ORIGINAL PAPER

Sardignaite, a new mineral, the second known bismuth molybdate: description and crystal structure

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Abstract The new mineral sardignaite, a bismuth molybdate with formula $BiMo_2O_7(OH)\cdot 2H_2O$, occurs in quartz veins within a granitic rock at Su Senargiu, near Sarroch, Sardegna, Italy. The name is after the locality. Sardignaite occurs a thin prismatic crystals up to 1 mm in length, with pale yellow color and a white streak. It is transparent with adamantine lustre, non fluorescent, and brittle with a conchoidal fracture. It is associated with bismuthinite, bismoclite, molybdenite, ferri-molybdite, koechlinite, wulfenite, and the new mineral IMA 2009–022. Mohs hardness is ca. 3. D_{calc} is 4.82 g/cm^3. The mineral is monoclinic, space group $P2_1/m$, with a 5.7797(7), b 11.567(1), c 6.3344(8) Å, β 113.360(9)°, V 388.8(1) Å^3. The strongest lines in the powder X-ray diffraction pattern are $d(I)(hkl)$: 3.206(100)(031), 5.03(80)(−101), 1.992(45)(221), 3.120(32)(130). The crystal structure of sardignaite was solved to $R(F)$ 0.056 using single-crystal X-ray diffraction data, and is characterized by edge-sharing dimers of $[MoO_5(H_2O)]$ octahedra, linked to each other through corner-sharing to give rise to corrugated columns running along b. Such columns are held together by Bi^{3+} cations, eight-fold coordinated by 7 O + 1 (OH). Both the mineral and its name were approved by the IMA-CNMNC.

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Introduction

In this paper, the new bismuth molybdate mineral sardignaite is described. The new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA No. 2008–040). The name sardignaite is after Sardigna (in Italian Sardegna, in English Sardinia), the region in which the mineral was found, as spelt in the local language, which is considered an independent Romance language, and not merely a variety (dialect) of Italian. The mineral collector who found the new mineral (Marzio Mamberti) is a native Sardinian and is very proud of its cultural roots. Sardinia is the fourth Italian region (after Piedmont, Tuscany and Latium) to have a mineral named after it. The holotype of sardignaite is deposited in the mineralogical collection of the "Museo di Storia Naturale e del Territorio" of the University of Pisa, under the catalogue No. 19350.

Geological outline

The presence of molybdenum mineralizations in Sardinia is known since the XIX Century (Jervis 1881). Later on, the exploitation of Sardinian ore deposits resulted in a number of notes on molybdenum mineralizations (Dessau 1956; Venerandi 1968). One of them was specifically devoted to Su Senargiu, the type locality of sardignaite (Caboi et al. 1978).

All the above studies agree in relating the molybdenum mineralizations of Sardinia to leucogranitic intrusions of Hercynic age (Ghezzo et al. 1981), formed by acid intrusive bodies characterized by a fairly homogeneous composition. Quartz is the most abundant mineral and K-feldspar prevails over plagioclase (An_{2-20}). The only femic mineral
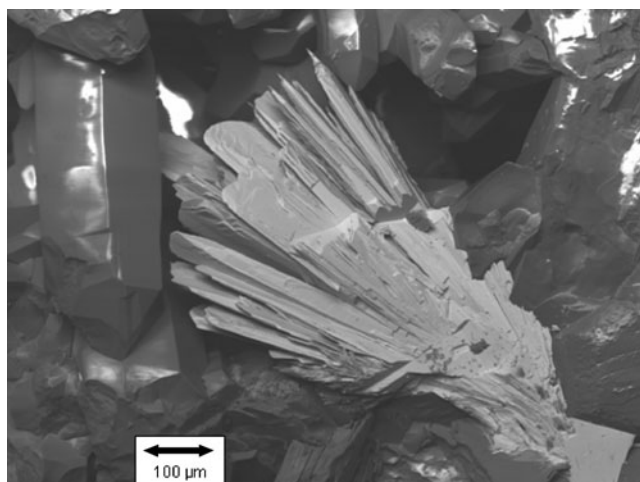
Fig. 1 SEM micrograph of a spray of flattened, 0.5 mm long, prismatic crystals of sardignaite

is biotite, and accessory minerals (apatite, allanite, monazite, zircon) are rare.

