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Lavoisierite, $Mn^{2+}_8[Al_{10}(Mn^{3+}Mg)][Si_{11}P]O_{44}(OH)_{12}$, a new mineral from Piedmont, Italy: the link between "ardennite" and sursassite

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Abstract The new mineral species lavoisierite, ideally $Mn^{2+}_8[Al_{10}(Mn^{3+}Mg)][Si_{11}P]O_{44}(OH)_{12}$, has been discovered in piemontite-bearing micaschists belonging to the Piedmontese Nappe from Punta Gensane, Viù Valley, Western Alps, Italy. It occurs as yellow-orange acicular to prismatic-tabular crystals up to a few millimeters in length, with white streak and vitreous luster, elongated along [010] and flattened on {001}. Lavoisierite is associated with quartz, "mica," sursassite, piemontite, spessartine, braunite, and "tourmaline." Calculated density is 3.576 g cm⁻³. In plane-polarized light, it is transparent, pleochroic, with pale yellow parallel to [010] and yellow-orange normal to this direction; extinction is parallel and elongation is positive. Birefringence is moderate; the calculated average refraction index n is 1.750. Lavoisierite is orthorhombic, space group *Pnmm*, with a 8.6891(10), b 5.7755(3), c 36.9504(20) Å, V 1854.3(2) Å³, $Z = 2$. Calculated main diffraction lines of the X-ray powder diffraction pattern are [d in Å, (I), (hkl); relative intensities are visually estimated]: 4.62 (m) (112), 2.931 (vs) (11$\underline{10}$), 2.765 (s) (11$\underline{11}$), 2.598 (s) (310), 2.448 (ms) (028). Chemical analyses by electron microprobe give (in wt%) P_2O_5 2.08, V_2O_5 0.37, SiO_2 34.81, TiO_2 0.13, Al_2O_3 22.92, Cr_2O_3 0.32, Fe_2O_3 0.86, Mn_2O_3 6.92, MnO 19.09, MgO 5.73, CaO 1.94, Na_2O 0.01, H_2O 5.44, sum 100.62 wt%. H_2O content was calculated from structure refinement. The empirical formula, based on 56 anions, is $(Mn^{2+}_{5.340}Mg_{1.810}Ca_{0.686}Na_{0.006})_{\Sigma=7.852}(Al_{8.921}Mn^{3+}_{1.739}Mg_{1.010}$ $Fe^{3+}_{0.214}Cr_{0.084}Ti_{0.032})_{\Sigma=12.000}(Si_{11.496}P_{0.582}V_{0.081})_{\Sigma=12.159}$ $O_{43.995}(OH)_{12.005}$. The crystal structure of lavoisierite was solved by direct methods and refined on the basis of 1743 observed reflections to $R_1 = 4.6$ %. The structure is characterized by columns of edge-sharing octahedra running along [010] and linked to each other by means of [SiO₄], [Si₂O₇], and [Si₃O₁₀] groups. Lavoisierite, named after the French chemist and biologist Antoine-Laurent de Lavoisier (1743–1794), displays an unprecedented kind of structure, related to those of "ardennite" and sursassite.

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Introduction

"Ardennite," "pumpellyite," and sursassite are structurally related mixed-anion silicates which typically occur in metamorphic environment. After the solution of the crystal structures of ardennite (Donnay and Allmann 1968) and pumpellyite (Galli and Alberti 1969), Allmann and Donnay (1971) pointed out the structural relationships between the two minerals. The crystal structure of sursassite was solved independently by Allmann (1984) and Mellini et al. (1984), who highlighted the structural affinity of this species with pumpellyite-group minerals. These three structures are characterized by chains of edge-sharing octahedra, developing along [010]; adjacent chains are connected to each other by means of inserted silicate groups. Pumpellyite-group minerals and sursassite have SiO₄ and Si₂O₇ groups, whereas in "ardennite" SiO₄ and Si₃O₁₀ groups occur. In addition, in the latter phase, a slightly larger tetrahedron is

occupied by As^{5+} and V^{5+} cations, which occur in the two members of the ardennite series, ardennite-(As) and ardennite-(V), respectively. In the cavities of the framework, sevenfold and sixfold coordinated cations (Mn^{2+}, Ca^{2+}, Mg^{2+}) are located.

Ferraris et al. (1986) interpreted the close relationships between sursassite, "pumpellyite," and "ardennite" considered as the members of a polysomatic family; Merlino (1990) described these structures as composed by two different kinds of layer occurring in regular alternation, according to the OD theory (Dornberger-Schiff 1966). HRTEM studies showed the frequent occurrence of sursassite-pumpellyite intergrowths (Mellini et al. 1984) and of polytypic features in selected specimens of ardennite (Pasero and Reinecke 1991), together with disordered sequences as well.

During a systematic study of specimens of "ardennite" from world-wide localities, Chimenti (2004) recognized the presence of an ardennite-like phase at Punta Gensane, Viù Valley, Piedmont, Italy, underlining its chemical peculiarity, that is, the high Si content. Previously, a chemically anomalous "ardennite," having a very high Si/(As + V + P) ratio, was described by Pasero and Reinecke (1991) from Mili, near Karystos, southern Evvia Island, Greece. Through a selected area electron diffraction (SAED) study of the Greek anomalous "ardennite," the latter authors reported a double c periodicity, that is, ca. 37 Å, interpreting it as a new "ardennite" polytype, coexisting with the "normal ardennite," which has a c axis of ca. 18.5 Å.

Besides the anomalous chemical composition, the phase from Punta Gensane had a doubled c parameter; therefore, it was a potentially new mineral species. The new mineral and its name have been approved by the IMA-CNMNC (no. 2012-009). The name lavoisierite is in honor of the French chemist and biologist Antoine-Laurent de Lavoisier (1743–1794), considered to be one of the fathers of the modern chemistry. The type material is deposited in the mineralogical collections of the Museo di Storia Naturale, University of Pisa, Via Roma 79, Calci (Pisa, Italy), under the catalog number 19637. A cotype specimen is kept in the mineralogical collections of the Museo Regionale di Scienze Naturali, Via Giovanni Giolitti 36, Torino (Italy), with catalog number M/U 16359.

