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Gelosaite, $BiMo^{6+}_{(2-5x)}Mo^{5+}_{6x}O_7(OH){\cdot}H_2O$ ($0 \leq x \leq 0.4$), a new mineral from Su Senargiu (CA), Sardinia, Italy, and a second occurrence from Kingsgate, New England, Australia

PAOLO ORLANDI,[1] FRANCESCO DEMARTIN,[2,*] MARCO PASERO,[1] PETER LEVERETT,[3]
PETER A. WILLIAMS,[3] AND DAVID E. HIBBS[4]

[1]Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, I-56126 Pisa, Italy
[2]Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università degli Studi di Milano, Via G. Venezian 21, I-20133 Milano, Italy
[3]School of Natural Sciences, University of Western Sydney, Locked Bag 1797, Penrith South DC, New South Wales 1797, Australia
[4]School of Pharmacy, University of Sydney, New South Wales 2006, Australia

ABSTRACT

Gelosaite, $BiMo^{6+}_{(2-5x)}Mo^{5+}_{6x}O_7(OH){\cdot}H_2O$ ($0 \leq x \leq 0.4$), occurs at the type locality in quartz veins hosted by granitic rocks at Su Senargiu, near Sarroch, Sardegna, Italy. The name is in memory of Mario Gelosa (1947–2006) who first found the mineral. The mineral also occurs in the oxidized zones of the Old 25 and Wolfram pipes at Kingsgate, New South Wales, Australia. Both the mineral and its name have been approved by the IMA CNMNC (IMA 2009-022). Gelosaite occurs as yellow, yellowish green, and pale blue, prismatic crystals with a white streak. It is transparent with an adamantine luster, non-fluorescent, brittle, and has a conchoidal fracture. Mohs hardness is ~3. The mineral is monoclinic, space group $P2_1/n$, with a = 5.8505(4), b = 9.0421(6), c = 13.917(1) Å, β = 100.42(1)°, V = 724.1(1) Å^3, Z = 4 (yellow Su Senargiu crystal); a = 5.8570(5), b = 9.0517(8), c = 13.992(1) Å, β = 100.44(1)°, V = 729.5(1) Å^3, Z = 4 (pale blue Su Senargiu crystal); a = 5.837(3), b = 9.040(5), c = 13.904(7) Å, β = 100.64(1)°, V = 721.0(6) Å^3, Z = 4 (blue Kingsgate crystal). Strongest lines in the powder X-ray pattern [d (Å)(I_{rel})] are 4.83(100), 3.41(21), 3.30(25), 3.015(50), 2.755(60), 2.080(50), 1.688(20), and 1.509(30). The single-crystal X-ray structure of gelosaite was determined for three separate crystals, two from Su Senargiu and one from Kingsgate. The structure consists of layers of distorted MoO_6 octahedra, plus minor amounts of interstitial Mo ions, and layers made up of eight-coordinate Bi^{3+} ions, plus further small amounts of interstitial Mo ions. The theoretical Mo(VI) end-member has the stoichiometry $BiMo^{6+}_2O_7(OH){\cdot}H_2O$ and excess Mo in the interstices requires increasing amounts of Mo(V) to be present. The theoretical Mo(V) end-member has the stoichiometry $BiMo^{5+}_{2.4}O_7(OH){\cdot}H_2O$.

Keywords: Gelosaite, new mineral, crystal structure, Su Senargiu, Kingsgate

INTRODUCTION

We describe here the first and second occurrences of gelosaite, $BiMo^{6+}_{(2-5x)}Mo^{5+}_{6x}O_7(OH){\cdot}H_2O$ ($0 \leq x \leq 0.4$), a new bismuth molybdenum hydrated oxide mineral from two different localities. The type locality is Su Senargiu, Sarroch (CA), Sardinia, Italy. After submission of the proposal for the new mineral from Su Senargiu to the IMA CNMNC, the Italian authors were informed by the Chairman of the Commission that Australian colleagues were studying the same phase from Kingsgate, Australia. After approval of the new mineral from Su Senargiu (Sardinia, Italy), it was decided to publish the description from both localities together. The new mineral and its name were approved by the IMA CNMNC (IMA 2009-022). The name gelosaite is in memory of Mario Gelosa (1947–2006), an Italian mineral collector from Porto Torres, Sardinia, Italy, who first explored the dumps of the small, abandoned molybdenite mine at Su Senargiu, where the new mineral sardignaite, $BiMo_2O_7(OH){\cdot}2H_2O$, is also found (Orlandi et al. 2010). The holotype of gelosaite is deposited in the mineralogical collection of the Museo di Storia Naturale e del Territorio of the University of Pisa, catalog number 18910.

