

Yazganite, $\text{NaFe}^{3+}_2(\text{Mg,Mn})(\text{AsO}_4)_3 \cdot \text{H}_2\text{O}$, a new mineral: its description and crystal structure

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Abstract: Yazganite, $\text{NaFe}^{3+}_2(\text{Mg,Mn})(\text{AsO}_4)_3 \cdot \text{H}_2\text{O}$, occurs in the andesitic rocks of the volcanic complex of Erciyes (prefecture of Kayseri, Turkey), associated with hematite, tridymite, cassiterite, magnetite, orpiment and realgar. It forms isolated prismatic crystals or aggregates formed by intergrown perfect crystals (10 x 3 x 2 mm maximum size). The crystals are brown to brown black color, showing a metallic luster. They are elongated along *c* and slightly flattened on {010}. Twinning was not observed. The mineral is monoclinic, *C* 2/c, *a* = 12.181(1), *b* = 12.807(1), *c* = 6.6391(5) Å, β = 112.441(9)°, *V* = 957.2(2) Å³, *Z* = 4, *D*_{meas} = 4.18(2) and *D*_{calc} = 4.19 g/cm³ based on the crystal structure refinement. The strongest lines in the X-ray powder diffraction pattern (*d*_{obs} in Å, (*hkl*), *I*_{obs}) are: 6.40, (020), 20; 5.630, (200), 20; 3.575, ($\bar{1}$ 31), 30; 3.202, (040)($\bar{1}$ 12), 40; 2.917, ($\bar{3}$ 12)($\bar{2}$ 22), 35; 2.780, (240), 100; 2.611, ($\bar{1}$ 32), 40. The Mohs' hardness is about 5. The crystals are translucent and have adamantine luster, streak is bright brown to yellow gray; crystals are biaxial (-) with α = 1.870(2), β = 1.897(2), γ = 1.900(2) at 589 nm; 2*V*_{obs} = 35(2), 2*V*_{calc} = 36.5(3). Pleochroism is moderate with α = orange brown, yellow; γ , β = grayish yellow, colorless. The crystal structure was solved by direct methods (Mo*K*α radiation) and refined using 1528 observed unique reflections to *Rw*(*F*²) = 0.073, *R*(*F*) = 0.029. The structure is a variant of the johillerite structure, which belongs to the alluaudite group. The mineral is the first example of a hydrated mineral from this group.

Key-words: yazganite, new mineral, X-ray powder pattern, crystal structure, arsenate, alluaudite group, hydrogen bonding, Erciyes (Turkey).

Introduction

Yazganite, $\text{NaFe}_2(\text{Mg,Mn})(\text{AsO}_4)_3 \cdot \text{H}_2\text{O}$, is a new mineral discovered in samples collected by Dr. Evren Yazgan in the andesitic rocks of the volcanic complex of Erciyes (10 km south of the prefecture of Kayseri, near Hisarcik, village Kiranardi, coordinates: x(N) 719500, y(E) 4279400).

The mineral name honors Dr. Evren Yazgan (1943–), a geologist in Turkey, who found the samples containing the mineral when working in this volcanic region in the collaboration with the Institute of mineral research and exploration of Turkey (M.T.A). The mineral and its name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Type material is preserved in the Department of Mineralogy of the Natural History Museum of Geneva, Switzerland, under reference no. 478.188. Here we report on the properties of the new mineral and its crystal structure.

Occurrence

The Erciyes volcanic complex within the Cappadocian volcanic province (CVP) with magnificent geomorphology and

distinct geological characteristics is located southwest of Kayseri. It has a circular shape with a diameter of about 40 km and a peak level of 3917 m (the highest elevation in the region). The eastern margin of the complex is defined by the eastern branch of the Ecemis fault zone. The Erciyes volcano is erected at a central part of the Kayseri-Sultansazligi depression that is a Quaternary pull-apart basin overprinted by the larger depression of the CVP. The Kayseri-Sultansazligi depression is formed by the activity of the left-lateral strike-slip Ecemis fault zone, one of the longest faults deforming central Anatolia. The distribution of the cones within the Erciyes volcanic complex displays a typical pattern of radial fracturing. The cones are aligned in various directions radiating from the central vent. This is an evidence for the fact that the volcanic activity has not used the fault system existing in the region for the recent eruptions.

The Erciyes volcanic complex is the largest and one of the youngest stratovolcanoes of the CVP. The complex volcanic edifice is composed of lava with intercalated pyroclastic deposits. Geochemical analyses identify the rocks as calc-alkaline basaltic andesites and dacites. The geotectonic settings, geological context and the observed geochemical characters of the Erciyes volcanic activity may account for A-type granitic melts (Toprak *et al.*, 1994).