Geological setting and mineral occurrence

The presence of Mn-bearing sorosilicates in the oceanic sequences of the Mesozoic Piedmont-Ligurian basin is well known since the study of Gennaro (1925) reporting the occurrence of "ardennite" in piemontite-bearing micaschists from the Lanzo Valleys, observing the similarity between these rocks and those described by Stella (1894). Recently, Barresi et al. (2007) described the new mineral

ardennite-(V) from Sparone, Locana Valley, Piedmont, Italy, not far from Lanzo Valleys.

Punta Gensane was not considered so far an important mineralogical locality and its mineralogy and petrography were never described; the occurrence of "ardennite" from this locality was reported by Piccoli et al. (2007), who quoted the results of Chimenti (2004). Old specimens labeled as "ardennite" were kept in the mineralogical collections of the Museo Regionale di Scienze Naturali of Torino, donated by Ferruccio Zambonini (1880–1932), at the beginning of XX century.

The crystallization of lavoisierite is related to the Alpine tectono-metamorphic events involving (Mn, Al)-rich metasediments. Associated minerals are quartz, "mica," sursassite, piemontite, spessartine, braunite, and "tourmaline."

Mineral characterization

Appearance and physical properties

Lavoisierite occurs as acicular and prismatic-tabular crystals, elongated on [010] and flattened on {001}, up to a few millimeters in length. It is yellow-orange in color, with white streak and vitreous luster. In plane-polarized light, lavoisierite is transparent and pleochroic, pale yellow parallel to [010] and yellow-orange normal to this direction. Between crossed polars, the mineral shows parallel extinction, with positive elongation parallel to [010]. Birefringence is moderate. Refractive indices were measured in white light using the Becke line method; along [010] and

Table 1 Chemical data (average of 3 analyses) for lavoisierite

Oxide	wt%	Range	Probe standard
P_2O_5	2.08	1.88–2.88	Apatite
V_2O_5	0.37	0.28–0.43	Metallic V
SiO_2	34.81	34.26–35.17	Diopside
TiO_2	0.13	0.05–0.20	Ilmenite
Al_2O_3	22.92	22.45–23.57	Plagioclase
Cr_2O_3	0.32	0.22–0.42	Chromite
Fe_2O_3	0.86	0.36–1.11	Ilmenite
MgO	5.73	5.57–5.83	Olivine
$MnO_{(tot)}$*	25.31	24.94–25.92	Bustamite
CaO	1.94	1.74–2.11	Diopside
Na_2O	0.01	0.00–0.02	Albite
$H_2O_{(calc)}$**	5.45		
Total***	100.63		

* Recalculated as MnO 19.09, Mn_2O_3 6.92, as to yield 32 total cations pfu and 100 positive charges

** Calculated so as to give 56 anions pfu and an O/OH ratio so as to achieve the charge balance

*** Including $H_2O_{(calc)}$ and the recalculated MnO and Mn_2O_3 instead of $MnO_{(tot)}$

Table 2 Observed powder X-ray diffraction data for lavoisierite

I_{obs}	d_{meas}	I_{calc}	d_{calc}	h k l	I_{obs}	d_{meas}	I_{calc}	d_{calc}	h k l
		17	8.46	1 0 1			13	2.327	2 2 4
w	7.13	18	7.10	1 0 3	m	2.318	7	2.324	3 1 7
w	6.07						21	2.314	1 1 14
vw	5.70	1	5.71	0 1 1			18	2.287	2 2 5
vw	5.45				m	2.263	43	2.258	3 1 8
w	4.99	5	5.02	1 0 6			14	2.256	2 0 14
w	4.73	9	4.77	1 1 1			18	2.240	2 2 6
m	**4.62**	100	4.65	1 1 2	mw	2.164	37	2.157	4 0 2
		16	4.62	0 0 8			16	2.143	2 0 15
w	4.52	13	4.51	1 0 7	mw	2.108	41	2.106	0 2 12
w	4.48	47	4.48	1 1 3			26	2.075	2 2 9
m	4.23	33	4.23	2 0 2			14	2.049	4 0 6
vw	3.961	10	3.93	2 0 4	w	2.045	6	2.045	3 2 0
m	3.747	66	3.745	2 0 5			9	2.039	2 0 16
		11	3.712	1 0 9	mw	2.019	17	2.021	4 1 2
w	3.556	14	3.550	2 0 6			34	2.016	2 2 10
w	3.440	2	3.457	2 1 1	vw	1.979	15	1.982	3 1 12
m	3.167	31	3.165	2 0 8			9	1.955	2 2 11
vw	3.037	8	3.024	2 1 6	w	1.874	8	1.873	4 0 10
		77	2.930	1 1 10			15	1.870	1 3 2
vs	**2.931**	33	2.896	3 0 0	m	1.808	31	1.804	0 2 16
		47	2.888	0 2 0			6	1.803	1 1 19
vw	2.815	12	2.815	2 0 10	w	1.788	11	1.781	4 1 10
		24	2.764	3 0 4	vw	1.681	7	1.675	1 3 10
s	**2.765**	17	2.756	0 2 4	w	1.657	6	1.657	5 1 2
		90	2.754	1 1 11			7, 11	1.649	5 1 3, 4 2 7
		25	2.710	1 2 2	vw	1.636	11	1.640	1 3 11
mw	2.659	57	2.657	2 0 11			10	1.611	4 1 14
		34	2.593	1 1 12	w	1.607	69	1.604	1 3 12
s	**2.598**	78	2.589	3 1 0			23	1.603	3 3 0
		13	2.583	3 1 1			16	1.599	4 2 9
w	2.517	22	2.512	2 0 12			12	1.586	1 1 22
		14	2.504	1 2 6	m	1.576	57	1.571	4 2 10
ms	**2.448**	80	2.449	0 2 8			6	1.566	2 0 22
		39	2.447	1 1 13			8	1.556	0 2 20
		6	2.414	2 1 11	m	1.544	33	1.542	4 2 11
w	2.403	13	2.405	2 2 0	w	1.517			
		17	2.400	2 2 1					

The d_{hkl} values were calculated on the basis of the unit cell refined by using single-crystal data. Intensities ($I/I_{100} \times 100 > 1$ only) were calculated on the basis of the structural model. Observed intensities were visually estimated

The five strongest reflections are shown in bold

vs very strong, *s* strong, *ms* medium-strong, *m* medium, *mw* medium-weak, *w* weak, *vw* very weak

normal to this direction, the measured refractive indices are >1.69. The mean refractive index *n* of lavoisierite, calculated using the Gladstone-Dale relationship (Mandarino 1979, 1981) and the empirical formula, is 1.750.

