

**ORLANDIITE, $Pb_3Cl_4(SeO_3) \cdot H_2O$, A NEW MINERAL SPECIES,
AND AN ASSOCIATED LEAD-COPPER SELENITE CHLORIDE
FROM THE BACCU LOCCI MINE, SARDINIA, ITALY**

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ABSTRACT

Orlandiite, ideally $Pb_3Cl_4(SeO_3) \cdot H_2O$, is a new mineral species from a selenium-rich part of the oxidation zone at the old lead-arsenic mine of Bacchu Locci, near Villaputzu, Sardinia, Italy. The mineral is colorless to white, translucent, brittle, has a vitreous to silky luster, and is not fluorescent in ultraviolet light. The calculated density is 5.66 g/cm^3 for the ideal formula, with $Z = 2$. The mineral is birefringent, with $n_{\text{meas.}} = n_{\text{calc.}} = 1.96 (\pm 0.05)$. An X-ray study carried out on a single crystal indicates a triclinic symmetry, space group $P\bar{1}$ (no. 2), a 8.136(3), b 8.430(6), c 9.233(7) Å, α 62.58(7), β 71.84(4), γ 75.13(4)°. The strongest six lines of the X-ray-diffraction pattern [d in Å(I)(hkl)] are: 4.000(100)(002), 3.258(75)($\bar{1}21$), 3.188(75)(201), 3.818(55)(201), 3.731(44)(122), and 2.103(40)(142). Orlandiite occurs as very small, elongate, tabular crystals up to 0.1 mm in length, colorless to white, in association with chalcocite, pseudobolite, anglesite, quartz and other selenites. The chemical formula has been determined from electron-microprobe data and a crystal-structure determination [final R index = 0.042 on 1226 reflections with $I > 3\sigma(I)$]. The structure contains two independent Pb atoms belonging to layers with idealized composition $PbCl_2$; a third disordered lead atom is located between these layers, together with a disordered SeO_3 group and the H_2O molecule. In most of the sites occupied by Cl atoms, there is a partial replacement by OH groups. Associated with orlandiite and chalcocite, and presently under study, is another new selenite, $Pb_4CuCl_3(SeO_3)_3(OH)$, in the form of minute lemon-yellow aggregates of tiny platy crystals. The strongest six lines of the X-ray diffraction pattern for this phase [d in Å(I)(hkl)] are: 8.279(100)(010), 6.674(80)(110), 11.100(76)(001), 7.344(70)(100), 5.788(65)(101), and 6.036(60)($\bar{1}12$), which leads to the following unit-cell data: a 8.290(8), b 10.588(13), c 13.587(15) Å, α 124.47(8), β 110.60(9), γ 63.26(9)°, and $Z = 2$.

Keywords: orlandiite, new mineral species, selenites, Bacchu Locci, Sardinia, Italy.

SOMMAIRE

Nous présentons ici les caractéristiques de la orlandiite, nouvelle espèce minérale dont la composition idéale serait $Pb_3Cl_4(SeO_3) \cdot H_2O$; elle provient de la partie riche en sélénium de la zone d'oxydation de l'ancienne mine de plomb-arsenic de Bacchu Locci, située près de Villaputzu, en Sardaigne, Italie. Le minéral est incolore ou blanc, translucide, cassant, ayant un éclat vitreux à soyeux; il n'émet aucune fluorescence en lumière ultraviolette. La densité calculée est 5.66 g/cm^3 pour la formule idéale, avec $Z = 2$. Le minéral est biréfringent, avec $n_{\text{mes.}} = n_{\text{calc.}} = 1.96 (\pm 0.05)$. Une étude en diffraction X sur cristal unique indique une symétrie triclinique, groupe spatial $P\bar{1}$ (no. 2), a 8.136(3), b 8.430(6), c 9.233(7) Å, α 62.58(7), β 71.84(4), γ 75.13(4)°. Les six raies les plus intenses du spectre de diffraction [d en Å(I)(hkl)] sont: 4.000(100)(002), 3.258(75)($\bar{1}21$), 3.188(75)(201), 3.818(55)(201), 3.731(44)(122) et 2.103(40)(142). La orlandiite se présente en très petits cristaux incolores à blancs, tabulaires, allongés, jusqu'à 0.1 mm en longueur, en association avec chalcocite, pseudobolite, anglesite, quartz et autres sélénites. La formule chimique a été établie à partir de données obtenues à la microsonde électronique et des résultats d'une ébauche de la structure cristalline [R final = 0.042, 1226 réflexions ayant $I > 3\sigma(I)$]. La structure contient deux atomes indépendants de Pb faisant partie de couches de composition idéale $PbCl_2$; un troisième atome est désordonné entre ces couches, en relation avec un groupe SeO_3 désordonné et la molécule de H_2O ; dans la plupart des sites occupés par le Cl, il y a un remplacement partiel par des groupes OH. Une deuxième nouvelle espèce, étroitement associée à la orlandiite et la chalcocite, fait présentement l'objet d'une étude; il s'agit d'un autre sélénite, $Pb_4CuCl_3(SeO_3)_3(OH)$, qui se présente sous forme d'aggrégats de plaquettes jaunecitron très petites. Les six raies les plus intenses du spectre de diffraction de cette phase [d en Å(I)(hkl)] sont: 8.279(100)(010),