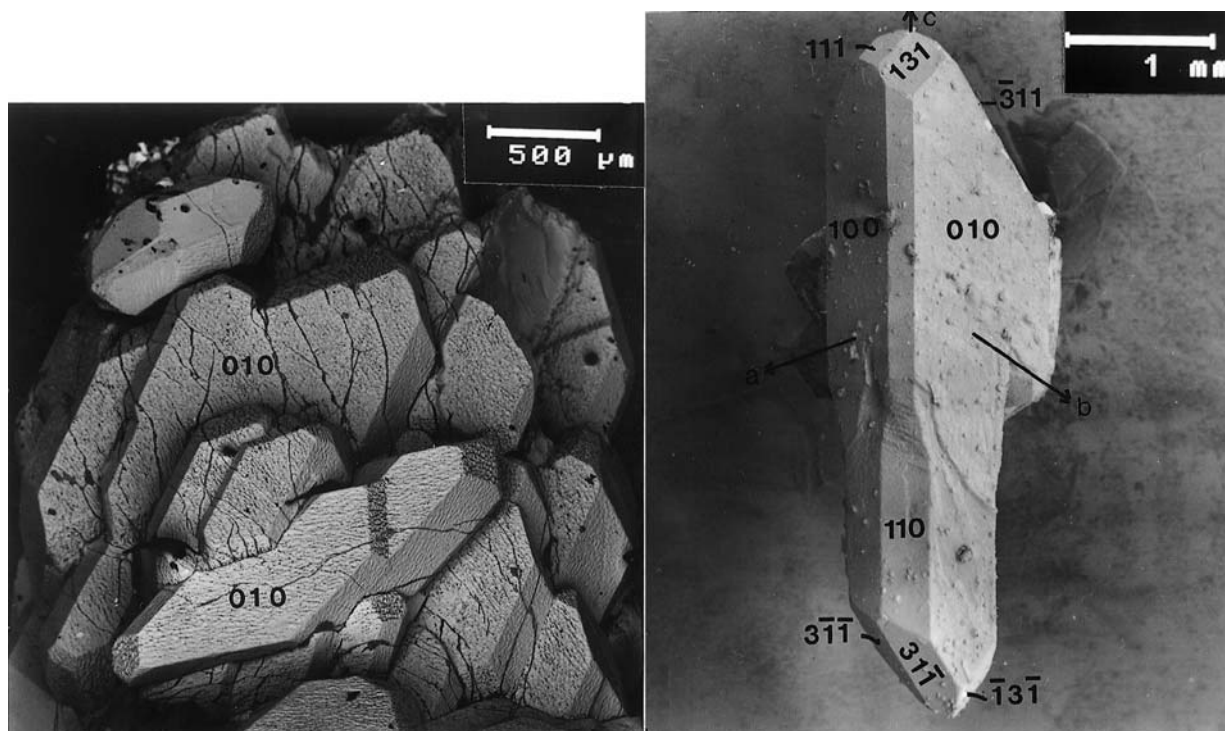


Fig. 1. SEM images of yazganite crystals, elongated parallel to c , and slightly flattened on $\{010\}$.

The samples containing the new mineral come from the edges of fissures (1 m thick) in the porphyric andesitic rocks. It is associated with hematite, magnetite, cassiterite, orpiment, realgar and tridymite. The origin of the mineral is probably hydrothermal.

Physical and optical properties

Yazganite occurs as masses and aggregates, which are formed by well developed intergrown or isolated prismatic perfect crystals with a maximum size of $10 \times 3 \times 2$ mm. The samples are often covered with a yellow brown amorphous crust which is easy to remove with compressed air or ultrasound. The crystals are elongated parallel to c , slightly flattened on $\{010\}$. Cleavage and parting are not observed, and the crystals are not twinned. The best developed forms are $\{010\}$, $\{100\}$, $\{110\}$, $\{131\}$, $\{111\}$ and $\{3\bar{1}1\}$ (Fig. 1). The crystals are brown, brown-black with a metallic aspect, translucent, with adamantine luster and bright brown, yellow-gray streak. The mineral is brittle with conchoidal fracture. The Mohs' hardness is about 5. The density, measured by flotation in a heavy liquid, is $4.18(2)$ g/cm³ and the calculated density is $4.182(1)$ g/cm³ (based on the empirical formula) and $4.19(1)$ g/cm³ (based on the ideal formula with $\text{Mg}_{0.66}\text{Mn}_{0.34}$). The mineral is not soluble in HCl. It is non-fluorescent and has moderate pleochroism: α = orange-brown; γ and β = grayish yellow. It is biaxial negative, with $\alpha = 1.870(2)$, $\beta = 1.897(2)$, $\gamma = 1.900(2)$ (determined at 589 nm), $2V_{\text{obs}} = 35(2)^\circ$ (Tobi's method, Tobi, 1956) and $2V_{\text{calc}} = 36.5(3)^\circ$. The dispersion ($r < v$) is strong. The optical orientation is: O.A.P. = (010) , $\alpha \wedge a = 5^\circ$, $\beta = b$, $\gamma \wedge c = 17^\circ$ (Fig. 2).