Density was not measured, due to the difficult in separating lavoisierite from the admixed phases and the small crystal size; the calculated density, based on the empirical formula used for the calculation of the mean refractive index, is 3.576 g cm^{-3}.

Lavoisierite is brittle; no cleavage or parting were observed. Hardness could not be measured, due to the small size of crystals.

Chemical data

Quantitative chemical data were collected using a JEOL JXA-8200 electron microprobe, using an acceleration

voltage of 15 kV and a beam current of 20 nA. The beam size was set to 1 μm. Analytical data are reported in Table 1.

The chemical data were processed in order to give a chemical formula based on 56 anions. The analytical values of $MnO_{(tot)}$ were split between MnO and Mn_2O_3 to yield 32 total non-H cations per formula unit (*pfu*) and 100 positive charges. The O/OH ratio was adjusted as to achieve the charge balance; consequently, the wt% of H_2O was calculated accordingly and included in Table 1.

The empirical formula, based on 56 anions *pfu*, is $(Mn^{2+}_{5.340}Mg_{1.810}Ca_{0.686}Na_{0.006})_{\Sigma=7.852}(Al_{8.921}Mn^{3+}_{1.739}Mg_{1.010}Fe^{3+}_{0.214}Cr_{0.084}Ti_{0.032})_{\Sigma=12.000}(Si_{11.496}P_{0.582}V_{0.081})_{\Sigma=12.159}O_{43.995}(OH)_{12.005}$. The empirical formula simplifies to $(Mn^{2+}_5Mg_2Ca)_{\Sigma8}(Al_9Mn^{3+}_2Mg)_{\Sigma12}(Si_{11}P)O_{44}(OH)_{12}$. However, since Mn^{2+} is the dominant cation at the *A* sites, and Al is the dominant cation at the *M*2, *M*3, and *M*4 sites (see below), the ideal formula could be written $Mn^{2+}_8[Al_{10}(Mn^{3+}Mg)](Si_{11}P)O_{44}(OH)_{12}$. At the *M*1 site, both Mn^{3+} and Mg^{2+} must occur, being a case of valency-imposed double site occupancy (Hatert & Burke, 2008).

X-ray crystallography and crystal structure determination

The powder X-ray diffraction pattern of lavoisierite was obtained using a 114.6-mm Gandolfi camera and Ni-filtered CuKα radiation (Table 2). Indexing of the reflections was based on a calculated powder pattern obtained by the structural model described below, using the software POWDERCELL (Kraus and Nolze 1996). The unit-cell parameters were not refined from the powder data, owing to the multiplicity of indices of the majority of the most intense diffraction lines.

Single-crystal X-ray diffraction data were collected using an Oxford Xcalibur single-crystal diffractometer equipped with a Sapphire 3 CCD area detector, with graphite-monochromatized MoKα radiation, at the Centro Interdipartimentale di Analisi e Determinazioni Strutturali (CIADS) of the University of Siena. The detector-to-crystal working distance was 45 mm. The data were corrected for Lorentz and polarization factors; an analytical numerical absorption correction using a multifaceted crystal model was applied (Clark and Reid 1995). Crystal data and experimental details are reported in Table 3.

The refinement of the unit-cell parameters gave $a = 8.6891(10)$, $b = 5.7755(3)$, $c = 36.9504(20)$ Å, $V = 1854.3(2)$ Å^3. The *a:b:c* ratio is 1.505:1:6.398. A total of 2382 independent reflections were collected, and the structure was solved and refined by means of the SHELX set of programs (Sheldrick 2008).

The $|E^2-1|$ value is 1.076, thus suggesting a possible presence of a center of symmetry; space group absences

suggest a possible space group *Pnmm*, the same as "ardennite". A trial was done in solving the crystal structure assuming this space group symmetry, using the SHELXS-97 (Sheldrick 2008) software. The positions of the heaviest atoms, that is, Mn, were located; through successive difference-Fourier maps, the crystal structure was completed. Scattering curves for neutral atoms were taken from the International Tables for X-ray Crystallography (1992).

The crystal structure of lavoisierite shows eight sixfold and sevenfold coordinated sites, seven tetrahedral sites, and 23 anion sites. The occupancy of the eight independent cation sites was refined using the following curves: Mn *versus* Ca at the *A*1 site; Mn *versus* Mg at the *A*2, *A*3, *A*4, and *M*1 sites; Al *versus* Mn at the *M*2, *M*3, and *M*4 sites.

The site occupancy of the *M*1 site points to $Mn_{0.492(6)}Mg_{0.508(6)}$, in good agreement with the expected value of $Mn_{0.50}Mg_{0.50}$, corresponding to the ideal valency-imposed double site occupancy; consequently, the site occupancy of this site was fixed at the ideal value. The site occupancy of the *M*4 site points to a full occupancy by

Table 3 Crystal data and summary of parameters describing data collection and refinement for lavoisierite

Crystal data	
Crystal size (mm^3)	$0.19 \times 0.10 \times 0.05$
Cell setting, space group	Orthorhombic, *Pnmm*
Unit-cell dimensions	
a (Å)	8.6891(10)
b (Å)	5.7755(3)
c (Å)	36.9504(20)
V (Å^3)	1854.3(2)
Z	2
Data collection and refinement	
Radiation type (λ)	MoKα (0.71073 Å)
Temperature (K)	∼298
Maximum observed 2θ (°)	58.09
Measured reflections	5683
Unique reflections	2382
Reflections $F_o > 4\sigma F_o$	1743
R_{int}	0.0257
$R\sigma$	0.0375
Range of *h, k, l*	$-3 \leq h \leq 10$
	$-6 \leq k \leq 7$
	$-49 \leq l \leq 49$
$R_1 [F_o > 4\sigma F_o]$	0.0464
R_1 (all data)	0.0666
wR_2 (on F_o^2)	0.1403
Goof	1.254
Number of l.s. parameters	239
$\Delta\rho_{max}$ and $\Delta\rho_{min}$	1.29, −1.46

aluminum. The tetrahedral *T* sites are occupied by silicon, with the exception of the small *T*4 site; its occupancy was fixed at (Si$_{0.50}$P$_{0.50}$), taking into account both the chemistry and the average *T*4–O bond length.

