Mejillonesite, a new acid sodium, magnesium phosphate mineral, from Mejillones, Antofagasta, Chile

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Abstract

Mejillonesite, ideally $NaMg_2(PO_3OH)(PO_4)(OH) \cdot H_5O_2$, is a new mineral approved by the CNMNC (IMA 2010-068). It occurs as isolated crystal aggregates in thin zones in fine-grained opal-zeolite aggregate on the north slope of Cerro Mejillones, Antofagasta, Chile. Closely associated minerals are bobierrite, opal, clinoptilolite-Na, clinoptilolite-K, and gypsum. Mejillonesite forms orthorhombic, prismatic, and elongated thick tabular crystals up to 6 mm long, usually intergrown in radiating aggregates. The dominant form is pinacoid {100}. Prisms {hk0}, {h0l}, and {0kl} are also observed. The crystals are colorless, their streak is white, and the luster is vitreous. The mineral is transparent. It is non-fluorescent under ultraviolet light. Mohs' hardness is 4, tenacity is brittle. Cleavage is perfect on {100}, good on {010} and {001}, and fracture is stepped. The measured density is 2.36(1) g/cm^3; the calculated density is 2.367 g/cm^3. Mejillonesite is biaxial (–), $\alpha = 1.507(2)$, $\beta = 1.531(2)$, $\gamma = 1.531(2)$, $2V(meas) = 15(10)°$, $2V(calc) = 0°$ (589 nm). Orientation is $X = \mathbf{a}$, Z = elongation direction. The mineral is non-pleochroic. Dispersion is r > v, medium. The IR spectrum contains characteristic bands of the Zundel cation ($H_5O_2^+$, or $H^+ \cdot 2H_2O$) and the groups P-OH and OH^-. The chemical composition is (by EDS, H_2O by the Alimarin method, wt%): Na_2O 9.19, MgO 26.82, P_2O_5 46.87, H_2O 19, total 101.88. The empirical formula, based on 11 oxygen atoms, is $Na_{0.93}Mg_{2.08}(PO_3OH)_{1.00}(PO_4)_{1.06}(OH)_{0.86} \cdot 0.95H_5O_2$. The strongest eight X-ray powder-diffraction lines [d in Å(I)(hkl)] are: 8.095(100)(200), 6.846(9)(210), 6.470(8)(111), 3.317(5)(302), 2.959(5)(132), 2.706(12)(113), 2.157(19)(333), and 2.153(9)(622). The crystal structure was solved on a single crystal (R = 0.055) and gave the following data: orthorhombic, Pbca, a = 16.295(1), b = 13.009(2), c = 8.434(1) Å, V = 1787.9(4) $Å^3$, Z = 8. The crystal structure of mejillonesite is based on a sheet (parallel to the **b-c** plane) formed by two types of MgO_6 octahedra, isolated tetrahedra PO_4 and PO_3OH whose apical vertices have different orientation with respect to the sheet. The sheets are connected by interlayer, 5-coordinated sodium ions, proton hydration complexes, and hydroxyl groups. The structure of mejillonesite is related to that of angarfite, $NaFe_5^{3+}(PO_4)_4(OH)_4 \cdot 4H_2O$ and bakhchisaraitsevite, $Na_2Mg_5(PO_4)_4 \cdot 7H_2O$.

Keywords: Mejillonesite, new mineral, Chile, phosphate

Introduction

Mejillonesite, ideally $NaMg_2(PO_3OH)(PO_4)(OH) \cdot H_5O_2$, from the Mejillones Peninsula, Antofagasta, Chile, has been approved by the CNMNC (IMA 2010-068). The name is for Cerro Mejillones, the type locality. Mejillonesite represents a new crystal structure type. No valid or invalid equivalent unnamed mineral exists (Smith and Nickel 2007, and updated lists on IMA-CNMNC's web site). Type material is deposited in the Museu de Geociências, Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, 05508-080 São Paulo, SP, Brazil, catalog number DR712, and in the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, registration number 4043/1 (fragment of holotype).

Occurrence

Mejillonesite occurs very sparsely as isolated crystal aggregates in thin zones on the north slope of Cerro Mejillones (23°05′44.56″S 70°30′53.78″W), Mejillones Peninsula, Mejillones, Antofagasta, II Region, Chile. Associated minerals are bobierrite, opal, clinoptilolite-Na, clinoptilolite-K, and gypsum. Iron-rich tinsleyite, which is very common in the upper part of the hill, gives a reddish tint to the otherwise colorless silicate matrix. The mineral formed at the contact between a granite and what is now a fine-grained, completely altered siliceous layer at the base of a Pliocene (ca. 2.5 Ma) coastal bird guano deposit.

Guano mining near Mejillones started around 1840, at first by a concession from the Bolivian government. The growing economic importance of the guano deposits at the Mejillones

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peninsula resulted in military conflicts between Chile and Bolivia (Wappäus 1870). The main guano mining and export period from Mejillones was in the decades 1860–1880. In the Mejillones guano, the agricultural chemist Bobierre (1868) discovered a new magnesium phosphate hydrate mineral in small, colorless prismatic crystals. Dana (1868) named the mineral in the same year as bobierrite, $Mg_3(PO_4)_2 \cdot 8H_2O$.