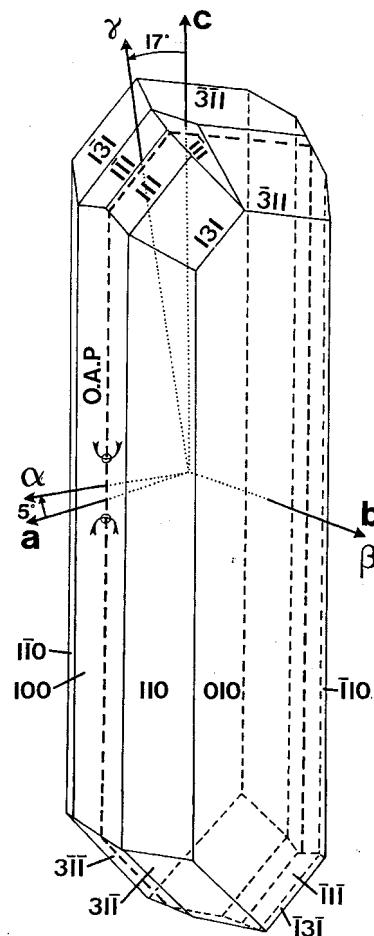


Fig. 2. Optical orientation of yazganite.

Chemical composition

The chemical composition of yazganite was analyzed with a Cameca electron microprobe, using an operating voltage of 15 kV, a beam current of 5.5 nA, and a beam size of 6 μm . Qualitative examination showed only Na, Fe, Mg, Mn, As and Zn. For quantitative analysis, albite (Na), hematite (Fe), spinel (Mg), rhodonite (Mn), trippkeite and arsenic metal (As) and sphalerite (Zn) were used as standards. The results are given in Table 1. The water content was estimated by difference and confirmed by infrared spectroscopy and by the structure determination. The infrared spectroscopy has been performed with the Perkin Elmer spectrometer in the range of 4000–200 cm^{-1} . The absorption bands are: 3400, 1630, 1110, 940, 880, 800, 745, 665, 555, 505, 400, 335. The band at 3400 cm^{-1} and 1630 cm^{-1} could indicate a presence of water molecules in the structure. The empirical formula based on 12 structural oxygen atoms is: $\text{Na}_{0.99}\text{Fe}^{3+}_{2.05}\text{Mg}_{0.61}\text{Mn}_{0.32}\text{Zn}_{0.02}\text{As}_{2.99}\text{O}_{12} \cdot 0.88\text{H}_2\text{O}$ and the idealized formula, $\text{NaFe}_2^{3+}(\text{Mg,Mn})(\text{AsO}_4)_3 \cdot \text{H}_2\text{O}$, was confirmed by X-ray crystallography.

In some crystals of the cotype specimens, the measured iron content increases and the magnesium and manganese content diminishes, giving: Na_2O 5.17; Fe_2O_3 26.63; MgO 2.89; MnO 2.96; FeO 2.27; ZnO 0.95; As_2O_5 56.73; H_2O 2.40. For these crystals, the excess of iron, calculated as bivalent Fe^{2+} , is located on the (Mg,Mn,Fe^{2+}) site giving the empirical formula:

$\text{Na}_{0.97}\text{Fe}^{3+}_{2.03}(\text{Mg}_{0.43}\text{Mn}_{0.26}\text{Fe}^{2+}_{0.20}\text{Zn}_{0.07})\text{As}_3\text{O}_{12} \cdot 0.79\text{H}_2\text{O}$, or ideally: $\text{NaFe}_2^{3+}(\text{Mg,Mn,Fe}^{2+})(\text{AsO}_4)_3 \cdot \text{H}_2\text{O}$. Yazganite is the magnesium dominant end-member. In this environment, we could observe also yazganite-Mn, yazganite- Fe^{2+} and yazganite-Zn.