Introducing anisotropic displacement parameters for cations and anions (with the exception of five oxygen atoms, that gave negative displacement parameters), R_1 converged to 0.046 for 1743 observed reflections and 239 parameters. The atomic coordinates and the equivalent or isotropic displacement parameters are given in Table 4; selected bond distances are given in Table 5.

Table 4 Atomic coordinates and equivalent isotropic or isotropic (*) displacement parameters (Å^2) for lavoisierite

Atom	Wyckoff site	Occupancy	x/a	y/b	z/c	U_{eq} or U_{iso}^*
A1	4f	Mn$_{0.58(1)}$Ca$_{0.42(1)}$	0.8689(2)	1/4	0.70330(4)	0.0077(5)
A2	4f	Mn$_{0.70(1)}$Mg$_{0.30(1)}$	0.4267(2)	3/4	0.70586(4)	0.0068(5)
A3	4f	Mn$_{0.74(1)}$Mg$_{0.26(1)}$	0.7841(2)	3/4	0.45668(4)	0.0073(5)
A4	4f	Mn$_{0.76(1)}$Mg$_{0.24(1)}$	0.7581(2)	3/4	0.54683(4)	0.0065(5)
M1	4e	Mn$_{0.50}$Mg$_{0.50}$	0.1327(2)	0.0055(3)	3/4	0.0054(4)
M2	4d	Al$_{0.98(1)}$Mn$_{0.02(1)}$	1/2	0	1/2	0.0050(8)
M3	8g	Al$_{0.97(1)}$Mn$_{0.03(1)}$	0.8166(2)	0.0001(3)	0.62447(4)	0.0032(5)
M4	8g	Al$_{1.00}$	0.3153(2)	−0.0012(3)	0.62469(5)	0.0037(4)
T1	4f	Si$_{1.00}$	0.4213(3)	3/4	0.42329(6)	0.0035(5)
T2	4f	Si$_{1.00}$	0.0522(3)	3/4	0.67290(6)	0.0033(5)
T3	4f	Si$_{1.00}$	0.5384(3)	1/4	0.67216(6)	0.0037(5)
T4	2a	Si$_{0.50}$P$_{0.50}$	0.7723(4)	3/4	3/4	0.0044(6)
T5	4f	Si$_{1.00}$	0.0932(3)	3/4	0.57618(6)	0.0032(5)
T6	4f	Si$_{1.00}$	0.8441(3)	1/4	0.50173(6)	0.0052(5)
T7	2b	Si$_{1.00}$	0.4800(4)	1/4	3/4	0.0040(7)
O1	8g	O$_{1.00}$	0.4396(5)	0.0164(8)	0.6667(1)	0.0052(5)
O2	4f	(OH)$_{1.00}$	0.9645(8)	1/4	0.5361(2)	0.0081(13)
O3	4f	O$_{1.00}$	0.6705(8)	3/4	0.7154(2)	0.0121(14)
O4	8g	O$_{1.00}$	0.9464(5)	−0.0241(8)	0.6657(1)	0.0057(9)
O5	4f	O$_{1.00}$	0.5095(8)	3/4	0.4634(2)	0.0059(12)*
O6	4f	O$_{1.00}$	0.1159(8)	1/4	0.7158(2)	0.0102(14)
O7	4f	O$_{1.00}$	0.9268(7)	3/4	0.5976(2)	0.0059(12)
O8	4f	O$_{1.00}$	0.7038(8)	1/4	0.6506(2)	0.0053(12)*
O9	4f	O$_{1.00}$	0.5974(8)	1/4	0.7154(2)	0.0068(13)*
O10	8g	O$_{1.00}$	0.7402(5)	−0.9877(8)	0.5007(1)	0.0088(9)
O11	4f	(OH)$_{1.00}$	0.9289(8)	1/4	0.6066(2)	0.0061(12)
O12	4f	(OH)$_{1.00}$	0.4312(8)	3/4	0.6065(2)	0.0050(12)
O13	4f	(OH)$_{1.00}$	0.7033(8)	3/4	0.6418(2)	0.0055(12)*
O14	8g	O$_{1.00}$	0.1923(5)	−0.0174(8)	0.5824(1)	0.0064(8)
O15	4f	O$_{1.00}$	0.1974(7)	3/4	0.6449(2)	0.0046(12)
O16	4f	O$_{1.00}$	0.5672(7)	3/4	0.3953(2)	0.0059(12)
O17	4f	O$_{1.00}$	0.1381(8)	3/4	0.7134(2)	0.0111(14)
O18	4f	(OH)$_{1.00}$	0.4864(7)	1/4	0.4665(2)	0.0073(13)*
O19	4f	(OH)$_{1.00}$	0.1986(7)	1/4	0.6418(2)	0.0062(12)
O20	8g	O$_{1.00}$	0.3137(5)	−0.0245(7)	0.4167(1)	0.0051(8)
O21	4f	O$_{1.00}$	0.9627(7)	1/4	0.4668(2)	0.0066(13)
O22	4e	O$_{1.00}$	0.8769(8)	−0.0251(13)	3/4	0.0151(15)
O23	4e	O$_{1.00}$	0.3812(7)	0.0100(11)	3/4	0.0067(13)

The occupancy values take into account the site multiplicity. Occupancies without esds mean that those values were held fixed

Description and discussion of the structure

General features and cation coordination

The crystal structure of lavoisierite is formed by chains of edge-sharing M octahedra connected by ortho-, di-, and trisilicate groups (Fig. 1). A slightly smaller tetrahedron has a mixed (P, Si) occupancy. Sixfold to sevenfold coordinated A sites are hosted in the cavities of the structure.

The chains of octahedra are formed by four independent M site.