GEOLOGICAL SETTING

Su Senargiu

The presence of Mo mineralization in Sardinia, details of which are given by Orlandi et al. (2010), has been known for more than a century (Jervis 1881; Lovisato 1886; Traverso 1898). All deposits are related to leucogranitic intrusions of Hercynic age (Ghezzo et al. 1981). The only primary Mo-bearing mineral is molybdenite, associated with pyrite and minor wolframite, sphalerite, and scheelite. The locality of Su Senargiu is located in the easternmost part of Sulcis, Sardinia, and Mo mineralization crops out on the slope of the Su Senargiu mountain at 260 m

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* E-mail: francesco.demartin@unimi.it

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above sea level, near the village of Sarroch, not far from the town of Cagliari. Here, molybdenite is associated with pyrite, bismuthinite, and sphalerite in quartz veins ranging from 5 to 15 cm thick and more rarely in the granite itself (Caboi et al. 1978). Study of samples collected from small dumps in front of the three galleries worked between 1934 and 1953 yielded in addition native bismuth, cassiterite, anatase, brookite, aeschynite-(Ce), synchysite-(Ce), xenotime-(Y), bismoclite, ferrimolybdite, koechlinite, wulfenite, powellite, and muscovite.

Kingsgate

The Kingsgate bismuth-molybdenite deposits are situated 28 km east of Glen Innes in the New England district of northeastern New South Wales, Australia. Mineralization is largely confined to quartz-rich pipes in a leucogranite of Permian age (Andrews 1916; Lawrence and Markham 1962). Primary minerals present have been described in detail (Lawrence and Markham 1962; Lawrence et al. 1998; Clissold et al. 2008), as well as the extensive range of secondary Mo and Bi minerals present in the oxidized zones of the pipes (England 1985; Sharpe and Williams 2004).

OCCURRENCE AND PHYSICAL PROPERTIES

Su Senargiu

Only three small samples of gelosaite were found at the type locality, where the mineral occurs in cavities in quartz veins within a granite rock. Gelosaite is a secondary mineral formed in the oxidation zone and is associated with sardignaite, ferrimolybdite, koechlinite, wulfenite, and muscovite. It occurs as prismatic and very thin, elongated [010] and tabular {100} crystals up to 1 mm in length and a few micrometers in diameter (Fig. 1). Twinning was not observed in material from this locality.

Colorless or pale blue and yellow crystals are transparent with an adamantine luster, have a white streak, are non-fluorescent, and are brittle with a conchoidal fracture. Mohs hardness is ~3. Density was not measured because its value was too high to be studied using conventional heavy liquids and there was not enough material available for weighing methods. The calculated density is 5.114 g/cm^3 (yellow crystal). Refractive indices were not determined due to their very high values (average n_{calc} = 2.04) and the small amount of material available. Gelosaite is anisotropic and birefringent, and pale blue crystals show blue and pale blue pleochroism.

Kingsgate

Gelosaite was originally recovered from a single boulder of quartz from the waste dumps of the Old 25 pipe. Crystals up to 0.5 mm in size are tabular {100} and range in color from pale yellow and greenish yellow to pale blue. These occur perched on quartz crystals in vugs (Fig. 2) associated with bismutite. Several dozens of specimens were collected by Noel and Ann Kennon and subsequent visits have unearthed further specimens. Recently, Vic Cloete located a few specimens of gelosaite of a similar nature in quartz from the dumps of the Wolfram pipe. Nearly all gelosaite crystals are twinned (twin law unknown); examination of more than 30 crystals located a single, apparently untwinned, platy crystal that was used for the single-crystal X-ray study.

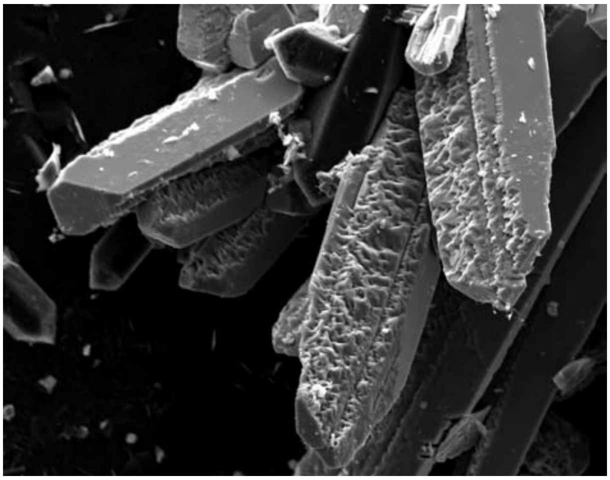

FIGURE 1. SEM BSE image of gelosaite crystals from Su Senargiu. Dimensions of the crystals about 100 μm. Photo: Paolo Orlandi.