The original paragenesis seems to have been affected by alteration phenomena, marked by the pronounced instability of biotite and plagioclase, transformed into sericitic products, chlorite and clay minerals. The only molybdenum-bearing mineral in the above mineralizations is molybdenite, associated with pyrite and minor wolframite, sphalerite, and scheelite. In some intrusions molybdenite occurs as lamellar crystals disseminated in the hosting rock; in other ones, as in the case of the mineralization of Su Senargiu, molybdenite is only found within quartz veins.

At this last locality, in the easternmost part of Sulcis, the mineralization is located at 260 m asl, on the slope of the Su Senargiu mount, in the proximity of the village of Sarroch, and not far from the town of Cagliari.

Molybdenite occurs within quartz veins with thickness ranging from 5 to 15 cm and also, more rarely, within the granitic rock itself (Caboi et al. 1978). The study of several samples, collected in the small dumps in front of the three galleries worked from 1934 to 1953, allowed an accurate

Table 1 Electron microprobe analysis of sardignaite (average of six points)

Constituent	Wt.%	Range	Probe standard
PbO	0.41	0.31–0.77	cerussite
Bi_2O_3	41.21	40.68–42.46	metallic Bi
MoO_3	52.14	51.84–52.73	$CaMoO_4$
WO_3	0.00	0.00–0.02	metallic W
H_2O_{calc}[a]	8.13		
Total	101.89		

[a] Two water molecules per formula unit, as resulting from the crystal-structure analysis.

Table 2 X-ray powder pattern of sardignaite. Gandolfi camera, 114.6 mm diameter, $CuK\alpha$ radiation

d_{obs}	hkl	d_{calc}	I/I_0	I_{calc}
5.79	001	5.82	25	28
5.20	011	5.20	3	1
5.03	−101	5.05	80	100
4.83	110	4.83	2	1
4.62	−111	4.62	4	11
3.91	120	3.91	4	16
3.327	101	3.327	28	9
3.206	031	3.210	100	57
3.120	130	3.117	32	32
3.060	−131	3.060	2	1
3.010	−112	3.021	3	0
2.907	002	2.912	11	4
2.883	−201	2.890	4	1
	040	2.885		3
2.827	012	2.824	1	2
2.660	200	2.660	6	1
2.590	210	2.592	30	7
	041	2.585		2
2.524	−202	2.523	25	15
2.465	−212	2.465	15	10
2.435	−132	2.427	5	9
2.315	−222	2.312	10	2
	−231	2.311		4
2.215	102	2.213	4	6
2.178	230	2.188	13	1
	141	2.180		1
2.115	201	2.123	30	1
	−103	2.113		2
2.067	122	2.066	20	5
2.052	042	2.050	5	1
1.992	221	1.992	45	4
1.947	003	1.942	4	3
1.919	060	1.923	13	10
	132	1.918		1
1.899	−242	1.899	5	3
	151	1.896		1
1.859	231	1.859	25	1
	−152	1.857		1
1.822	−321	1.823	3	1
1.791	−322	1.788	3	4
1.761	−233	1.765	9	5
1.712	241	1.710	11	4
1.696	320	1.695	8	3
plus 15 more lines				