$M1$ is a distorted octahedron, with four shorter and two longer bonds, as observed in "ardennites" by Pasero et al. (1994). The distortion may be due to the presence of Mn^{3+} in this site, but an important role may be played also by the O22 site, which is linked to two cations with different charge, that is, (Mn^{3+}, Mg^{2+}) at $M1$ and (P^{5+}, Si^{4+}) at $T4$. This octahedron is bonded to the isolated $T4$ tetrahedron, to the middle-tetrahedron in the trisilicate groups, to the $T2$ tetrahedra. Along $\mathbf{b}$, it forms chains of $M1$ octahedra through edge-sharing.

$M2$, $M3$, and $M4$ are Al-centered octahedra, with a small proportion of heavier cations, that is, Mn^{3+}. $M2$ is bonded to the $T6$ tetrahedra of the disilicate groups, to the isolated $T1$ tetrahedra, and forms chains of octahedra along b through edge-sharing. $M3$ and $M4$ octahedra forms chains

along [010] through edge-sharing, connected each other through silicate tetrahedra.

All the T sites but $T4$ host Si^{4+} cations, whereas the $T4$ site is a mixed (P, Si) site. The average bond lengths of the Si tetrahedra range between 1.630 and 1.646 Å; the $T4$ site is significantly smaller, with an average bond length of 1.570 Å, in agreement with the partial substitution of Si^{4+} by the smaller P^{5+} cation. $T1$, $T2$, and $T4$ are isolated tetrahedra; $T5$ and $T6$ are bonded through corner-sharing, forming disilicate groups, whereas $T3$-$T7$-$T3$ form trisilicate groups.

The larger A sites are hosted in the cavities of the structure. $A1$ and $A4$ are sevenfold coordinated and are mixed (Mn^{2+}, Ca) and (Mn^{2+}, Mg) sites, with average bond length of 2.30 and 2.28 Å, respectively. The $A2$ and $A3$ sites are sixfold coordinated, with an average bond length of about 2.23 Å; an additional bond at ~ 2.95–3.00 Å arises the coordination number up to seven. These two sites are occupied by Mn^{2+}, with minor Mg.

Bond-valence balance in lavoisierite

Table 6 reports the bond valence sums (BVS) for the sites of lavoisierite, calculated following Brese and O'Keeffe (1991).

A sites are mixed manganese-, magnesium-, and calcium-bearing sites. During the bond valence calculation, it was assumed that Ca^{2+} is completely distributed at the $A1$

Table 5 Selected bond distances (Å) for lavoisierite

| $A1$	–O6	2.195(7)	$A2$	–O1 × 2	2.115(4)	$A3$	–O14 × 2	2.124(4)	$A4$	–O20 × 2	2.172(4)
	–O4 × 2	2.212(4)		–O3	2.148(7)		–O2	2.200(7)		–O18	2.182(6)
	–O22 × 2	2.346(5)		–O23 × 2	2.253(4)		–O10 × 2	2.255(5)		–O10 × 2	2.286(5)
	–O9	2.401(7)		–O17	2.523(7)		–O5	2.400(6)		–O7	2.381(6)
	–O8	2.419(9)		Average	2.234		Average	2.226		–O21	2.478(6)
	Average	2.304		–O15	3.008(6)		–O16	2.950(7)		Average	2.280
$M1$	–O6 × 2	1.900(4)	$M2$	–O18 × 2	1.905(4)	$M3$	–O13	1.861(4)	$M4$	–O12	1.879(4)
	–O17 × 2	2.002(4)		–O5 × 2	1.980(4)		–O11	1.864(4)		–O19	1.880(4)
	–O23	2.159(6)		–O10 × 2	2.089(5)		–O4	1.900(4)		–O1	1.894(4)
	–O22	2.230(7)					–O20	1.903(4)		–O14	1.895(4)
	Average	2.032		Average	1.991		–O8	1.994(4)		–O15	1.916(4)
							–O7	1.998(4)		–O16	1.921(4)
							Average	1.920		Average	1.898
$T1$	–O20 × 2	1.621(4)	$T2$	–O4 × 2	1.618(4)	$T3$	–O1 × 2	1.612(4)	$T4$	–O3 × 2	1.553(6)
	–O16	1.637(6)		–O15	1.632(6)		–O8	1.645(6)		–O22 × 2	1.586(7)
	–O5	1.668(6)		–O17	1.673(6)		–O9	1.678(6)		Average	1.570
	Average	1.637		Average	1.635		Average	1.637			
$T5$	–O14 × 2	1.612(4)	$T6$	–O10 × 2	1.644(5)	$T7$	–O23 × 2	1.629(6)			
	–O7	1.648(6)		–O2	1.644(6)		–O9 × 2	1.636(6)			
	–O21	1.660(6)		–O21	1.652(7)		Average	1.632			
	Average	1.633		Average	1.646						
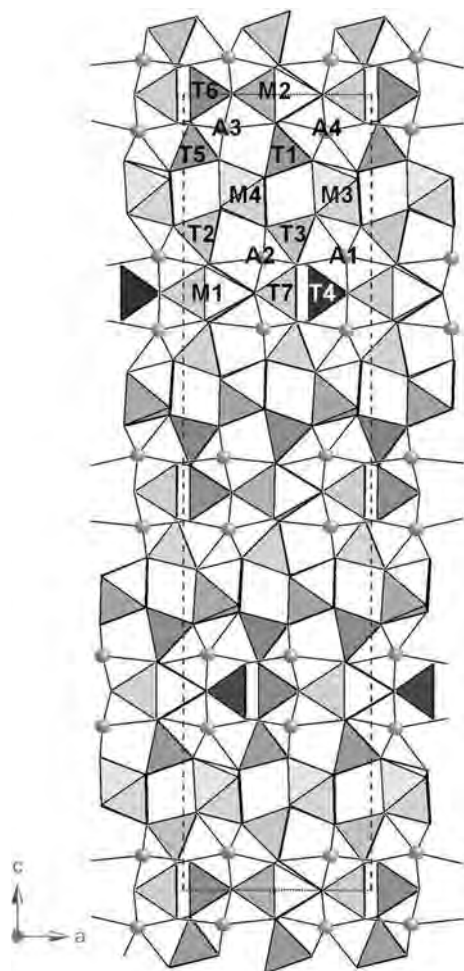
Fig. 1 Crystal structure of lavoisierite, as seen down [010]

site, whereas the other three remaining sites have a mixed (Mn^{2+}, Mg^{2+}) occupancy. Owing to the slight oversaturation at $A1$ site and under saturation at $A2$, $A3$, and $A4$ sites, it is possible that the substitution of calcium and magnesium for manganese takes place randomly at all the four independent sites, since the refined site-scattering values of the four A sites are rather similar, that is, 22.9, 21.1, 21.6, and 21.8 electrons per formula unit (*epfu*) for $A1$, $A2$, $A3$, and $A4$ sites, respectively.