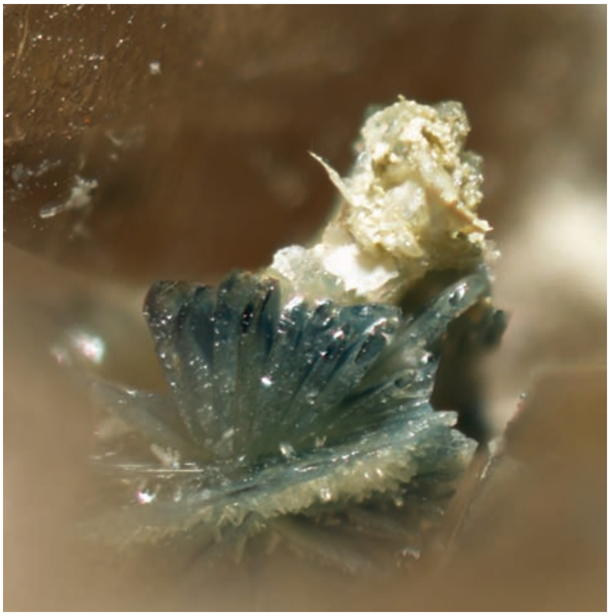

FIGURE 2. Blue gelosaite crystals and cream colored bismutite on quartz, Old 25 pipe, Kingsgate; field of view 1.5 mm. Photo: John Haupt; specimen: Merv and Lil Legg.

CHEMICAL DATA

Chemical analyses (11) of a pale-blue specimen from Su Senargiu were carried out using an electron microprobe (WDS mode, 15 kV, 20 nA, 6 μm beam diameter). Preliminary SEM-EDS analyses revealed the presence only of Bi, Mo, and traces of Pb and W, and only those elements were probed. H_2O was calculated by stoichiometry from the results of the crystal-structure analysis, which also confirmed that neither CO_2 nor other light elements are detectable. Analytical data are given in Table 1.

If all Mo were present as Mo^{6+}, the empirical formula based on 9 O atoms is $Bi_{1.00}Mo_{2.01}H_{2.94}O_9$ and the simplified formula is $BiMo_2O_7(OH){\cdot}H_2O$, which requires Bi_2O_3 42.52, MoO_3 52.54,

TABLE 1. Analytical data for gelosaite (pale blue Su Senargiu crystal)

Constituent	wt% 1	wt% 2	Range	e.s.d.	Probe standard
PbO	0.01	0.01	0.00–0.10	0.03	cerussite
Bi_2O_3	42.87	42.87	42.05–44.13	0.87	metallic Bi
Mo_2O_5		14.97		0.46	
MoO_3	53.00	37.85	52.28–53.72	0.46	$CaMoO_4$
WO_3	0.02	0.02	0.00–0.10	0.03	metallic W
H_2O*	4.85	4.85			
Total	100.75	100.57			

Notes: 1 = Mo content based on MoO_3. 2 = Mo content partitioned between Mo_2O_5 and MoO_3 based on the single-crystal structure study.
* Calculated (see text).

H_2O 4.93, total 99.99 wt%. However, in all three single-crystal used for X-ray structure determination, a Mo content >2.00 apfu was found. This necessitates the presence of mixed oxidation states for Mo, Mo^{6+}, and Mo^{5+}. Table 1 includes recalculated Mo contents partitioned between Mo_2O_5 and MoO_3 based on the initial single-crystal X-ray structure study undertaken of a Su Senargiu crystal. For this case, the empirical formula based on 9 O atoms is $Bi_{1.03}Mo^{6+}_{1.47}Mo^{5+}_{0.62}H_{3.01}O_9$ and the simplified formula is $BiMo^{6+}_{1.48}Mo^{5+}_{0.62}O_7(OH)\cdot H_2O$, allowing for rounding errors. Taking into account partial site occupation for Mo3 and Mo4 obtained from crystal structure refinement (yellow crystal, see below) a better balanced formula is obtained: $Bi_{1.00}Mo^{6+}_{1.49}Mo^{5+}_{0.61}O_7(OH)\cdot H_2O$. Since the total charge of the metal cations must be 15+, gelosaite can range in composition from $BiMo^{6+}_2O_7(OH)\cdot H_2O$ to $BiMo^{5+}_{2.4}O_7(OH)\cdot H_2O$ and the series may be expressed as $BiMo^{6+}_{(2-5x)}Mo^{5+}_{6x}O_7(OH)\cdot H_2O$ ($0 \leq x \leq 0.4$).

X-RAY DIFFRACTION STUDIES

X-ray powder diffraction data for gelosaite were collected with a 114.6 mm diameter Gandolfi camera, using Cu*K*α radiation, and are reported in Table 2.