Table 3 Final positional and displacement parameters for sardignaite

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi	0.15761(7)	0.75	0.26334(7)	0.0238(1)	0.0264(2)	0.0217(2)	0.0212(2)	0.0	0.0074(1)	0.0
Mo	0.6926(1)	0.59567(5)	0.6545(1)	0.0200(2)	0.0206(3)	0.0162(3)	0.0201(3)	−0.0009(2)	0.0050(2)	0.0002(2)
O1	0.886(1)	0.6153(7)	0.511(1)	0.032(1)	0.033(3)	0.028(3)	0.036(3)	0.002(3)	0.016(3)	0.001(2)
O2	0.886(1)	0.6187(6)	0.937(1)	0.030(1)	0.031(3)	0.026(3)	0.025(2)	−0.001(2)	0.002(2)	0.000(2)
O3	0.656(1)	0.4333(5)	0.634(1)	0.0225(9)	0.024(2)	0.017(2)	0.023(2)	−0.001(2)	0.006(2)	−0.000(2)
O4	0.531(2)	0.75	0.592(1)	0.022(1)	0.027(3)	0.016(3)	0.022(3)	0.0	0.008(3)	0.0
O5	0.381(2)	0.75	0.075(2)	0.038(2)	0.046(6)	0.046(6)	0.031(4)	0.0	0.025(4)	0.0
O6	0.400(1)	0.5737(6)	0.825(1)	0.026(1)	0.031(3)	0.023(2)	0.024(2)	−0.001(2)	0.010(2)	−0.001(2)

definition of the mineralogical association at Su Senargiu: besides molybdenite, native bismuth, bismuthinite, pyrite, sphalerite, cassiterite, anatase, brookite, aeschynite-(Ce), bismoclite, ferrimolybdite, koechlinite, wulfenite, muscovite, and synchysite-(Ce) were observed.

Occurrence and physical properties

The new mineral sardignaite occurs within cavities of quartz veins in granitic rock at Su Senargiu, Sarroch, (CA), Sardinia, Italy. Associated minerals are bismuthinite, bismoclite, molybdenite, ferrimolybdite, koechlinite, wulfenite, and the new mineral IMA 2009–022. Sardignaite is a secondary mineral formed in the oxidation zone of a molybdenite-bismuthinite deposit.

At the type locality, sardignaite occurs as prismatic and very thin elongated [010] and tabular {100} crystals up to 1 mm in length and a few microns in diameter (Fig. 1). Bundles of crystals with parallel elongation are also common. Crystals are pale yellow with a white streak, transparent with adamantine lustre, non fluorescent, and brittle with a conchoidal fracture. Mohs hardness is ca. 3. Density was not measured because its value was too high to be reached with heavy liquids and there was not enough material for weighting methods. The calculated density is 4.82 g/cm^3. The sign of the optical elongation is positive on [010]. Birefrincence is high. The mean refractive index, obtained from Gladstone-Dale equilibrium using chemical composition and calculated density, is 2.04.

Chemical data

Chemical analyses of sardignaite were performed with an ARL-SEMQ electron microprobe. Operating conditions were: WDS mode, 15 kV, 20 nA, beam diameter 6 μm. According to preliminary SEM-EDS analyses, which revealed the presence of Pb, Bi, Mo, and W, only those elements were probed. No S was observed during EPMA, which could have been overlooked due to overlap with lines of Pb and Bi in the SEM-EDS. Analytical data and probe standards are given in Table 1. H_2O and CO_2 were not determined directly. H_2O_{calc} was included in the chemical analysis according to the chemical formula resulting from the single-crystal X-ray diffraction study, which also confirmed that neither CO_2 nor other light elements occur. The high analytical total (101.89 wt.%) is likely to result from minor dehydration under the electron beam. The empirical formula of sardignaite, based on 10 oxygen atoms, is: $Bi_{0.980}Pb_{0.010}Mo_{2.007}O_7(OH)_{1.000} \cdot 2H_2O$. The simplified formula is $BiMo_2O_7(OH) \cdot 2H_2O$.

X-ray diffraction study

The X-ray powder diffraction pattern of sardignaite was collected with a 114.6 mm diameter Gandolfi camera, using CuKα radiation, and is reported in Table 2. The unit-cell parameters, refined from 27 unequivocally indexed reflections, are: a=5.793(3), b=11.540(5), c=6.341(4) Å, β=

Table 4 Selected bond distances (Å) for sardignaite

Bi – O5	2.076(10)	Mo – O1	1.711(7)	O5 ... O6 (×2)	2.61(1)
Bi – O4	2.329(8)	Mo – O2	1.712(6)		
Bi – O3 (×2)	2.350(6)	Mo – O3	1.888(6)		
Bi – O2 (×2)	2.544(7)	Mo – O4	1.981(4)	O6 ... O6'	2.67(1)
Bi – O1 (×2)	3.052(7)	Mo – O3	2.143(6)	O6 ... O1	2.88(1)
		Mo – O6	2.353(7)		
< Bi – O >	2.537				
		< Mo – O >	1.965		