HABIT AND PHYSICAL PROPERTIES

Mejillonesite occurs as orthorhombic prismatic and elongated thick tabular crystals up to 6 mm long, usually intergrown in radiating aggregates. The dominant form is the pinacoid {100}. Prisms {$hk0$}, {$h0l$}, and {$0kl$} are also observed (Fig. 1). Twinning was not observed. The crystals are colorless, their streak is white, and the luster is vitreous. The mineral is transparent. It is non-fluorescent under both long- and short-wave ultraviolet light. The Mohs' hardness is 4, tenacity is brittle. The cleavage is perfect on {100}, good on {010} and {001}, parting was not observed and fracture is stepped. The measured density is 2.36(1) g/cm^3 by flotation in heavy liquids; the calculated density is 2.367 g/cm^3 based on the empirical formula and unit-cell parameters derived from the single-crystal structure study.

In transmitted light, mejillonesite is biaxial (–) and has α = 1.507(2), β = 1.531(2), γ = 1.531(2), $2V$ (meas) = 15(10)°, $2V$ (calc) = 0° (589 nm). The optical orientation is $X = \mathbf{a}$, Z = elongation direction. The mineral is non-pleochroic. Dispersion is r > v, medium.

Mejillonesite was mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) with the resolution of 4 cm^{-1}. Sixteen scans have been obtained in the range of 390–4000 cm^{-1}. The spectrum of a pure KBr pellet was used as reference. Absorption bands in the infrared spectrum of mejillonesite (Fig. 2) and their assignments are as follows (in cm^{-1}, s = strong band): 3530, 3385, 3330 (O-H stretching vibrations of OH groups and H_2O groups); 2990, 2770, 2000, 1760 (O-H stretching vibrations of acid OH groups); 1515 (H-O-H bending vibrations); 1230, 1151s, 1137s, 1087, 1054s, 1037s, 995s, 954 (P-O stretching vibrations of phosphate ions); 910, 877, 848, 813, 775 (P-O-H and Mg···O-H bending vibrations); 610, 580, 570, 543 (O-P-O bending vibrations); 461 (Mg···O stretching vibrations); 395 (doubtful value at the edge of the measurement range). There are no bands in the spectra that are indicative of carbonate ions. The O-H modes at 2990, 2770, 1760 and, possibly, 1515 cm^{-1} are close to those calculated and measured for the oxonium cation, H_3O^+, or its hydrated complexes like Zundel cation, $H_5O_2^+$, which is formed by a proton H^+ coordinated by two H_2O groups forming very strong hydrogen bonds with the central cation H^+ (Kim et al. 2002; Sobolewski and Domcke 2002; Christie 2004; Park et al. 2007). The infrared spectrum contains all absorption bands expected for a Zundel cation. These bands mentioned above cannot be assigned to other hydrogen atom bearing groups. Moreover, typical bands of the HOH bending vibrations of isolated H_2O groups (the range of 1600–1690 cm^{-1}) are absent in the IR spectrum of mejillonesite.

Among minerals, the existence of Zundel-type complexes $H_5O_2^+$ has been reliably confirmed only in rhomboclase, (H_5O_2) $Fe^{3+}(SO_4)_2 \cdot 2H_2O$ (Peterson et al. 2009), and in afwillite, $Ca_{12}(H_2O)_8[SiO_4]_4[SiO_2(OH)_2]_4$ where such complexes are

formed as a result of protonation of pairs of adjacent H_2O molecules (Rastsvetaeva et al. 2009).

CHEMICAL DATA

Electron microprobe analyses (5 point analyses) were carried out using VEGA TS 5130MM SEM equipped with EDX analyzer [INCA Si(Li) detector], at an operating voltage of 15.7 kV and a beam current of 0.5 nA. The electron beam was rastered over an area of $16 \times 16 \, \mu m^2$. H_2O was determined by the Alimarin method [Penfield method modified for small samples involving selective sorption of H_2O on $Mg(ClO_4)_2$ from the gaseous products obtained by heating the mineral at 1050 °C in oxygen, Alimarin and Petrikova 1974]. Mean analytical results are given in Table 1.

The empirical formula, based on 11 O atoms, is $H_{6.61}Na_{0.93}$ $Mg_{2.08}(PO_4)_{2.06}O_{2.76}$ or, taking into account structural and IR data (see below), $Na_{0.93}Mg_{2.08}(PO_3OH)_{1.00}(PO_4)_{1.06}(OH)_{0.86} \cdot 0.95H_5O_2$. Hydrogen is divided among OH, H_5O_2, and PO_3OH taking charge balance into account. The simplified formula is $NaMg_2(PO_3OH)$ $(PO_4)(OH) \cdot H_5O_2$ (see below), which requires: Na_2O 9.79, MgO 25.46, P_2O_5 44.83, H_2O 19.92, total 100 wt%.

X-RAY DIFFRACTION: METHODS

Powder X-ray diffraction data obtained using a Siemens D5000 diffractometer equipped with a Göbel mirror and a position-sensitive detector (for Cu$K\alpha$, 40 kV and 40 mA) are given in Table 2. Unit-cell parameters refined from powder data (CellCalc program, Miura 2003) in the same space group $Pbca$ as obtained by single-crystal X-ray diffraction (see below) are a = 16.270(3), b = 12.901(5), c = 8.430(3) Å, V = 1769(2) Å^3, Z = 8, in close agreement with those obtained from the single-crystal study.