Three single-crystal X-ray structures have been determined for gelosaite. For the first (yellow Su Senargiu crystal), rotation and Weissenberg photographs indicated monoclinic symmetry, space group $P2_1/n$. Diffraction data were collected from a crystal fragment (0.06 × 0.06 × 0.04 mm) with Mo*K*α radiation (λ = 0.71073 Å), using a Bruker Apex II diffractometer equipped with a 2K CCD detector. A one-minute frame-time and 0.3° frame width were used. A total of 8921 reflections, corresponding to complete scanning of the reciprocal lattice up to 2θ = 64.24°, were measured. Of these, 2356 were unique (R_{int} = 0.031). Unit-cell dimensions were refined by least-squares from 3389 reflections with $I > 2\sigma(I)$. These are given in Table 3, together with other details concerning data collection and refinement. Data were reduced using the Bruker program SAINT, and were corrected for Lorentz, polarization, and background effects. No violations of the systematic absences of space group $P2_1/n$ were observed. An absorption correction was applied (minimum transmission factor 0.728) using the SADABS program (Sheldrick 2000). The structure was solved by direct methods using SHELXS (Sheldrick 1997) and refined using the SHELXL97 program (Sheldrick 2008) implemented in the WinGX suite (Farrugia 1999).

Full lists of crystallographic data excluding structure-factor tables have been deposited with the Inorganic Crystal Structure Database (ICSD), Fachinformationszentrum, Karlsruhe, Germany; CRYSDATA@FIZ-Karlsruhe.DE and with MSA[1].

TABLE 2. Powder X-ray diffraction data (Å) for gelosaite

I_{rel}	d_{obs}	d_{calc}*	*hkl*
10	7.51	7.545	011
1	6.81	6.844	002
5	5.63	5.684	$\bar{1}01$
100	**4.83**	4.855	110
1	4.53	4.521	020
5	4.28	4.280	$\bar{1}\bar{1}2$
8	3.70	3.702	112
12	3.54	3.555	120
21	**3.41**	3.422	004
25	**3.30**	3.310	$\bar{1}\bar{2}2$
		3.297	103
50	**3.015**	3.020	122
5	2.823	2.842	$\bar{2}02$
60	**2.755**	2.758	032
8	2.655	2.666	$\bar{1}05$
12	2.614	2.620	015
		2.616	$\bar{1}24$
		2.615	114
4	2.498	2.496	202
5	2.390	2.394	$\bar{1}33$
4	2.336	2.338	124
6	2.227	2.230	041
		2.224	133
50	**2.080**	2.081	230
5	2.051	2.049	$\bar{1}\bar{4}2$
5	2.027	2.029	204
12	1.967	1.972	$\bar{2}25$
		1.969	$\bar{2}06$
12	1.890	1.895	$\bar{3}03$
		1.891	$\bar{2}\bar{3}4$
6	1.835	1.836	135
6	1.792	1.795	027
4	1.759	1.757	107
12	1.726	1.727	150
20	**1.688**	1.688	$\bar{3}\bar{2}4$
		1.683	234
14	1.647	1.648	206
		1.645	322
4	1.599	1.600	$\bar{1}46$
		1.600	028
		1.599	054
4	1.576	1.576	$\bar{1}54$
6	1.541	1.542	118
30	**1.509**	1.509	155
3	1.478	1.478	$\bar{3}41$
2	1.460	1.459	$\bar{1}29$

Notes: The strongest lines are marked in bold. The experimental error for the *d*-spacings is about ±0.01 Å for low-angle values and about ±0.002 Å for high-angle values
* Calculated from single-crystal unit-cell dimensions (yellow Su Senargiu crystal).

The introduction of one bismuth, two molybdenum (Mo1 and Mo2), and nine O atoms in the structure model led to an *R* index of 0.0334, but two residual peaks of 10.4 and 4.6 e Å^{-3} were observed in a difference Fourier map. After having excluded the presence of additional elements in gelosaite by chemical analysis, and on the basis of stereochemical considerations, these were interpreted as a small fraction of interstitial molybdenum atoms [with partial occupancy of 0.028(1) and 0.074(1) for Mo3

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[1] Deposit item AM-11-004, observed and calculated structure factors. Deposit items are available from MSA two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.
To request the ICSD for this material, please quote the full literature citation and the CSD-numbers 421733 (filename Bi Mo2.39 O9), 421734 (filename Bi H3 Mo2.19 O9), or 421735 (filename Bi H3 Mo2.10 O9); refer to Table 3 and text to identify the particular structure concerned.

