.00	706.8	Baur (1969a)
Sigfoite	Fe <sup>3+</sup> Al <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>3</sub> •7H <sub>2</sub> O	$P\bar{1}$	5.190	10.419	7.033	105.00	111.31	70.87	330.5	Hawthorne (1988)
Stewartite	Mn <sup>2+</sup> (Fe <sup>3+</sup> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub> •8H <sub>2</sub> O	$P\bar{1}$	10.398	10.672	7.223	90.10	109.10	71.83	715.1	Moore & Araki (1974)
Ushkovite	Mg(Fe <sup>3+</sup> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub> •8H <sub>2</sub> O	$P\bar{1}$	5.20	10.70	7.14	108.6	106.9	72.7	351.0	Galliski & Hawthorne (2002)

Note: <sup>a</sup>Erroneously listed as  $P\bar{1}$  by Leavens & Rheingold (1988).



from the alteration of phosphate minerals in pegmatites or in sediments, with paravauxite and sigloite also present as a weathering product in epithermal Sn-Pb-Zn-As mineralizations. The association of maghrebite with cabalzarite,  $\text{Ca}(\text{Mg}, \text{Al}, \text{Fe}^{3+})_2(\text{AsO}_4)_2 \cdot 2(\text{OH}, \text{H}_2\text{O})$ , hints to unusual geochemical conditions during weathering at the Aghbar open cut, favoring Al mobility in carbonate-rich ores (high Mg). However, the existence of maghrebite as the first arsenate of the paravauxite-lauzeite group raises the question of the rarity of the As-substitution in these minerals. This question may be answered by experimental studies of the stability of maghrebite in arsenate-phosphate solutions.

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