Table 5 Bond valence analysis (v.u.) for sardignaite (Brese and O'Keeffe 1991), including the contribution of the hydrogen bonds (Ferraris and Ivaldi 1988). Left and right superscript indicate the number of equivalent bonds for the cation and for the anion, respectively

	Bi	Mo	$\Sigma'_a v$	H bonds	$\Sigma_a v$
O1	2× 0.074	1.698	1.772	+0.158	1.930
O2	2× 0.293	1.693	1.986		1.986
O3	2× 0.495	1.053	2.076		2.076
		0.528			
O4	0.524 2×	0.819	1.867		1.867
O5 (OH)	1.040		1.040	−0.280	1.040
				+0.280	
O6 (H₂O)		0.300	0.300	+0.280 0.5×	0.142
				−0.280 0.5×	
				−0.158	
$\Sigma_c v$	3.288	6.096			

113.28(3)°, $V=389.4(3)$ Å^3. These values are in fair agreement with those determined from the single-crystal study (see below).

The single-crystal X-ray diffraction study was started with the collection of rotation and Weissenberg photographs, which indicated monoclinic symmetry, and systematic absences pointing to either $P2_1$ or $P2_1/m$ as possible space groups.

Then a selected, relatively thick single crystal (dimensions ca. $0.18 \times 0.12 \times 0.30$ mm) was mounted on a conventional Siemens P-4 four-circle diffractometer equipped with a X-ray tube using graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The following unit-cell parameters were refined through least-squares fit of 2θ values of 46 accurately centered reflection ($24° < 2\theta < 36°$): $a=5.7797$ (7), $b=11.567(1)$, $c=6.3344(8)$, $\beta=113.360(9)°$, $V=388.8$ (1) Å^3. The intensity data collection was carried out in θ–2θ scan mode up to $2\theta_{max}=70°$, with scan width (in θ) $\pm 0.50°$, and scan speed 2°/min. The 2,372 measured intensities were reduced to a set of 1,785 independent squared structure amplitudes after correction for Lorentz, polarisation and absorption, the latter based on a set of ψ-scan measurements.

The crystal structure of sardignaite was solved with direct methods in the space group $P2_1/m$. At first the positions of Bi and Mo were found, and then six out of the most relevant residual electron density maxima were interpreted as oxygen atoms and selected so as to model reasonable coordination polyhedra around the cations. The nature of coordinating anions (whether oxygens, hydroxyls, or water molecules) was assessed on the basis of the bond-valence sums. Any attempt to locate the hydrogen atoms was unsuccessful. The full matrix refinement of the structural model, with anisotropic displacement parameters for all atoms, converged to

R1 (conventional $R(F)$ factor) = 0.056 for 1,651 non-zero $[F_o > 4\sigma(F_o)]$ reflections, wR2 (weighted R on F^2) = 0.1491, S (goodness of fit) = 1.131. A total of 65 parameters were refined. The maximum and minimum peaks in the final difference-Fourier map were +9.19 and −3.37 e/Å^3, respectively. All highest peaks are in the close surroundings of the cation sites, and are likely to be the result of minor inaccuracies in the absorption surface modeling which may have caused small distortions of the thermal ellipsoids. Structure solution and refinement were carried out with the SHELX-97 package of programs (Sheldrick 2008), implemented within the WinGX program system (Farrugia 1999). Final positional and displacement parameters are given in Table 3; bond distances are given in Table 4, and a bond-valence analysis in Table 5.

Description of the structure

The crystal structure of sardignaite is shown in Fig. 2. The structure is characterized by edge-sharing dimers of [MoO₅(H₂O)] octahedra. Dimers in turn link each other through corner-sharing to give rise to corrugated columns running along b. Columns are held together by Bi^{3+} cations, eight-fold coordinated by 7 O + 1 (OH). The cross-linking of columns by Bi^{3+} is not evenly distributed, being stronger along [100] and weaker along [−101]. Along this latter direction, columns are held together only by the weak, 3.05 Å long Bi-O1 bonds and by the system of hydrogen bonds (Fig. 3).