Single-crystal X-ray studies were carried out using a four-circle STOE STADI IV single-crystal diffractometer equipped with an Oxford Diffraction CCD detector [Mo$K\alpha$ radiation, omega-scan 1°, exposure time 60 s, R = 0.055 for 754 reflections with $F_o > 4\sigma(F_o)$; 2599 total reflections to $2\theta = 60(°)$ and gave the following data: orthorhombic, $Pbca$, a = 16.295(1), b = 13.009(2), c = 8.434(1) Å, V = 1787.9(4) Å^3, Z = 8]. The a:b:c ratio calculated from the unit-cell parameters is 1.253: 1: 0.648 (single-crystal data). All the crystal-structure refinement data are reported in Table 3. (The CIFs are on deposit[1].) Calculations using the Gladstone-Dale relationship for the empirical formula and the cell data derived from the single-crystal studies yield –0.017, indicating superior compatibility (Mandarino 1979).

CRYSTALLOGRAPHY OF MEJILLONESITE

The crystal structure of mejillonesite is characterized by zigzag chains of alternating $Mg1O_6$ (in blue) and $Mg2O_6$ (in orange) octahedra running along the **c** axis (see the thick yellow zigzag line in Fig. 3a). The chains are connected via common OZ-atom vertices of octahedra (see Fig. 3b). This gives a sheet of octahedra parallel to the **b-c** plane. The $P1O_4$ (yellow) and $P2O_4$ (light blue) tetrahedra are unconnected. While the $P2O_4$ tetrahedron shares O21, O22, and O23 with $Mg1O_6$ and $Mg2O_6$ octahedra, $P1O_4$ only shares two oxygen atoms with $Mg1O_6$ and $Mg2O_6$, O11 and O13. If the crystal structure is viewed along the **b** axis (Fig. 4), it is seen that the octahedral sheet has tetrahedra above and below pointing with their apical oxygen atoms (O14 for $P1O_4$ and O24 for $P2O_4$) out of the plane. The octahedral sheets are connected by inter-layered, 5-coordinated sodium ions (colored
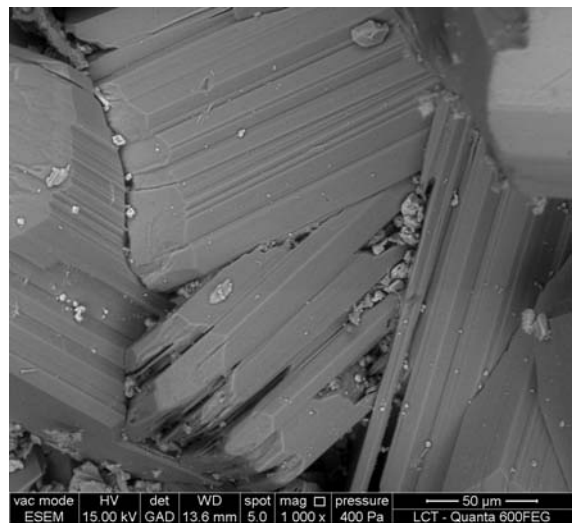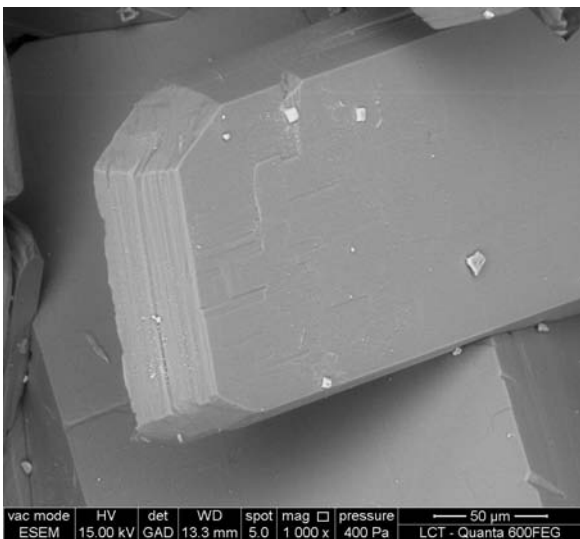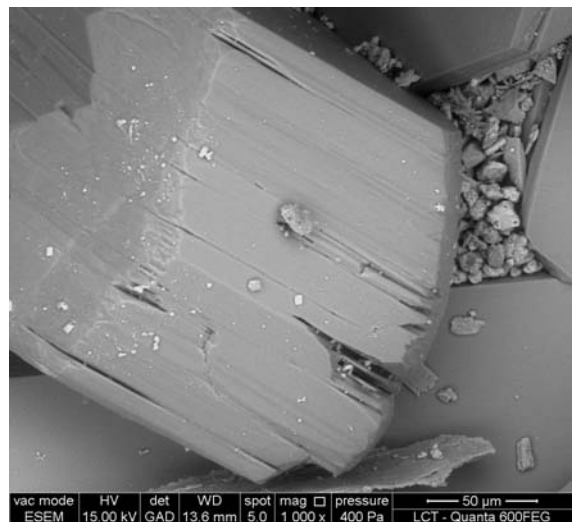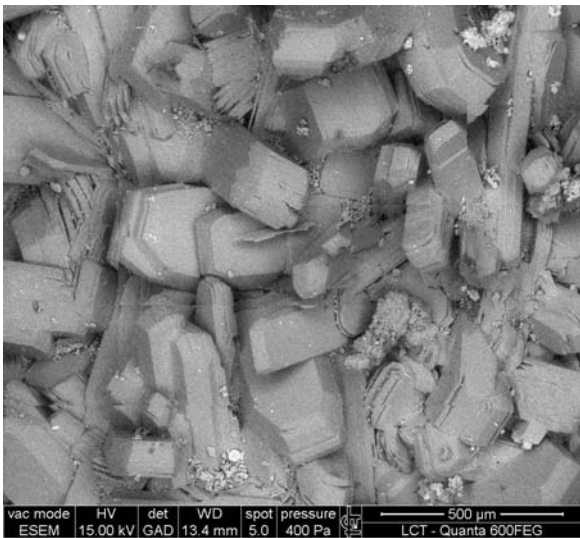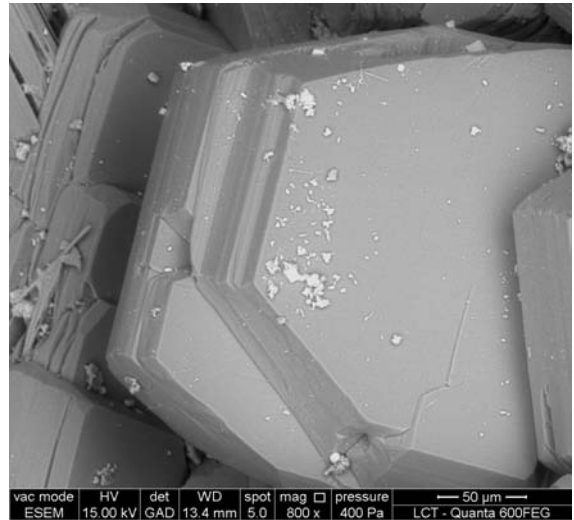
Figure 1. Mejillonesite crystals.
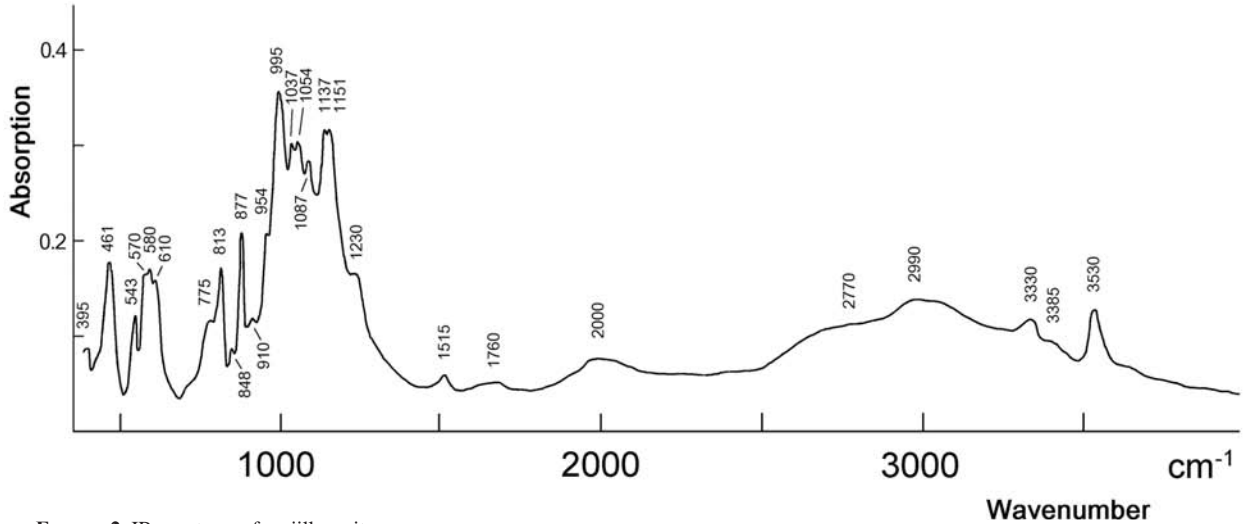
Figure 2. IR spectrum of mejillonesite.