The Gladstone-Dale constants of Mandarino (1981) along with the oxide proportions, as determined from the electron-microprobe data and from the crystal structure analysis, lead to Kc values of 0.213 and 0.212 respectively. The value of Kp, calculated using the average index of refraction (1.889), and the calculated density from the empirical formula, is 0.213. For the same average index of refraction and the calculated density from the idealized formula, Kp is 0.212. The compatibility index is 0.00 for the empirical and the idealized formula, indicating superior compatibility (Mandarino, 1981) between the physical and chemical data.

Table 1. Chemical analysis [wt.%] of yazganite.

	Average of 5 analysis	Range of 5 analysis	Standard deviation	Ideal formula**
Na_2O	5.10	4.5–5.9	0.6	5.13
MgO	4.12	3.9–4.4	0.2	4.40
MnO	3.70	3.5–3.9	0.2	3.99
ZnO	0.30	0–0.6	0.1	–
Fe_2O_3	27.20	25.1–28.5	1.3	26.43
As_2O_5	56.94	56.0–58.2	0.8	57.07
H_2O^*	2.64			2.98

*by difference,

**according to the refined composition ($\text{Mg}_{0.66}\text{Mn}_{0.34}$)

Table 2. X-ray powder diffraction data for yazganite (Guinier-Hägg camera, $\text{CuK}\alpha_1$ radiation d in Å).

<i>hkl</i>	<i>d</i> (calc)	<i>d</i> (obs)	<i>I</i> (obs)	<i>hkl</i>	<i>d</i> (calc)	<i>d</i> (obs)	<i>I</i> (obs)
020	6.404	6.400	20	$\bar{4}22$	2.437	2.438	<<5
$\bar{1}11$	5.823	5.818	5	$\bar{2}42$	2.287	2.285	<<5
200	5.629	5.630	20	510	2.218		
111	4.403	4.401	<<5			2.216	5
220	4.228	4.225	<5	042	2.215		
$\bar{3}11$	3.766	3.766	15	350	2.116		
$\bar{1}31$	3.574	3.575	30			2.115	5
040	3.202			440	2.114		
		3.202	40	312	2.001	2.000	<<5
$\bar{1}12$	3.193			530	1.992	1.992	<<5
221	3.092	3.091	<<5	$\bar{3}33$	1.941	1.941	<5
002	3.068	3.070	<5	$\bar{1}33$	1.929	1.927	<<5
$\bar{3}12$	2.923			152	1.861	1.859	5
		2.917	35	$\bar{2}43$	1.820	1.821	5
$\bar{2}22$	2.911			170	1.806	1.806	<<5
041	2.839	2.838	5	460	1.701		
$\bar{3}30$	2.819					1.698	<5
		2.817	5	$\bar{6}23$	1.694		
400	2.815			$\bar{6}42$	1.678	1.676	<5
240	2.783	2.780	100	370	1.645	1.645	15
022	2.767	2.763	<<5	640	1.619	1.617	5
$\bar{4}02$	2.635	2.637	10				
$\bar{1}32$	2.609	2.611	40				
$\bar{4}20$	2.577	2.576	<<5				

X-ray crystallography

X-ray powder-diffraction data (Table 2) were obtained using a Guinier-Hägg camera ($\text{CuK}\alpha_1$ radiation). The relative intensities of the reflections were estimated visually.

A single-crystal of yazganite, 0.30 x 0.25 x 0.10 mm in size, was examined by the precession method (Ni-filtered $\text{CuK}\alpha$) and the same crystal was measured on a Stoe IPDS diffractometer with monochromatized $\text{MoK}\alpha$ radiation and with an image plate detector. The details of the data collection are given in Table 3. The observed extinction symbol, $C1c1$, corresponded to the space group $C2/c$ or its non-centrosymmetrical subgroup Cc . The structure was solved in the space group $C2/c$ ($Z = 4$) by using the program FOX (Favre-Nicolin & Černý, 2002) for an *ab initio* crystal structure determination by direct space approach. The program uses a global optimization algorithm (parallel tempering) to find the correct structure by making trials in the direct space. The program describes the structural building blocks (polyhedra, free atoms etc.) with their internal coordinates (Z -matrices), thus allowing natural constraints on interatomic distances and angles. Identical atoms shared between neighboring building blocks, and special positions are handled with an automatic, adaptive method (dynamical occupancy correction). The starting model contained 3 AsO_4 tetrahedra, 2 FeO_6 octahedra, 1 MnO_6 octahedron, 1 sodium atom and 1 water molecule. The correct structural model contains 2 AsO_4 tetrahedra, 1 FeO_6 octahedron, 1 $(\text{Mg,Mn})\text{O}_6$ octahedron, 1 sodium atom and 1 water molecule. The excessive AsO_4 tetrahedron and FeO_6 octahedron were successfully merged with their respective equivalent polyhedra.