M sites can be divided into the mixed (Mn^{3+}, Mg^{2+}) $M1$ site, on one side, and the three independent $M2$, $M3$, and $M4$ sites, on the other side. The latter are preferentially occupied by aluminum, with small substitutions by Mn^{3+}, Fe^{3+}, Cr^{3+}, and Ti^{4+}, probably concentrated in $M2$.

$M1$ site is slightly oversaturated, deviating of about 12 % from the ideal value; probably, this deviation could be related with the uncertainties of the anion position, owing to the different crystal-chemical behavior of Mn^{3+} and Mg^{2+}, with the former displaying Jahn–Teller effect (Greenwood and Earnshaw 1997). Another possibility is

that aluminum partially substitutes for magnesium, in agreement with the substitution required for the introduction of silicon in $T4$.

The discrepancy between the observed and expected BVS for the $M2$ site can be related with the substitution of the small Al^{3+} cation with larger ones, that is, Mn^{3+}, Fe^{3+}, Cr^{3+}. However, the refined site-scattering value, 13.2 *epfu*, does not indicate significant deviations from a full site occupancy by aluminum.

Considering the anions, the BVSs are significantly different from 2 valence units (*vu*) for O2, O3, O6, O11, O12, O13, O18, and O19. The examination of the O···O distances shorter than 3.0 Å between atoms not belonging to the same polyhedron suggests that those oxygens are involved in the hydrogen bond system (see Table 7). The under saturation of O3 and O6 oxygen atoms is removed by their linkages with O13 (for O3) and O19 (for O6); on the contrary, the remaining sites are occupied by hydroxyls. The allocation of hydroxyls results in 44 oxygens and 12 hydroxyls.

The chemical formula obtained through the structural study is $(Mn_{6.00}Mg_{1.36}Ca_{0.64})_{\Sigma8.00}[Al_{9.08}Mn_{0.92}(Mn_{1.00}Mg_{1.00})]_{\Sigma12.00}(P_{0.50}Si_{0.50}O_4)(SiO_4)_4(Si_2O_7)_2(Si_3O_{10})(OH)_{12}$. This formula is not charge balanced, owing to the partial substitution of phosphorus by silicon, that requires an additional substitution. This issue is discussed in the following paragraph.

Phosphorus : silicon substitution at the T4 site

Ideally, lavoisierite should have $[T^{4+}_{11}T^{5+}]$; in the studied sample, the T^{5+} cation is partially substituted by T^{4+}. The substitution of P^{5+} by Si^{4+} at the $T4$ site agrees with both chemical and structural data. In fact, chemical data show the presence of only 0.58 P *apfu* and an excess of Si (11.50 *apfu*); the average bond distance in the $T4$ site is in accord with a mixed (P, Si) site. Consequently, it is important to discuss the possible mechanism involved in $P^{5+} \rightarrow Si^{4+}$ substitution.

We can hypothesize two possible mechanisms, involving both cation and anion sites:

1. $^{T4}P^{5+} + {}^{M1}Mg^{2+} = {}^{T4}Si^{4+} + {}^{M1}Me^{3+}$,
   where $Me^{3+} = Mn^{3+}, Al^{3+}$;
2. $^{T4}P^{5+} + {}^{O3}O^{2-} = {}^{T4}Si^{4+} + {}^{O3}OH^-$.

Assuming a $T4$ site population of $P_{0.50}Si_{0.50}$, the site occupancy of $M1$ site, according to the first mechanism, would be $(Mn^{3+}_{0.50}Al_{0.25}Mg_{0.25})$. This cation distribution matches well the refined electron density of $M1$ site. In fact, it corresponds to ~ 18.8 *epfu*, to be compared with the refined value of 18.5 *epfu*. In this way, the slight oversaturation observed in the BVS would be removed, obtaining 2.71 *vu*, to be compared with an expected value of 2.75 *vu*.

Table 6 Bond–valence calculations for lavoisierite, according to Brese and O'Keeffe (1991)

Site	A1	A2	A3	A4	M1	M2	M3	M4	T1	T2	T3	T4	T5	T6	T7	Σν (O–X)	Σν (O–X)$	Species
O1		0.39*					0.52				1.03*					1.94	1.94	O^{2-}
O2			0.31											0.95		1.26	0.99	OH^-
O3		0.35										1.18*				1.53	1.74	O^{2-}
O4	0.40*						0.52			1.02*						1.94	1.94	O^{2-}
O5		0.18			0.41*·**			0.89								1.89	1.89	O^{2-}
O6	0.42				0.63*·**											1.68	1.85	O^{2-}
O7				0.19		0.40**							0.94			1.93	1.93	O^{2-}
O8	0.23					0.40**						0.95				1.98	1.98	O^{2-}
O9	0.24											0.86			0.97*	2.07	2.07	O^{2-}
O10			0.27*	0.25*	0.31*								0.95*			1.78	1.78	O^{2-}
O11						0.57**										1.14	1.17	OH^-
O12							0.54**									1.08	1.03	OH^-
O13						0.57**										1.14	1.16	OH^-
O14			0.38*				0.52						1.03*			1.93	1.93	O^{2-}
O15		0.03					0.49**		0.98							1.96	1.96	O^{2-}
O16			0.04				0.48**		0.97							1.97	1.97	O^{2-}
O17		0.13			0.48*·**					0.88						1.97	1.97	O^{2-}
O18				0.33	0.51*·**											1.35	1.17	OH^-
O19							0.54**									1.08	1.15	OH^-
O20				0.34*			0.51		1.01*							1.86	1.85	O^{2-}
O21				0.15									0.91	0.93		1.99	1.99	O^{2-}
O22	0.28*·**				0.26							1.08*				1.90	1.90	O^{2-}
O23		0.27*·**			0.31										0.99*	1.84	1.84	O^{2-}
Σν (X–O)	2.25	1.83	1.83	1.85	2.79	2.46	2.97	3.09	3.88	3.90	3.87	4.52	3.91	3.78	3.92			
Expected value	2.00	2.00	2.00	2.00	2.50	3.00	3.00	3.00	4.00	4.00	4.00	4.50	4.00	4.00	4.00			