TABLE 1. Analytical data for mejillonesite

Constituent	wt%	Range	Probe standard
Na_2O	9.19	9.09–9.28	albite
MgO	26.82	26.70–26.97	diopside
P_2O_5	46.87	46.72–47.00	$LaPO_4$
H_2O^*	19(2)		
Total	101.88		

* Single measurement with accuracy in parentheses.

TABLE 2. Powder X-ray diffraction data for mejillonesite*

I (%)	d_{meas} (Å)	d_{calc} (Å)	h	k	l
100	**8.09**	8.135	2	0	0
9	**6.85**	6.881	2	1	0
8	**6.47**	6.474	1	1	1
2	5.31	5.331	2	1	1
2	4.04	4.067	4	0	0
3	3.807	3.802	2	3	0
2	3.468	3.466	2	3	1
5	3.317	3.328	3	0	2
2	3.221	3.223	3	1	2
4	3.190	3.185	4	2	1
5	2.959	2.960	1	3	2
3	2.823	2.825	2	4	1
3	2.745	2.747	5	2	1
12	**2.706**	2.707	1	1	3
2	2.532	2.531	6	1	1
5	2.187	2.181	1	5	2
19	**2.157**	2.158	3	3	3
9	**2.153**	2.150	6	2	2
2	2.090	2.090	1	0	4
2	2.008	2.009	8	1	0
2	1.887	1.888	1	5	3
4	1.838	1.839	8	3	0
4	1.833	1.832	8	0	2
3	1.722	1.722	4	5	3
		1.721	7	4	2
3	1.624	1.624	1	5	4
3	1.619	1.619	4	4	4
2	1.453	1.453	10	4	0
3	1.348	1.348	12	1	0
		1.348	8	7	1
2	1.344	1.344	3	7	4

Notes: Indexed with a = 16.270(3), b = 12.901(5), c = 8.430(3) Å refined from the powder diffraction data. All lines were used for unit-cell refinement. The strongest lines are marked in bold. The experimental error for the d-spacings is about ±0.02 Å for low-angle values and about ±0.003 Å for high-angle values.