Table 3. Experimental conditions of the single-crystal X-ray crystallography and crystal parameters for yazganite.

Formula	NaFe ₂ (Mg _x Mn _{1-x})[AsO ₄] ₃ · H ₂ O (x=0.656)
Space group	C2/c
Cell parameters from 2000 reflections:	INDEX and CELL (Stoe & Cie, 1999)
<i>a</i> [Å]	12.181(1)
<i>b</i> [Å]	12.807(1)
<i>c</i> [Å]	6.6391(5)
β [°]	112.441(9)
<i>V</i> [Å ³]	957.2(2)
<i>Z</i>	4
μ [mm ⁻¹]	13.93
Crystal size [mm]	0.30 x 0.25 x 0.10
Calculated density [g cm ⁻³]	4.19
Data collection	Stoe IPDS (Stoe & Cie, 1999)
Radiation	graphite-monochromatized MoKα
Max 2θ	63.78°
Measured reflections	5'701
<i>hkl</i> limits	-15 < <i>h</i> < 18, -18 < <i>k</i> < 18, -8 < <i>l</i> < 9
Unique reflections	1528
<i>R</i> _{int}	.086
Analytical absorption correction and data reduction	X-RED (Stoe & Cie, 1999)
Structure solution	FOX (Favre-Nicolin & Černý, 2002)
Refinement	SHELXL-97 (Sheldrick, 1997)
Refinement coefficient, condition for observed reflections	<i>F</i> ² _{obs} , all
Data / parameters	1528 / 97
Weighting scheme	1 / [<i>u</i> ² (<i>F</i> ² _{obs}) + (0.02 <i>P</i>) ² + 3.34 <i>P</i>] <i>P</i> = (max(0, <i>F</i> ² _{obs}) + 2 <i>F</i> ² _{calc})/3
GoF	1.16
<i>R</i> (<i>F</i>)	.029
<i>wR</i> (<i>F</i> ²)	.073
Residua in difference electron-density map	-1.15, 1.45

Table 4. Atom positional and displacement parameters for yazganite.

Atom	site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} / <i>U</i> _{iso} (Å ²)
As1	4 <i>e</i>	0	0.27992(3)	¼	0.0085(1)
As2	8 <i>f</i>	0.24268(3)	0.10706(2)	0.12897(5)	0.0087(1)
Fe	8 <i>f</i>	0.28082(4)	0.34398(3)	0.36711(7)	0.0082(1)
Me	4 <i>e</i>	0	0.73268(8)	¼	0.0142(4)
Na	4 <i>b</i>	0	½	0	0.0175(4)
O1	8 <i>f</i>	0.3291(3)	0.4919(2)	0.3890(4)	0.0162(5)
O2	8 <i>f</i>	0.3854(2)	0.0911(2)	0.1883(4)	0.0175(5)
O3	8 <i>f</i>	0.1071(2)	0.3627(2)	0.2441(4)	0.0129(4)
O4	8 <i>f</i>	0.3282(2)	0.3317(2)	0.1126(4)	0.0125(4)
O5	8 <i>f</i>	0.2254(2)	0.1814(2)	0.3303(4)	0.0113(4)
O6	8 <i>f</i>	0.0468(2)	0.2044(2)	0.4759(4)	0.0138(4)
OW*	8 <i>f</i>	-0.003(1)	0.0004(4)	0.272(2)	0.020(2)

Me = Mg_{0.656(8)}Mn_{0.344(8)}, refined isotropically

* Split from the 4*e* position, occupancy 50%.

The equivalent isotropic atomic displacement parameters are expressed as $U_{eq} = (1/3) \sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

The structural model was refined (without hydrogen atoms) by the program SHELXL97 (Sheldrick, 1997) using |*F*² of all 1528 unique reflections. In the final cycle 97 parameters were varied, including anisotropic-displacement parameters of all atoms with the exception of the mixed (Mg,Mn) site, which was refined isotropically. The position of the water molecule oxygen located in a channel of a polyhedral framework was found to be split from a special position 4*e* to two half-occupied general positions 8*f* (see below). The details of the refinement can be found in Table 3, the atomic parameters in Table 4 and selected interatomic distances in Table 5.

No hydrogen atoms were detected in the difference electron-density map, therefore the concept of bond valences (Brown & Wu, 1976) was used to locate the hydrogen bonds (see below).