* Two bonds for each cation

** Two bonds for each anion

$ Bond valence sum obtained after considering the hypothesized hydrogen bonds

Table 7 O···O distances (in Å) in the suggested hydrogen-bonding scheme, with corresponding bond-valence values (vu) according to Ferraris and Ivaldi (1988)

O···O bond donor → acceptor	d (Å)	vu
O2 (OH) → O11 (OH)	2.623(8)	0.27
O11 (OH) → O19 (OH)	2.680(9)	0.24
O13 (OH) → O3 (O)	2.738(8)	0.21
O12 (OH) → O13 (OH)	2.700(8)	0.23
O18 (OH) → O12 (OH)	2.790(8)	0.19
O19 (OH) → O6 (O)	2.830(8)	0.17

Unfortunately, such a distribution involves a lower magnesium and a higher aluminum content than those observed.

The second mechanism could lead to the hydroxylation of O3 site. BVS indicates that this anion site is under satured and consequently it could be potentially a mixed (O, OH) site. Also in this case, an unequivocal confirmation of our hypothesis is lacking.

Relationship with other species

Lavoisierite is chemically and structurally related to sursassite and "ardennite" (Fig. 2; Table 8); repeats along **a** and **b** are similar for all minerals, whereas $c_{(Lav)} = c_{(Ard)} + 2c_{(Srs)}\sin\beta$. As previously described, in sursassite, chains of edge-sharing octahedra are connected to each other through SiO_4 and Si_2O_7 groups; in "ardennite," columns of edge-sharing octahedra are bonded by means of SiO_4 and Si_3O_{10} groups. In lavoisierite, both modes of connection are present: there are slabs with SiO_4 and Si_2O_7 groups (sursassite-type slab) and slabs with SiO_4 and Si_3O_{10} groups (ardennite-type slab). The regular alternation, along [001], of sursassite-type and ardennite-type slabs, in 1:1 ratio, gives rise to the crystal structure of lavoisierite. Its ideal chemical formula may be obtained as the result of the sum of the chemical formulae of sursassite and "ardennite," as follows:

Sursassite:	Mn_4^{2+}	Al_6	$(SiO_4)_2(Si_2O_7)_2$	$(OH)_6$
"Ardennite":	Mn_4^{2+}	$M_5^{3+}Mg$	$(SiO_4)_2(T^{5+}O_4)(Si_3O_{10})$	$(OH)_6$
Lavoisierite:	Mn_8^{2+}	$M_{11}^{3+}Mg$	$(SiO_4)_4(Si_2O_7)_2$ $(T^{5+}O_4)(Si_3O_{10})$	$(OH)_{12}$

Here, $M^{3+} = Al^{3+}$, Mn^{3+}; $T = As^{5+}$ in ardennite-(As), V^{5+} in ardennite-(V), P^{5+} in lavoisierite. In the ardennite series, there are two mineral species, ardennite-(As) and ardennite-(V), in which the dominant T^{5+} cations are arsenic and vanadium, respectively (Barresi et al. 2007). Lavoisierite is the first case in which phosphorus is the dominant T^{5+} cation. The occurrence of T^{5+} in place of silicon at the insulated $T4$ tetrahedra is related to local charge balance requirements.

Pasero and Reinecke (1991) described an "anomalous ardennite" from Evvia Island, Greece, with a very high Si/(As + V + P) ratio, having a chemical composition $(Mn_{2.62}^{2+}Ca_{0.90}Mg_{0.44})_{\Sigma3.96}(Al_{4.16}Mn_{1.18}^{3+}Mg_{0.34}Fe_{0.25}^{3+}Ti_{0.04}Cu_{0.03})_{\Sigma6.00}(Si_{5.78}As_{0.20}P_{0.04}V_{0.01})_{\Sigma6.03}O_{22}(OH)_6$. A HRTEM study of this phase indicated the widespread occurrence of domains with a 37 Å c periodicity, which were interpreted by Pasero and Reinecke (1991) as a non-MDO polytype of "ardennite". Actually, this domain could be a new phase
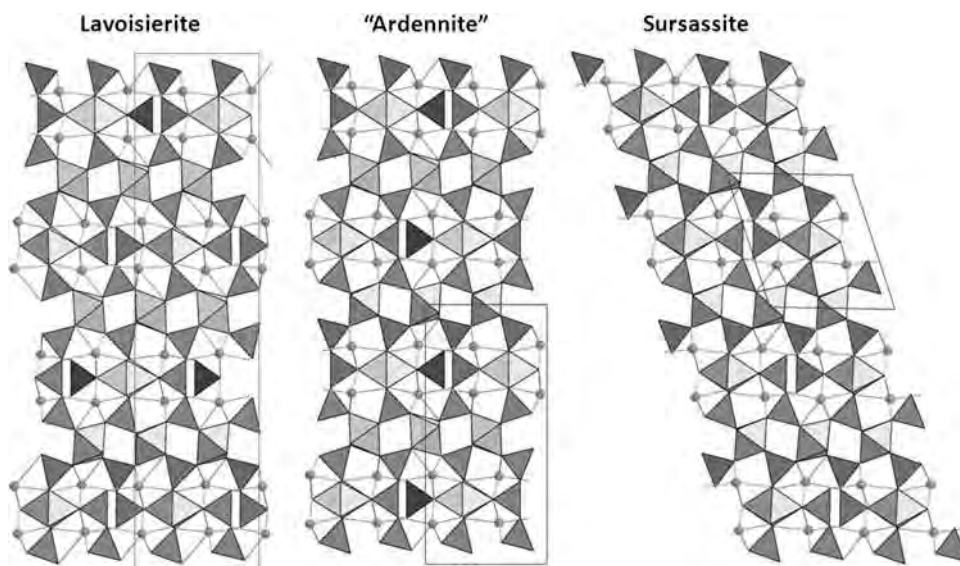
Fig. 2 Comparison between the crystal structures of lavoisierite, "ardennite," and sursassite