TABLE 3. Crystallographic data and refinement parameters for mejillonesite

Crystal data	
Simplified chemical formula	$NaMg_2(PO_3OH)(PO_4)(OH)·H_5O_2$
Crystal system	orthorhombic
Space group	*Pbca*
Unit-cell parameters a, b, c (Å)	16.295(1), 13.009(2), 8.434(1)
Unit-cell volume (Å³)	1787.9(4)
Software for the unit-cell parameter determination	CrysAlis (Oxford Diffraction)
Z	8
Crystal size (mm)	0.080 × 0.060 × 0.030
Data collection	
Diffractometer	STOE STADI IV (CCD detector, Oxford Diffraction)
Temperature (K)	298(2)
Radiation, wavelength (Å)	Mo$K\alpha$, 0.71073
θ range for data collection (°)	1.00–30.00
h, k, l ranges	−22 +22, −18 +17, −9 +11
Omega scan width (°), exposure time (s)	1, 60
Total reflections collected	23492
Redundancy	
Unique reflections (R_{int})	2599 (0.13)
Unique reflections $F > 4\sigma(F)$	754
Absorption correction method	XRED, XSHAPE (Stoe and Cie 1999, 2001)
Structure refinement	
Structure solution and refinement software	SHELXS-SHELXL-97
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2599/0/169
R_1 [$F > 4\sigma(F)$]	0.056
R_1 all	0.164
Goodness-of-fit on F^2	0.83
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.0010 \times P)^2 + 0.00 \times P]$ where P = [Max (F_o^2, 0) + 2×F_c^2]/3 (SHELXL-97)
Largest diff. peak and hole (e⁻/Å³)	0.77, −1.23
Secondary extinction	0.00000(15)

Notes: R_{int} = (n /n − 1)1/2[F_o^2 − F_o(mean)²]/ΣF_o^2; R1 = $\Sigma||F_o| − |F_c||/\Sigma|F_o|$; GooF = {$\Sigma[w(F_o^2 − F_c^2)2]/(n − p)$}$^{1/2}$, where n = number of reflections, p = number of refined parameters.

yellow in Fig. 4) and the H4-OH group (indicated in the figure).

Atomic coordinates are reported in Table 4 and bond lengths in Table 5. The bond P2-O24 is elongated (1.63 Å) because O24

forms a covalent bond with H6. Thus the P2-centered tetrahedron corresponds to the acid phosphate group HPO_4^{2-}. This is definitively demonstrated by the bond valence calculation for which the O24 atom shows 1.38 v.u., which is a typical value for a OH group (e.g., Nagashima et al. 2008). A more detailed view relative to the distribution of H atoms is shown in Figure 5.

Taking into account the IR data (see above), we can conclude that the cluster $(H_2O)_2$ including the sites OZ1 and OZ2 is protonated being really a Zundel-type cation complex, $H_5O_2^+$. OZ1 has 0.58 v.u. and OZ2 has a value of 0.46 v.u. Calculated O–O

FIGURE 3. Crystal structure of mejillonesite viewed along the **a** axis; the black solid rectangle represents the unit cell. On the left side (**a**), the figure shows only the $Mg1O_6$ (in orange) and $Mg2O_6$ (in blue) octahedra; whereas, on the right side (**b**), the P1O4 (yellow) and P2O4 (light blue) tetrahedra are added with respect to the octahedral sheet. The thick yellow line in **a** indicates the zigzag motif of the chain of octahedra.

distance for isolated (gas-phase) Zundel cation is about 2.4–2.5 Å (Agmon 1995, Paddison and Elliott 2005), but in condensed substances O–O distances in hydrated proton complexes can have different values: 2.8 Å (Laria et al. 2004), from 2.3 to 2.8 Å (Xu et al. 2007), 2.55–3.0 Å (Gustafsson 1985), 3.1–3.4 Å (Jagoda-Cwiklik et al. 2011). The distance OZ1–OZ2 in mejillonesite is 3.135 Å. At such a distance the proton has two equilibrium states (near OZ1 and near OZ2) separated by an energy barrier (Agmon 1995; Woutersen and Bakker 2006). Consequently the crystal-chemical formula of mejillonesite is written as follows: $NaMg_2(PO_3OH)(PO_4)(OH)\cdot H_5O_2$.
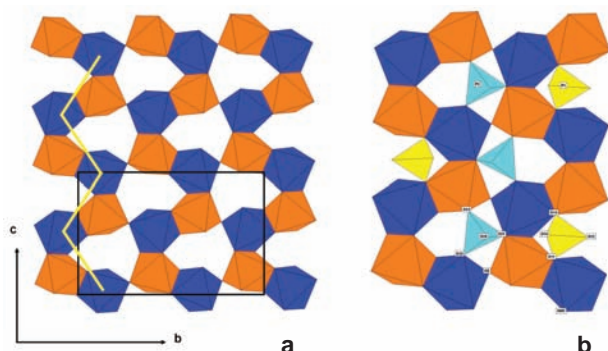
RELATION TO OTHER SPECIES