TABLE 3. Crystal data and structure refinement details for gelosaite*

Empirical formula	$BiMo_{2.10}O_7(OH)\cdot H_2O$; $BiMo_{2.19}O_7(OH)\cdot H_2O$; $BiMo_{2.39}O_7(OH)\cdot H_2O$
Formula weight	557.47; 566.11; 581.80
Temperature	292(2); 292(2); 150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit-cell dimensions	a = 5.8505(4); 5.8570(5); 5.837(3) Å b = 9.0421(6); 9.0517(8); 9.040(5) Å c = 13.9173(10); 13.9923(12); 13.904(7) Å β = 100.42(1); 100.44(1); 100.64(1)°
V	724.1(1); 729.5(1); 721.0(6) $Å^3$
Z	4
Density (calculated)	5.114; 5.127; 5.360 g/cm^3
Absorption coefficient	27.84; 27.78; 28.43 mm^{-1}
$F(000)$	984.8; 999.9; 1020.7
Crystal size	0.06 × 0.06 × 0.04; 0.06 × 0.04 × 0.03; 0.15 × 0.10 × 0.02 mm
θ range for data collection	2.70 to 32.12; 2.69 to 31.22; 2.70 to 28.37°
Index ranges	$-8 \le h \le 8, -13 \le k \le 13, -20 \le l \le 20$; $-8 \le h \le 8, -13 \le k \le 13, -19 \le l \le 19$; $-7 \le h \le 7, 0 \le k \le 11, 0 \le l \le 18$
Reflections collected	8921; 10605; 1798
Independent reflections	2356 [R(int) = 0.031]; 2233 [R(int) = 0.066]; 1687 [R(int) = 0.054]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2356/1/131; 2233/0/119; 1687/0/60
Goodness-of-fit on F^2	0.975; 1.063; 1.101
Final R indices†	$R_1 = 0.0226$, $R_w = 0.0484$ [1827 reflections with $I > 2\sigma(I)$]; $R_1 = 0.0439$, $R_w = 0.1109$ [1661 reflections with $I > 2\sigma(I)$]; $R_1 = 0.0757$, $R_w = 0.1972$ [1356 reflections with $I > 2\sigma(I)$]
R indices (all data)	$R_1 = 0.0345$, $R_w = 0.0507$; $R_1 = 0.0628$, $R_w = 0.1216$; $R_1 = 0.0893$, $R_w = 0.2115$

* Successive values refer to yellow gelosaite from Su Senargiu described in some detail above (supplementary data file number CSD-number 421735), blue gelosaite from Su Senargiu (supplementary data file number CSD-number 421734), and blue gelosaite from Kingsgate (supplementary data file number CSD-number 421733).

† The weighting schemes used were $w = 1/[\sigma^2(F_o)^2 + (0.022P)^2]$; $w = 1/[\sigma^2(F_o)^2 + (0.066P)^2 + 10.33P]$; $w = 1/[\sigma^2(F_o)^2 + (0.1237P)^2 + 63.57P]$, where $P = [\mathrm{Max}(F_o)^2 + 2(F_c)^2]/3$ as defined by SHELX-97 (Sheldrick 2008).

TABLE 4. Atomic coordinates and displacement parameters [$U_{eq}/U_{(i,j)}$] for gelosaite (yellow Su Senargiu crystal)

Atom	occupancy	x/a	y/b	z/c	U_{eq}
Bi	1.00	0.403568(13)	0.416894(10)	0.106492(6)	0.01002(2)
Mo1	1.00	0.86623(3)	0.10399(2)	0.157185(13)	0.00901(4)
Mo2	1.00	0.63232(3)	0.22137(2)	0.340837(13)	0.00927(4)
Mo3	0.028(1)	0.6321(12)	−0.0443(8)	0.3396(5)	0.0124(14)
Mo4	0.074(1)	1.0937(5)	0.2597(4)	0.3943(2)	0.0204(6)
Ow	1.00	0.9606(3)	0.4172(2)	0.34252(12)	0.0199(4)
O2	1.00	0.7548(3)	0.09301(19)	0.03404(11)	0.0159(4)
O3	1.00	0.3999(3)	0.10589(18)	0.33664(13)	0.0184(5)
O4	1.00	0.6397(3)	0.24002(19)	0.19069(10)	0.0129(4)
O5	1.00	0.7450(3)	0.2435(2)	0.46385(11)	0.0179(4)
OH	1.00	0.8231(3)	−0.08846(18)	0.48180(11)	0.0127(4)
O7	1.00	1.0121(3)	−0.08756(18)	0.18310(11)	0.0117(4)
O8	1.00	0.8649(3)	0.08618(18)	0.31149(11)	0.0114(4)
O9	1.00	1.1009(3)	0.21738(19)	0.16456(12)	0.0202(5)
H(1w)	1.00	1.028(6)	0.426(4)	0.303(2)	0.048(10)
H(2w)	1.00	1.041(5)	0.428(3)	0.393(2)	0.034(9)
H3	1.00	0.7578(15)	−0.1696(6)	0.4894(14)	0.050(11)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi	0.01155(3)	0.00916(3)	0.00921(3)	0.00044(3)	0.00151(2)	−0.00037(3)
Mo1	0.01043(7)	0.00849(8)	0.00829(7)	0.00109(6)	0.00220(6)	0.00045(6)
Mo2	0.01168(8)	0.00809(8)	0.00835(8)	0.00165(6)	0.00261(6)	0.00116(7)
Ow	0.0218(8)	0.0222(8)	0.0162(7)	0.0017(8)	0.0048(6)	0.0025(8)
O2	0.0210(7)	0.0161(8)	0.0103(7)	−0.0006(7)	0.0019(6)	0.0042(7)
O3	0.0150(7)	0.0170(9)	0.0236(8)	0.0074(7)	0.0049(6)	−0.0025(7)
O4	0.0177(7)	0.0110(7)	0.0109(6)	0.0023(6)	0.0049(6)	0.0055(6)
O5	0.0289(8)	0.0140(7)	0.0109(7)	0.0045(7)	0.0042(6)	0.0106(7)
OH	0.0139(6)	0.0127(7)	0.0129(6)	−0.0060(7)	0.0063(5)	−0.0079(7)
O7	0.0121(6)	0.0092(6)	0.0137(7)	−0.0008(7)	0.0020(5)	0.0008(7)
O8	0.0145(6)	0.0112(7)	0.0084(6)	0.0044(6)	0.0019(5)	0.0047(7)
O9	0.0202(8)	0.0199(9)	0.0201(8)	0.0018(7)	0.0026(7)	−0.0070(7)