Crystal structure

Yazganite, NaFe₂(Mg_xMn_{1-x})[AsO₄]₃ · H₂O (x = 0.656), is the first hydrated mineral from the allaudite, (Na,Ca,Mn)(Mg,Fe)₂(Li,Mg,Mn)[PO₄]₃, group. It contains trivalent iron, sodium and water. It is therefore a secondary phase that is probably a product of alkali-leached oxidation. It can be more closely compared to nickenichite, Na_xCa_y(Mg,Fe,Al)₃Cu_z[AsO₄]₃ (Auernhammer *et al.*, 1993), johillerite, Na(Mg,Zn)₃Cu[AsO₄]₃, and o'danielite, Na(Zn,Mg)₃H₂[AsO₄]₃ (Keller & Hess, 1988). Magnesium

Table 5. Coordination of cations (distances in Å) in yazganite. The following parameters are calculated: The average bond-length <1>, the root-mean-square deviation of bond-lengths (l_i) from the average bond-length Δ (= {1/CN Σ_{CN} [(l_i - <1>)/<1>]²})^{1/2}, where CN is a coordination number) and bond angle variance σ² (= 1/(BA-1) Σ_{BA} [θ_i - θ₀]², where BA is a number of independent bond angles, 12 for an octahedron and 6 for a tetrahedron, and θ₀ is a bond angle in the ideal polyhedron, 90° in an octahedron and 109.47° in a tetrahedron, Robinson *et al.*, 1971). Oxygen-oxygen distances in possible hydrogen bonds OW ... O1 are given too.

Fe-O3	1.971(2)	Me-O2 x 2	2.229(3)
Fe-O1	1.972(2)	Me-O6 x 2	2.253(3)
Fe-O4	1.989(2)	Me-O4 x 2	2.316(2)
Fe-O6	2.051(2)	<1>	2.266
Fe-O5	2.065(2)	Δ	0.017
Fe-O5	2.173(2)	σ ²	312.5
<1>	2.037	Me=Mg _{0.656} Mn _{0.344}	
Δ	0.032		
σ ²	72.4		
		As2-O2	1.641(3)
As1-O6 x 2	1.691(2)	As2-O4	1.696(2)
As1-O3 x 2	1.693(2)	As2-O1	1.695(2)
<1>	1.692	As2-O5	1.719(2)
Δ	5 · 10 ⁻⁴	<1>	1.688
σ ²	13.3	Δ	0.017
		σ ²	7.8
OW...O1	2.44(1)	Na-O2 x 2	2.322(3)
OW...O1	2.45(1)	Na-O3 x 2	2.410(2)
		Na-O2 x 2	2.492(3)
		Na-O3 x 2	3.062(3)

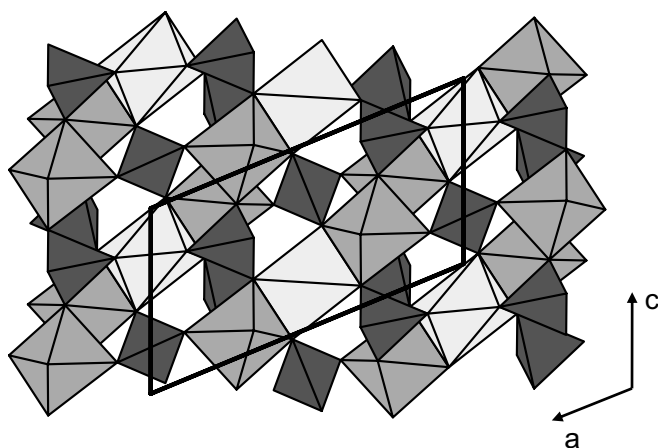


Fig. 3. Heteropolyhedral sheet as a structural unit in yazganite as projected along the **b**-axis (program Atoms; Dowty, 1993). AsO_4 tetrahedra are shown in dark gray, FeO_6 octahedra in medium gray, and $(\text{Mg,Mn})\text{O}_6$ octahedra in light gray.

and bi- or trivalent transition metal are disordered in sites $8f$ and $4e$ in nickenichite, johillerite and o'danielite, while they are partly ordered in yazganite with trivalent iron in $8f$ and magnesium and manganese in $4e$ site. The site $4e$ occupied by sodium in nickenichite, johillerite and o'danielite is occupied in yazganite by a water molecule. The other $4e$ site occupied in nickenichite and johillerite by copper and vacant (more precisely replaced by two hydrogen atoms forming two hydrogen bonds along opposite edges of the former CuO_4 square) in o'danielite is vacant in yazganite. The site $4b$ occupied in nickenichite by calcium and vacant in johillerite and o'danielite is occupied by sodium in yazganite.