The known Na-Mg phosphate minerals with no other metal cations are bakhchisaraitsevite and hylbrownite. Both mejillonesite and bakhchisaraitsevite, $Na_2Mg_5(PO_4)_4\cdot 7H_2O$ (Yakubovich et al. 2000), have topologically identical sheets of Mg octahedra coplanar with the **b-c** and **b-a** planes, respectively. The sheets consist of zigzag columns of edge-sharing octahedra and are connected with each other via common vertices. The sheets are decorated, above, and below, with PO4 tetrahedra to form TOT layers. In bakhchisaraitsevite, unlike mejillonesite, these layers are joined by pairs of Mg octahedra having common edges
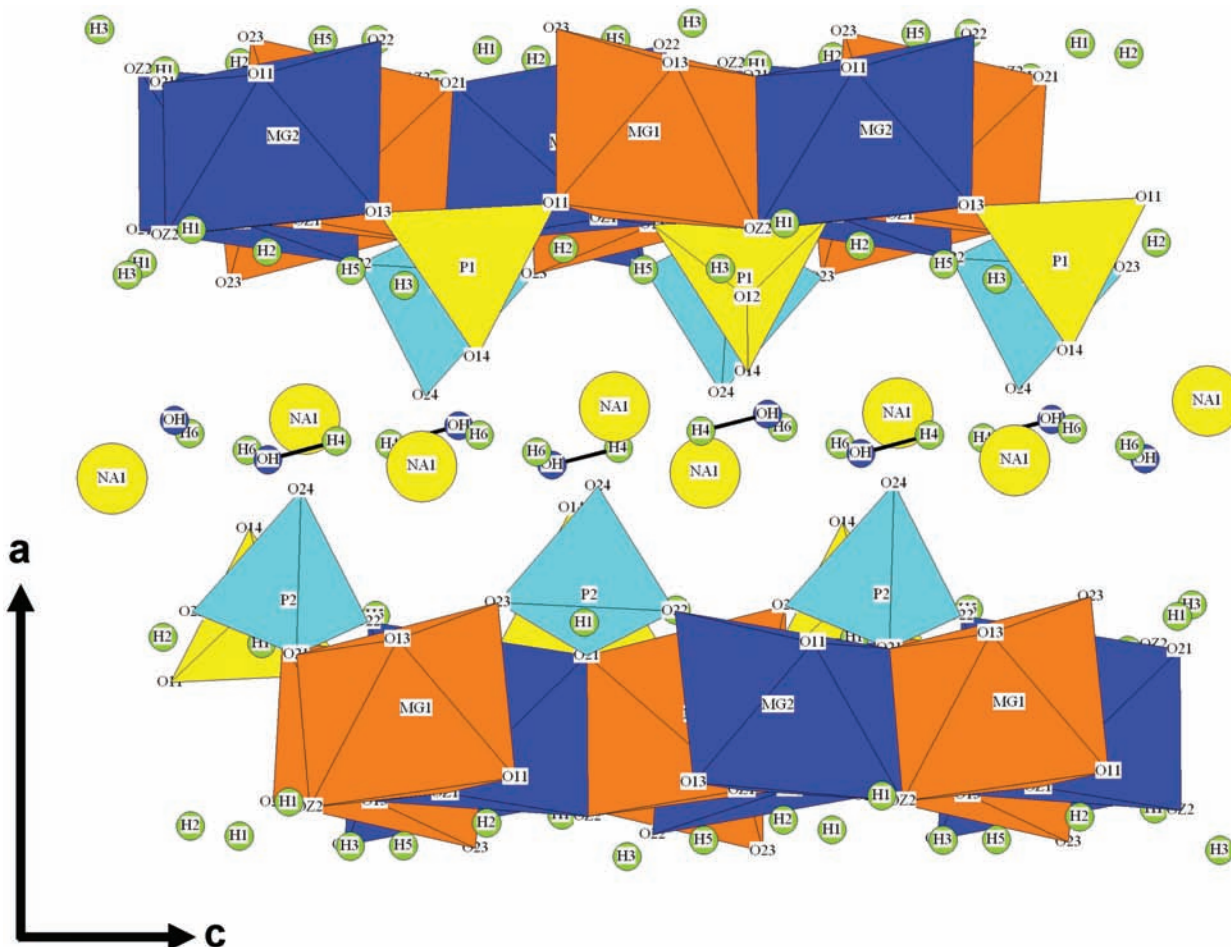