The Bi-centered coordination polyhedron may be roughly described as an augmented pentagonal bipyramid. The cation lies more or less at the centre of the pentagonal basis of the bipyramid, which is terminated on one side by a strongly bonded O5 (OH), and on the other side by a pair of weakly bonded O1 (Fig. 4a).
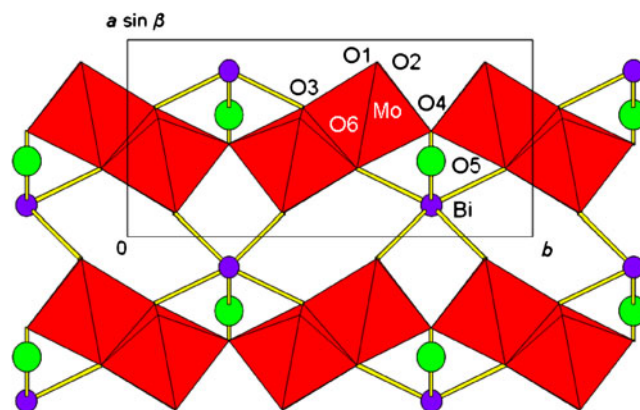

Fig. 2 The crystal structure of sardignaite, as viewed down c. The unit cell is outlined. Labeled atoms are those corresponding to the asymmetric unit
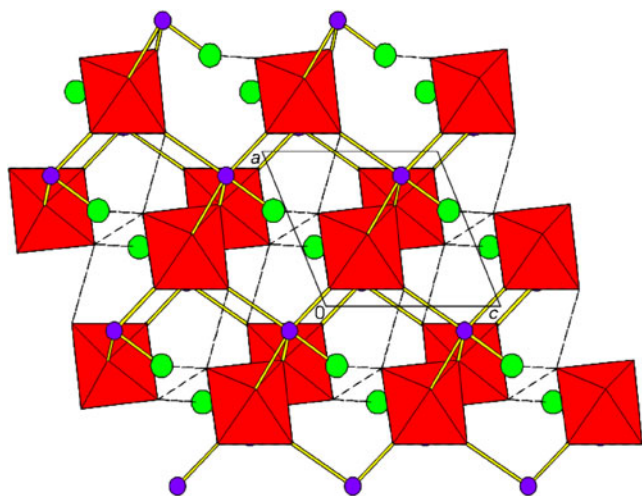
Fig. 3 The crystal structure of sardignaite, as viewed down *b*. The unit cell is outlined. The hydrogen bonds are indicated by dashed lines

The Mo-centered coordination polyhedron has six ligands in the range 1.711–2.353 Å. The longest bond distance is to O6 (H_2O). The six ligands define a fairly regular octahedron, with the central cation displaced off the central position (Fig. 4b).

Although hydrogen atoms could not be located, a plausible hydrogen-bonding scheme can be suggested on the basis of the O ... O interactions between oxygens not belonging to the same coordination polyhedron (Table 4) and of the bond-valence analysis (Table 5).

O5, which belongs to a hydroxyl group, has two contacts with two equivalent O6 atoms (water molecules), above and below the mirror on which O5 lies. O6 has two contacts with another O6 and with O1.

In the proposed hydrogen-bonding scheme, O5 (OH) could be donor of a hydrogen bond toward either of the two O6, and the other O6 (H_2O) could be donor of two hydrogen bonds towards O5 and O1, with an O1 - O6 - O5 angle of 90°. This scheme is, however, not consistent with the $P2_1/m$ symmetry, which should reduce to $P2_1$.

In an alternative scheme, O5 (OH) could be donor of two statistically distributed hydrogen bonds (or a so-called bifurcated hydrogen bond) toward the two equivalent O6 atoms, whereas O6 (H_2O) could be donor of two hydrogen bonds toward a symmetry-equivalent O6 and toward O1, with an O1 - O6 - O6 angle of 132°.