Note: The anisotropic displacement factor exponent takes the form: $-2\pi^2[U_{11}h^2(a^*)^2+...+2U_{12}hka^*b^*+...]$; $U_{eq} = 1/3(U_{11}+U_{22}+U_{33})$.

TABLE 5. Selected bond lengths (Å) for gelosaite (yellow Su Senargiu crystal)

Bi-OH	2.186(2)	Bi-O5	2.498(2)
Bi-OH	2.312(2)	Bi-O7	2.881(2)
Bi-O3	2.685(2)	Bi-O8	2.219(2)
Bi-O4	2.292(2)	Bi-O9	2.750(2)
Mo1-Ow	2.552(2)	Mo1-O7	1.936(2)
Mo1-O2	1.723(2)	Mo1-O8	2.155(2)
Mo1-O4	1.926(2)	Mo1-O9	1.702(2)
Mo2-Ow	2.609(2)	Mo2-O5	1.731(2)
Mo2-O3	1.707(2)	Mo2-O7	1.926(2)
Mo2-O4	2.105(2)	Mo2-O8	1.927(2)
Mo3-OH	2.127(7)	Mo3-O4	2.442(8)
Mo3-Ow	2.518(7)	Mo3-O8	1.895(8)
Mo3-O3	1.916(7)	Mo3-O9	2.545(7)
Mo4-OH	2.303(3)	Mo4-O3	2.512(4)
Mo4-Ow	1.718(4)	Mo4-O5	2.415(4)
Mo4-O2	2.405(3)	Mo4-O8	2.241(3)

and Mo4, respectively, after refinement]. By adding these to the structure model, together with the hydrogen atoms of the water molecule and the hydroxyl group that were clearly seen in the final difference Fourier map, the *R* index significantly lowered to 0.0226 for 1827 observed reflections with $I > 2\sigma(I)$. This led to the overall composition $BiMo_{2.10}O_7(OH)\cdot H_2O$. Since the charge corresponding to the total amount of Mo+Bi is 15+ to counterbalance the anionic charge, a fraction of the Mo atoms is in the 5+ oxidation state rather than 6+. The two fractionally occupied molybdenum sites are about 2.4–2.7 Å apart from the others, a distance that is not unusual in molybdenum clusters. Variation in color from yellow to blue, sometimes in the same crystal, is therefore likely to be related to charge transfer between Mo atoms of different oxidation states, and present in different amounts. Final atom coordinates and displacement parameters are listed in Table 4 and selected interatomic distances in Table 5.

A separate structure refinement was carried out on a pale blue crystal from Su Senargiu with unit-cell parameters $a = 5.8570(5)$, $b = 9.0517(8)$, $c = 13.992(1)$ Å, $\beta = 100.44(1)°$ (Table 3), and an occupancy of 0.06(1) and 0.13(1) for the Mo3 and Mo4 sites, respectively, thus leading to the formula $BiMo_{2.19}O_7(OH)\cdot H_2O$. No H atoms were detected in the final ΔF map and therefore not introduced in the refined model. The final *R* index for this crystal is 0.0439 for 1661 observed reflections with $I > 2\sigma(I)$. For final coordinates, please consult supplementary data[1]. It is sufficient to state that this crystal contains more Mo^{5+} than does the yellow crystal from Su Senargiu. There are no significant variations between the two structures other than the fractional site occupancies of Mo3 and Mo4.

Independently, a third single-crystal X-ray structure of a pale blue crystal of gelosaite from Kingsgate was determined. After an extended search a pale blue-green platy crystal fragment (0.15 × 0.10 × 0.02 mm), which was not twinned or fractured was eventually found and mounted on a Bruker SMART CCD diffractometer. Data were collected at 150(2) K using an Oxford Cryosystems COBRA cryogenics unit, with graphite-monochromatized Mo*K*α radiation and corrected for Lorentz and polarization effects (SAINT). An empirical absorption correction (SORTAV) was applied (Blessing 1995). Unit-cell dimensions were determined by least-squares refinement of the complete data set and are listed in Table 3 together with associated crystal data and structure refinement details. The structure was determined by a combination of direct methods using SHELXS (Sheldrick 1997) and subsequent difference Fourier syntheses, and refined on F^2 by full-matrix least-squares using SHELXL97 (Sheldrick 2008).