FIGURE 4. Crystal structure of mejillonesite viewed along the **b** axis. The atoms are labeled in the figure.
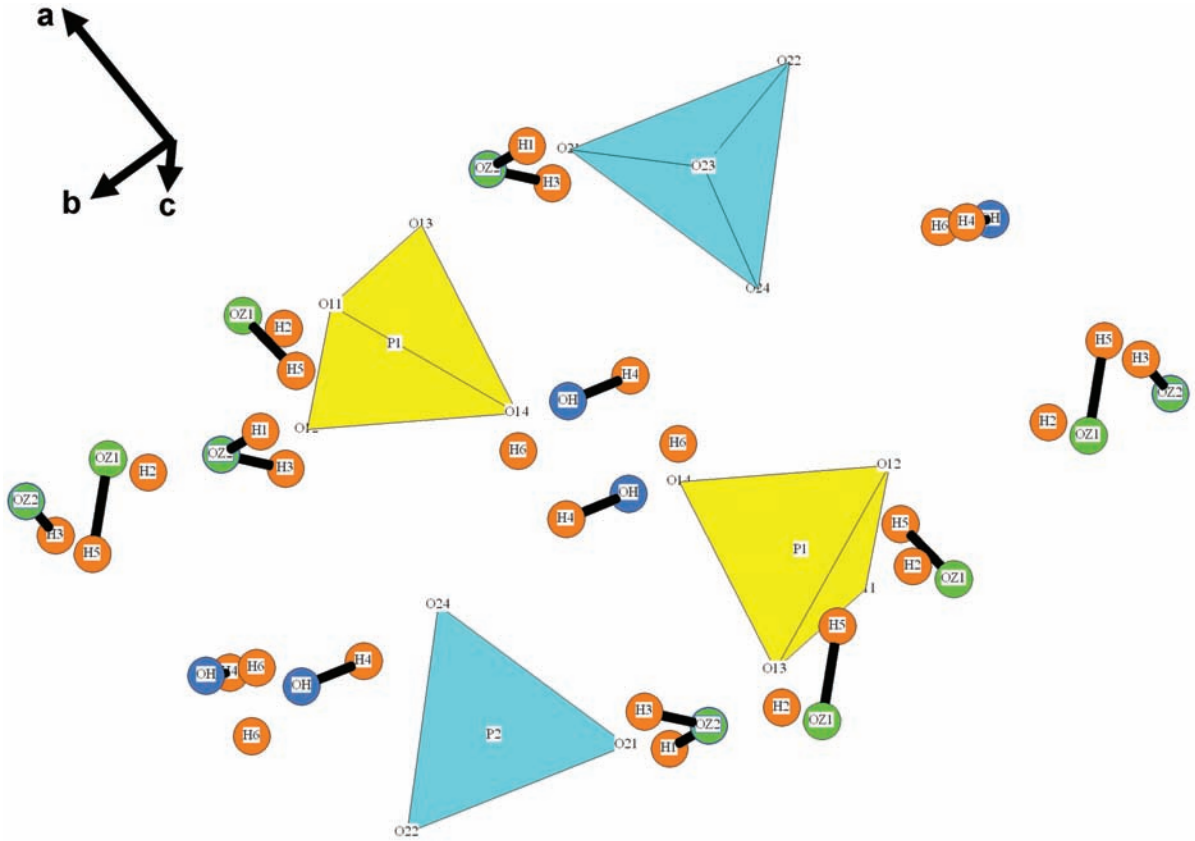
Figure 5. Crystal structure of mejillonesite in a perspective view to better show the positions of different hydrogen atoms. The atoms are labeled in the figure.

Table 4. Final atom positions and equivalent isotropic displacement parameters (Å²) for mejillonesite

Atom	x/a	y/b	z/c	U_{eq}
P1	0.1382(1)	0.0534(1)	0.1427(3)	0.0097(5)
P2	0.1432(1)	0.7876(1)	0.6463(3)	0.0100(5)
Mg1	0.2434(1)	0.8832(2)	0.9481(2)	0.0128(7)
Mg2	0.2437(1)	0.8881(2)	0.3390(2)	0.0127(6)
Na1	0.0322(2)	0.8839(2)	0.9341(3)	0.0218(9)
O11	0.1933(3)	0.0297(3)	0.2903(4)	0.0154(11)
O12	0.1180(3)	0.1703(3)	0.1361(5)	0.0165(10)
O13	0.1870(3)	0.0243(3)	0.9902(4)	0.0180(11)
O14	0.0585(2)	0.9910(3)	0.1507(5)	0.0225(10)
O21	0.1930(2)	0.8130(3)	0.1433(5)	0.0180(10)
O22	0.1599(3)	0.6425(3)	0.0080(4)	0.0222(12)
O23	0.1502(3)	0.8420(3)	0.8054(4)	0.0206(11)
O24	0.0475(2)	0.7451(4)	0.1263(5)	0.0238(10)
OH	0.9897(3)	0.8748(4)	0.3494(6)	0.0327(12)
OZ1	0.1866(2)	0.2492(4)	0.8895(5)	0.0200(10)
OZ2	0.1701(3)	0.4291(3)	0.1347(5)	0.0221(11)
H1	0.173(5)	0.486(4)	0.821(8)	0.053(1)
H2	0.160(4)	0.249(5)	0.179(8)	0.044(1)
H3	0.135(4)	0.448(6)	0.068(8)	0.053(1)
H4	0.005(3)	0.604(4)	0.964(6)	0.024(1)
H5	0.142(4)	0.212(4)	0.959(8)	0.052(1)
H6	0.000(4)	0.820(4)	0.319(8)	0.055(1)

Notes: O1 oxygen atoms coordinate the P1 atom, whereas the O2 oxygen atoms coordinate the P2 one. OZ1 and OZ2 are two oxygen atoms forming two water molecules belonging to the Zundel cation group together with H1, H2, H3, and H5 hydrogen atoms (see the text). OH is a hydroxyl group. H4 belongs to this OH group and H6 belongs to a OH group linked to P2.