The basic structural unit of yazganite is the same as in the minerals from the allaudite group: zig-zag chains, running in yazganite along $[10\bar{1}]$, formed by edge sharing $\text{Me}^{2+,3+}\text{O}_6$ octahedra (Fig. 3). The chains are interconnected by AsO_4 (or PO_4 in other members of the allaudite group) tetrahedra into (101) sheets, which have direct inter-sheet contacts forming a three-dimensional network. Similar sheets can be found in many other minerals with $\text{M}=\text{M-T}$ type sheets, according to the classifications of Eby & Hawthorne (1993), like (speaking only about arsenates) yvonite, koritnigite (as noted for johillerite-koritnigite relation already in Keller & Hess, 1988) *etc.* However, in these minerals the sheets do not have direct contacts, and they are interconnected by hydrogen bonds, where water molecules usually participate. The polyhedral framework in yazganite has, as other related minerals (Auernhammer *et al.*, 1993), two types of channels parallel to $[001]$ (Fig. 4). Channel I, which contains a monovalent atom (Na, K, Ag) in related minerals and in many synthetic compounds (Frerichs & Mueller-Buschbaum, 1994; Keller *et al.*, 1981), hosts in yazganite a water molecule that is fixed in the channel by hydrogen bonds (see below). Channel II has three different atomic positions occupied in related minerals by different atoms: Ca^{2+} in $[6+2]$ coordination, Cu^{2+} in square planar coordination and hydrogen atoms forming short hydrogen bonds. In yazganite the channel II is occupied by the Na^{+} cation that is located on the position of Ca^{2+} . Yazganite is the second example (be-

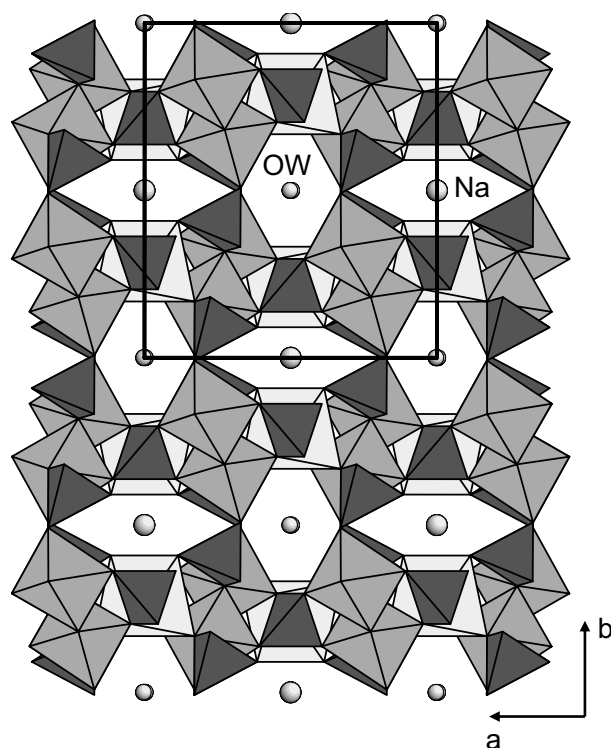


Fig. 4. Projection of the crystal structure of yazganite along the **c**-axis (program Atoms; Dowty, 1993). AsO_4 tetrahedra in dark gray, FeO_6 octahedra in medium gray, and $(\text{Mg,Mn})\text{O}_6$ octahedra in light gray. The positions of sodium (Na) cation and of the oxygen of the water molecule (OW) are shown, too.

sides nickenichite) of a mineral from the allaudite group with this position occupied. Contrary to nickenichite and similarly to johillerite and o'danielite, both channels are fully ordered.

Coordination of the cations

Two independent $\text{Me}^{2+,3+}$ sites have a distorted octahedral coordination by oxygen atoms. As in related minerals the octahedron around the site $4e$, occupied in yazganite by Mg^{2+} and Mn^{2+} , is more distorted but shows smaller variation of the individual Me-O bond distances than that around the site $8f$, occupied in yazganite by Fe^{3+} (see the bond angle variance σ^2 and the root-mean-square deviation Δ given in Table 5). In agreement with a larger size of Mg^{2+} and Mn^{2+} compared to Fe^{3+} the average Me-O bond distance ($2.266 \text{ \AA}$) around the site $4e$ is bigger than that around the site $8f$ ($2.037 \text{ \AA}$). The average Me-O bond distance of the site $4e$ is much larger, and the deformation of the octahedron around this site, is much more pronounced in yazganite than in related minerals. The ratio between magnesium and manganese on the $4e$ site is $0.656/0.344$ in the type specimen (neglecting the traces of zinc). However, another crystal from the cotype sample investigated by X-ray crystallography had the occupancy of the site $4e$, as deduced from the observed chemical composition: $\text{Mg}_{0.43}\text{Mn}_{0.26}\text{Fe}_{0.20}\text{Zn}_{0.07}$. The refinement of the occupation of this site using X-ray diffraction and constraining the occupation of the site only to magnesium and

Table 6. Bond valence (*vu*) table for yazganite.