The positions of the Bi, Mo1, and Mo2 atoms were readily located by direct methods with a subsequent difference synthesis revealing the positions of all the O atoms. Isotropic refinement of the structure gave an *R*1 value of 0.090 but a subsequent attempt to refine the structure anisotropically resulted in unacceptable thermal parameters for most atoms (with many being non-positive definite) and this was attributed to the quality of the data. Accordingly, the structure was refined with isotropic thermal parameters for all atoms except Bi, which was allowed to refine anisotropically, giving an *R*1 value of 0.080. It was noted that the thermal parameters for Mo1 and O8 had become quite small, and hence these two thermal parameters were subsequently held fixed at reasonable values. At this stage, the main features in the difference map were two small peaks, each being located in a distorted 5+1 octahedron of O atoms, and these were attributed to the fractionally occupied Mo atoms, Mo3 and Mo4. A final refinement, with the occupancies of Mo3 and Mo4 adjusted to give acceptable isotropic thermal parameters for each atom, gave an *R*1 of 0.076 and *wR*2 of 0.211 (Table 3). The only remaining feature in the final difference map was a small peak of ~5*e* at (0.101, 1.572, 0.398) that again was located in a distorted 5+1 octahedron of O atoms and could be attributed to yet another fractionally occupied Mo atom. However, attempts to include this atom in the structure led to unstable thermal parameters for the other Mo atoms and several of the O atoms and hence, given the quality of the data, it was concluded that this peak was an artifact and probably had no structural significance.

The refined occupancies of Mo3 and Mo4 are 0.115 and 0.27, respectively. This leads to the stoichiometry $BiMo_{2.39}O_7(OH){\cdot}H_2O$, which is within error identical to that of the Mo^{5+} end-member $BiMo_{2.4}O_7(OH){\cdot}H_2O$.

Description of the structure

The structure of gelosaite consists of layers of distorted MoO_6 octahedra, plus a minor amount of interstitial Mo atoms (Mo3), and layers made up by eight-coordinate Bi^{3+} ions, plus another small amount of interstitial Mo (Mo4) (Figs. 3 and 4). The presence of differently populated Mo3 and Mo4 sites in the three crystals examined by single-crystal X-ray diffraction, accounts for the stoichiometric variability of the mineral. Neglecting the fractional Mo3 and Mo4 atoms, the layers containing Mo atoms only display zigzag chains, running along [010] made up of MoO_6 octahedra, which share edges defined by the Ow-O4 and O7-O8 atoms. This arrangement is different from that observed in sardignaite, $BiMo_2O_7(OH){\cdot}2H_2O$ (Orlandi et al. 2010) and its synthetic counterpart (Hriljac and Torardi 1993), where dimeric Mo_2O_{10} units are instead corner-linked to form chains running along [010] (Fig. 5). Mo1 and Mo2 are surrounded by a distorted octahedron of O atoms with two short bonds [in the range 1.702(2)–1.731(2) Å], two normal bonds [from 1.926(2) to 1.936(2) Å], and two longer bonds [from 2.105(2) to 2.609(2) Å]; bond lengths given here refer to the yellow Su Senargiu crystal and are perfectly compatible with those found for the other two structures (supplementary data). With respect to the latter, the longest distances are those involving the water molecule, which is coordinated to both Mo1 and Mo2 atoms. This geometry is the classical one observed for nearly all Mo^{6+} compounds (Cotton and Wilkinson 1988). The interstitial Mo3 and Mo4 atoms are located in separate octahedral holes in the structural motif described above, with interactions with neighboring O atoms comparable with those found for Mo1 and Mo2.

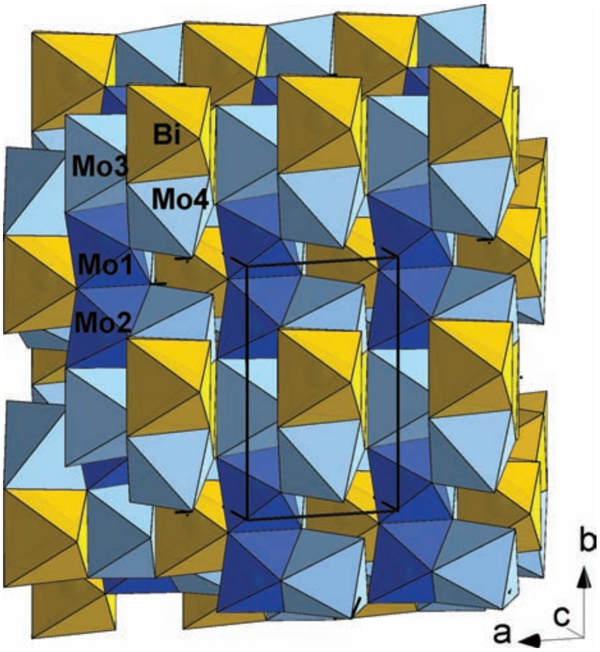

FIGURE 3. A perspective view of the structure of gelosaite. The dark blue polyhedra are those fully occupied by molybdenum, the light blue ones are those with only partial occupation.