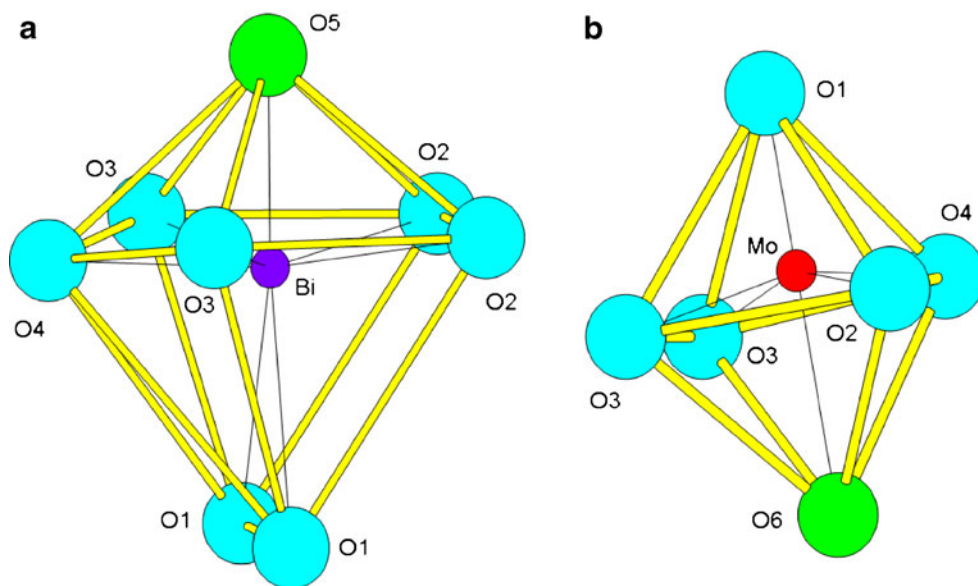A third scheme could be possible, which would involve O5 and O6 only, and no hydrogen bonds reaching O1.

Since the actual positions of the hydrogen atoms could not be located, all the above schemes seem plausible. The first one, however, is preferable since it improves the charge balance for O1, which shows some undersaturation, as well as for O5 and O6 (see Table 5).

A synthetic analogue of sardignaite is known (Hriljac and Torardi 1993). We did not use it as a starting model for our structure analysis, since we were not aware yet of it when we solved the structure of sardignaite. Consequently, different axial setting and asymmetric unit were chosen. If we compare the two structural models, after the necessary changes, the unit cell parameters, the atomic coordinates, and the bond lenghts are in good agreement.

Related species

Among all known mineral species, those having molybdenum as an essential component are less than forty. Out of

Fig. 4 a The [BiO7(OH)] polyhedron, and **b** the [MoO5(H2O)] polyhedron in the crystal structure of sardignaite

these, there are only three which also have bismuth as an essential component: koechlinite, $(BiO_2)MoO_4$ (Schaller 1916); chiluite, $Bi_6Mo_2Te_2O_{21}$ (Yang et al. 1989); and schlegelite, $Bi_7O_4(MoO_4)_2(AsO_4)_3$ (Krause et al. 2006).

Of the three previously known bismuth molybdate minerals, koechlinite is chemically closer to sardignaite, having only bismuth and molybdenum as major cations. Its crystal structure, however, has no relationship with that of sardignaite (Van den Elzen and Rieck 1973; Teller et al. 1984). Schlegelite is a bismuth molybdate-arsenate, whose crystal structure is described in detail (Krause et al. 2006). Chiluite was reported to be a bismuth molybdate-tellurate (Yang et al. 1989). However, chiluite is a mineral that needs further study: a synthetic compound with the same chemical formula as that of chiluite has been described (Deng and Yang 1993), whose unit-cell parameters do not match those of the mineral.

As a matter of fact, beyond being a simple bismuth molybdate, sardignaite displays an unprecedented structure topology among minerals, and has no evident crystal-chemical relations with known species.

More recently, another bismuth molybdate with ideal chemical formula $BiMo_2O_7(OH)\cdot H_2O$ was found at the same locality and approved as a new mineral (IMA No. 2009–022). It will be described in detail elsewhere.

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