	As1	As2	Fe	Mg _{0.656} , Mn _{0.344}	Na	H1	H2	Σ excluding hydrogen	Σ including hydrogen
O1		1.23	0.53			0.24/2	0.24/2	1.76	2.00
O2		1.41		Mg: 2×0.26 Mn: 2×0.33	2×0.25 2×0.15			2.09	2.09
O3	2×1.23		0.53		2×0.19 2×0.03			1.98	1.98
O4		1.23	0.51	Mg: 2×0.20 Mn: 2×0.26				1.95	1.95
O5		1.13	0.41 0.31					1.85	1.85
O6	2×1.23		0.43	Mg: 2×0.23 Mn: 2×0.30				1.92	1.92
OW						0.76	0.76	0	1.52
Σ	4.92	5.00	2.72	Mg: 1.36 Mn: 1.76	1.24	1	1	The bond valences for hydrogen atoms were fixed to 1.	

manganese, has given the ratio Mg/Mn of 0.478/0.522. An exact distribution of more than two *bivalent* cations on the site 4e cannot be determined by the X-ray diffraction using only one measurement.

The two As⁵⁺ cations have tetrahedral coordination by oxygen atoms. Both tetrahedra are quite regular, the tetrahedral angles for As1O₄ are in the interval of 102.5–112.2°, and those for As2O₄ are in the interval of 105.9–113.2°. However, the As2O₄ tetrahedron shows a smaller average As–O bond distance (1.688 Å) than the As1O₄ tetrahedron (1.692 Å), and much larger variation of the individual As–O bond distances than the As1O₄ tetrahedron (see Table 5). The difference between the AsO₄ tetrahedra is much more pronounced in yazganite than in related minerals, for example in nickenichite, and it is probably due to different bonding schemes in the channels I and II (see below).

The water molecule in the channel I is located in a [4+4] cage formed from four closer oxygen atoms in a square arrangement and four oxygen atoms with longer average distance in a disphenoid arrangement, as described by Auernhammer *et al.* (1993). The oxygen atom OW is located slightly out of the centre of the cage showing a positional disorder. The water molecule is fixed in the cage by hydrogen bonds involving its two hydrogen atoms (see below).

The Na¹⁺ cation in the channel II is coordinated in a [6+2] arrangement of oxygen atoms with the average distance of <2.406 Å> for 6 closer oxygen atoms and 3.064 Å for two distant oxygen atoms. The NaO₈ cubes are less deformed (for *cis*-O atoms the angles O–Na–O vary from 56.2 to 114.9°) than in nickenichite, and they form rows in the [001] direction by sharing two opposite faces. Hydrogen bonds formed in the channel II (as in o'danielite) can be excluded for yazganite, because the interatomic distance between the two corresponding oxygen atoms (O2–O3) is 2.956 Å compared to 2.502–2.539 Å, as observed in the related compounds where the hydrogen bridge occurs (Keller & Hess, 1988).

Bond valences and hydrogen bonds

The data of Brese & O'Keeffe (1991) were used to calculate the bond valences for all non-hydrogen atoms (Table 6). The bond valences for all cations sum to their expected values with the exception of the site 4e occupied by *bivalent* cations Mg²⁺ and Mn²⁺, which sum to lower values than expected, especially for magnesium (see Table 6). As already discussed the average *Me*–O bond distance around this site is much bigger than in related minerals. However, the bond valences of corresponding ligand oxygen atoms, as well as those of all other oxygen atoms, sum to expected value of 2 *vu*, with the exception of O1, which can be saturated (see below) with the proposed hydrogen bond of the water molecule.

Based on the dependence of H...O bond valence on O...O distance (assuming stretched O–H...O bond angles) according to Brown & Altermatt (1985) we propose in Table 6 also possible hydrogen bonds. The water molecule is fixed by hydrogen bonds of its two H atoms to the cage of the polyhedral framework. Due to the offset of the water molecule from the square formed by four oxygen atoms O1, there are only 2 close atoms O1 at the distance 2.44 and 2.45 Å, and with a bonding angle O1–OW–O1 of 104.1°, close to the ideal angle in a water molecule. A dynamical disorder of the water molecule on the split position including a bifurcation of both hydrogen bonds is possible.

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