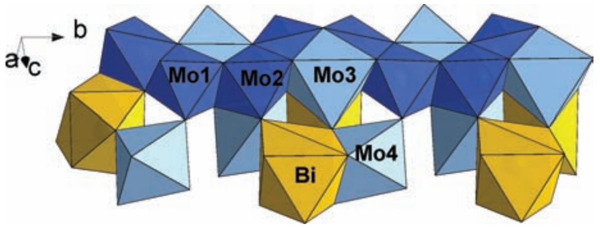

FIGURE 4. A portion of the layers made by MoO_6 distorted octahedra and eight-coordinate Bi^{3+} ions.

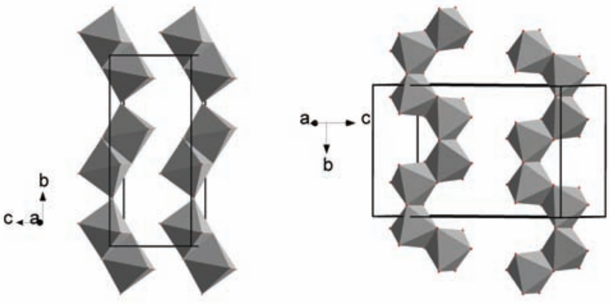

FIGURE 5. A comparison of the arrangement of the fully occupied MoO_6 polyhedra in sardignaite (**left**) and gelosaite (**right**).

The Bi^{3+} coordination environment may be described as a slightly distorted trigonal prism, bicapped on two of the three side faces. The uncapped side face, which is slightly folded, probably corresponds to the location of the bismuth electron lone pair. The Bi eight-coordinate polyhedra are arranged to form dimeric units, $Bi_2O_{12}(OH)_2$, by sharing an edge where two symmetry-related OH groups are located (Fig. 6). Each Bi polyhedron shares two edges (O7···O8 and O4···O7) and three corners (O3, O5, and O9) with the adjacent Mo polyhedra. The location of hydrogen atoms of the hydroxyl group and the water molecule allows establishing the pattern of hydrogen bonds. Several interatomic O···O contacts below the sum of the van der Waals radii are present in the structure, eventually ascribable to possible hydrogen bonds that contribute to holding together the building blocks of the structure. Among these the hydroxyl group and the water molecule display a short contact with O2 [OH···O2 2.918(2) Å, H3···O2 2.170(6) Å, OH-H3···O2 147.8(5)°; Ow···O2 2.901(2) Å, H(2w)···O2 2.13(3) Å, Ow-H(2w)···O2 168(3)°]. In addition two longer contacts between the water molecule and O3 and O7 are observed [Ow···O3 3.245(3) Å, Ow···O7 3.169(2) Å] (Fig. 7).

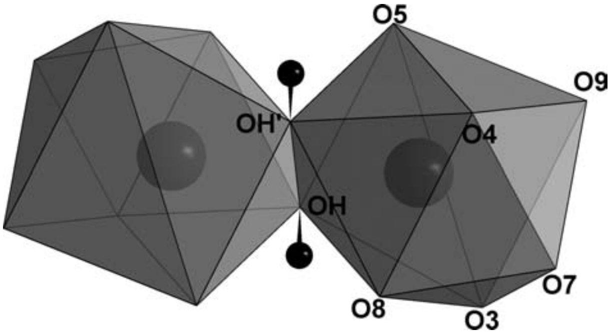

FIGURE 6. The dimeric unit $Bi_2O_{12}(OH)_2$.The coordination polyhedron about each Bi^{3+} ion is a trigonal prism bicapped on two of the three side faces. The triangular bases of the trigonal prism are defined by atoms O4, O5, O9 and O3, O8, OH, respectively, the two side caps are O7 and OH′.

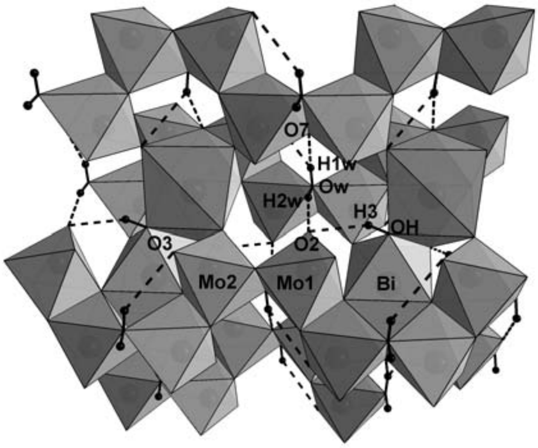

FIGURE 7. The hydrogen bond pattern. Interstitial fractional Mo atoms excluded for the sake of clarity.

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