Table 5. Bond lengths and angles for mejillonesite (Å)

P1-O14	1.533(4)	Mg1-O23	2.010(5)	Na1-O23	2.275(5)
P1-O12	1.556(3)	Mg1-O11	2.029(4)	Na1-O14	2.312(4)
P1-O11	1.566(4)	Mg1-O21	2.055(4)	Na1-O14	2.337(5)
P1-O13	1.559(4)	Mg1-O13	2.083(5)	Na1-O24	2.439(5)
\<P1-O\>	1.554	Mg1-OZ1	2.141(5)	Na1-O12	2.615(4)
		Mg1-OH	2.195(5)	\<Na-O\>	2.396
		\<Mg1-O\>	2.086		
				OZ1-H2	0.72
				OZ1-H5	1.05
P2-O22	1.504(4)	Mg2-O22	2.014(4)	OZ2-H1	0.83
P2-O23	1.521(4)	Mg2-O13	2.049(4)	OZ2-H3	0.87
P2-O21	1.539(4)	Mg2-O11	2.058(4)		
P2-O24	1.626(4)	Mg2-O21	2.089(4)	OH-H4	1.03
\<P2-O\>	1.540	Mg2-OZ1	2.159(5)		
		Mg2-OH	2.285(5)	H2-OZ1-H5	91.8°
		\<Mg2-O\>	2.108	H1-OZ2-H3	92.7°
				OZ1···OZ2 (Zundel group)	3.135

to form octahedral pseudo-framework. As a result, "in-plane" lattice parameters of bakhchisaraitsevite ($b = 12.906$ and $a = 8.3086$ Å) are close to that of mejillonesite ($b = 13.009$ and $c = 8.434$ Å), whereas "out-of-plane" parameters of these minerals are different (16.295 Å for mejillonesite and 17.486 Å for bakhchisaraitsevite). Note that the zigzag chain of edge-sharing MgO_6 octahedra parallel to **c** is a structural element of hydromagnesite, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$, which accounts for the very similar c repeats of that mineral and mejillonesite (8.38 vs. 8.43 Å). In bakhchisaraitsevite, Na⁺ cations and H_2O molecules occupy sites in channels of a 3D framework formed by Mg octahedra and P

tetrahedra. In mejillonesite, Na^+, $H_5O_2^+$, and OH^- are situated in the interlayer space.

Hylbrownite, $MgNa_3P_3O_{10} \cdot 12H_2O$ (Elliot et al. 2011), is the Mg analog of kanonerovite, $MnNa_3P_3O_{10} \cdot 12H_2O$ (Popova et al. 2002). No structural study of kanonerovite has been completed, but the structure of synthetic $MnNa_3P_3O_{10} \cdot 12H_2O$ is known (Lightfoot and Cheetham 1987): it is composed of discrete $[MnP_3O_{10} \cdot 3H_2O]^{3-}$ units, held together by intervening Na^+ ions and H_2O groups via a complex system of Na-O and hydrogen bonds.

The structure of mejillonesite is related to that of angarfite (IMA 2010-082—Kampf et al. 2011), $NaFe_3^{3+}(PO_4)_4(OH)_4 \cdot 4H_2O$. Its crystal structure contains zigzag chains of edge-sharing Fe^{3+}-O_6 octahedra along **c**, which are linked into sheets parallel to {010} by sharing corners with octahedra in adjacent chains. As in mejillonesite, the sheets are decorated with PO_4 tetrahedra. Unlike mejillonesite, in angarfite insular octahedra between the sheets share two sets of *trans* corners with tetrahedra in adjacent sheets, thereby linking the sheets into a framework. Channels in the framework parallel to **c** contain a partially occupied Na site and contain a disordered H_2O site. There are a few synthetic Na-Mg phosphates, including $MgNa(PO_4) \cdot 7H_2O$, isostructural with struvite (Mathew et al. 1982).

The compound $(H_3O)[Co_2(OH)_2(HPO_4)(H_2PO_4)]$ (compound 1), with unit-cell parameters $a = 8.443(2)$, $b = 13.093(4)$, $c = 15.484(4)$ Å, and space group is *Pcab*, has a structure closely related to that of mejillonesite (Hamanaka and Imoto 1998). As compared with mejillonesite, this compound contains Co instead of Mg and additional H atom instead of Na. Both structures are based on the same octahedral sheets decorated with isolated PO_4 tetrahedra. Unfortunately, the positions of H atoms in compound 1 could not be determined; IR spectrum and bond-valence calculations are also not given in the paper by Hamanaka and Imoto (1998). However from cation-anion distances one can conclude that in each tetrahedron only one vertex is occupied by OH that results in elongated P-OH distances of 1.592 and 1.583 Å. Moreover, Hamanaka and Imoto (1998) noted: "Because the compounds are prepared in acidic conditions, the oxygen atoms between the layers cannot be hydroxide anions and in the following discussion we regard them to be water molecules that can accommodate one more proton." Really, the substitution of Na for H results in the formation of a second acid phosphate anion PO_3OH^{2-}, and the correct formula of the synthetic compound could be written as $Co_2(HPO_4)_2(OH)(H_3O+H_2O)$ or $Co_2(HPO_4)_2(OH) \cdot H_5O_2$. On the other hand, taking into account that enlarged P–O distances in the synthetic compound are significantly shorter than P2–O24 bond in mejillonesite (1.626 Å), one cannot exclude that distances P–OH of 1.592 and 1.583 Å in compound 1 are due to H-bonds like P-O⋯(H⋯O-H) between P-O and strongly polarized H_2O molecules.

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