Table 8 Structurally related mixed-anion sorosilicates

	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	$\alpha(°)$	$\beta(°)$	$\gamma(°)$	s.g.	Chemical formula	Reference
Lavoisierite	8.69	5.78	36.95	90	90	90	$Pnmm$	$Mn_8[Al_{10}(Mn^{3+}Mg)](PO_4)(SiO_4)_4(Si_2O_7)_2(Si_3O_{10})(OH)_{12}$	[1]
Ardennite group									
Ardennite-(As)	8.71	5.81	18.52	90	90	90	$Pnmm$	$Mn_4(Al_5Mg)(AsO_4)(SiO_4)_2(Si_3O_{10})(OH)_6$	[2]
Ardennite-(V)	8.76	5.84	18.56	90	90	90	$Pnmm$	$Mn_4(Al_5Mg)(VO_4)(SiO_4)_2(Si_3O_{10})(OH)_6$	[3]
Sursassite group									
Macfallite	8.97	6.09	10.24	90	110.8	90	$P2_1/m$	$Ca_4Mn_6^{3+}[(SiO_4)(Si_2O_7)]_2(OH)_6$	[4]
Sursassite	8.70	5.79	9.78	90	108.9	90	$P2_1/m$	$Mn_4Al_6[(SiO_4)(Si_2O_7)]_2(OH)_6$	[5]
Pumpellyite-group									
Julgoldite-(Fe^{2+})	8.92	6.08	19.43	90	97.6	90	$A2/m$	$Ca_4(Fe_4^{3+}Fe_2^{2+})[(SiO_4)(Si_2O_7)]_2(OH)_4·2H_2O$	[6]
Julgoldite-(Fe^{3+})	8.89	6.06	19.33	90	97.5	90	$A2/m$	$Ca_4(Fe_4^{3+}Fe_2^{3+})[(SiO_4)(Si_2O_7)]_2O_2(OH)_2·2H_2O$	[7]
Julgoldite-(Mg)	No unit-cell parameters available							$Ca_4(Fe_4^{3+}Mg_2)[(SiO_4)(Si_2O_7)]_2 (OH)_4·2H_2O$	[8]
Okhotskite	8.89	6.00	19.53	90	97.1	90	$A2/m$	$Ca_4(Mn^{2+},Mg,Mn^{3+},Al,Fe^{3+})_6[(SiO_4)(Si_2O_7)]_2(O,OH)_6$	[9]
Poppiite	8.88	6.04	19.29	90	97.3	90	$A2/m$	$Ca_4(V^{3+},Fe^{3+},Mg,Mn^{2+})_2(V^{3+},Al)_4(Si,Al)_6O_{21}(OH)_7$	[10]
Pumpellyite-(Al)	8.82	5.90	19.13	90	97.3	90	$A2/m$	$Ca_4Al_6[(SiO_4)(Si_2O_7)]_2(OH)_4·2H_2O$	[11]
Pumpellyite-(Fe^{2+})	8.84	5.95	19.18	90	97.5	90	$A2/m$	$Ca_4(Al_4Fe_2^{2+})[(SiO_4)(Si_2O_7)]_2(OH)_4·2H_2O$	[12]
Pumpellyite-(Fe^{3+})	8.82	5.94	19.13	90	97.5	90	$A2/m$	$Ca_4(Al_4Fe_2^{3+})[(SiO_4)(Si_2O_7)]_2O_2(OH)_2·2H_2O$	[8]
Pumpellyite-(Mg)	8.82	5.92	19.13	90	97.4	90	$A2/m$	$Ca_4(Al_4Mg_2)[(SiO_4)(Si_2O_7)]_2(OH)_4·2H_2O$	[12]
Pumpellyite-(Mn)	8.85	5.93	19.12	90	97.0	90	$A2/m$	$Ca_4(Al_4Mn_2^{2+})[(SiO_4)(Si_2O_7)]_2(OH)_4·2H_2O$	[13]
Shuiskite	8.90	5.84	19.41	90	98.0	90	$A2/m$	$Ca_4[(Cr,Al)_4(Mg,Al)_2][(Si,Al)O_4]_2(Si_2O_7)_2(O,OH)_6$	[14]

[1] this work; [2] Donnay and Allmann (1968); [3] Barresi et al. (2007); [4] Moore et al. (1985); [5] Mellini et al. (1984); [6] Allmann and Donnay (1973); [7] Artioli et al. (2003); [8] Passaglia and Gottardi (1973); [9] Togari and Akasaka (1987); [10] Brigatti et al. (2006); [11] Hatert et al. (2007); [12] Artioli and Geiger (1994); [13] Artioli et al. (1996); [14] Ivanov et al. (1981)

structurally related to lavoisierite, with Si > P at the $T4$ site.

Summary and conclusion

Lavoisierite is the paradigm of the words by Galileo Galilei (Dialog concerning the two chief world systems—The second day; Florence 1632) «*Nature does not act by means of many things when it can do so by means of few*», used by Ferraris et al. (2008) in the introduction of their book about modular crystallography.

Lavoisierite is in fact an amazing example of polysomatism, being composed by alternating "ardennite-like" and "sursassite-like" slabs. This alternation gives rise to a peculiar crystal structure, showing three different kinds of polymerization of SiO_4 tetrahedra, that is, SiO_4, Si_2O_7, and Si_3O_{10} groups. Only another silicate displays three different kinds of SiO_4 polymers, that is, charoite, showing the presence of $[Si_6O_{17}]^{10-}$, $[Si_{12}O_{30}]^{12-}$, and $[Si_{17}O_{43}]^{18-}$ chains (Rozhdestvenskaya et al. 2010).

The role of P as pentavalent cation in "ardennite-like" slab and the substitution of P^{5+} by Si^{4+} open other research fields, suggesting the possibility of other new mineral phases (*e.g.* an hypothetical "ardennite-(P)" and a Si-analog of lavoisierite) among the mixed-anion silicates.

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