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6.674(80)(110), 11.100(76)(001), 7.344(70)(100), 5.788(65)(101) et 6.036(60)($\bar{1}\bar{1}2$), ce qui mène à la maille élémentaire: a 8.290(8), b 10.588(13), c 13.587(15) Å, α 124.47(8), β 110.60(9), γ 63.26(9)°, et $Z = 2$.

(Traduit par la Rédaction)

Mots-clés: orlandiite, nouvelle espèce minérale, sélénites, Bacu Locci, Sardaigne, Italie.

INTRODUCTION

The old lead and arsenic mine at Bacu Locci near Villaputzu, in southeastern Sardinia, is one of several hydrothermal ore deposits hosted in the Paleozoic "black shales" occurring in the well-known silver-rich mining zone of Sarrabus–Gerrei. The mine is situated at the northern border of this region and was exploited for about a century until the 1960s, when it was finally abandoned. Chalcomenite constitutes an interesting find in the dumps; the quality of the crystals permitted the structure refinement to be carried out on natural samples for the first time (Pasero & Perchiazzi 1989). Our first visit to the old underground workings in 1996 resulted in the discovery of exceptional specimens of chalcomenite in some abundance, with crystals up to 2 cm in length, together with other secondary copper minerals (see below), in some cases even in fine specimens, and a number of other selenites. In a Se-rich area in the mine, and in close connection with chalcomenite, two new lead selenites containing essential amounts of chlorine have also been discovered, one of them being orlandiite, and the other $Pb_4CuCl_3(SeO_3)_3(OH)$, which is presently under study.

Orlandiite is named in honor of Paolo Orlandi (b. 1946), Associate Professor of Mineralogy at the University of Pisa, who has been very active in determining new minerals and mineral occurrences in Italy. The new mineral and name have been approved by the IMA Commission on New Minerals and Mineral Names (No. 98–038): Type specimens, including the holotype, are deposited in the mineral collection of the Department of Earth Sciences at the Università degli Studi, Milan, Italy.

OCCURRENCE

A description of the Bacu Locci mineral deposit is given in Zucchetti (1958a, b) and Bakos *et al.* (1991). The ore mainly consists of galena and arsenopyrite, and occurs within sedimentary and igneous formations of lower Silurian age; these formations are covered by a transgressive formation of Eocene age (Monte Cardiga transgression). The Paleozoic sedimentary rocks are typically represented by black shales, whereas the igneous rocks are typically represented by porphyries. The unconformity between the Silurian and Eocene sediments is quite distinct, and can be easily noticed in the landscape of the nearby mountains.

The Paleozoic terranes are crossed by a series of subparallel fractures and faults oriented along a NNW–

SSE direction. Such discontinuities were formed as a result of tectonic readjustments after the last episode of intrusive activity, and were subsequently mineralized by hydrothermal solutions. Veins are more or less frequent within fractures, since the distribution of the ore minerals deposited by the mineralizing fluids was controlled by the mechanical behavior of the host rocks. Such an origin explains why stockwork-type structures are observed within the porphyries, whereas elongate orebodies can be observed within the shale unit.

The tectonic breccia filling the fractures was probably impregnated by the ores, thereby resulting in an unusual mineralization mainly consisting of galena and arsenopyrite in almost equal amounts. Accessory minerals are sphalerite, chalcopyrite, pyrite and pyrrhotite. The deposit is typically zoned, as can easily be observed in the upper part of the mine, where a surface zone, an oxidation zone and a secondary enrichment zone can be identified.

In the oxidation zone of the deposit (upper Santa Barbara level), there is a notable concentration of secondary minerals, mainly anglesite, azurite, brochantite and gypsum, with minor linarite, together with subordinate amounts of several other species, such as atacamite, bayldonite, beaverite, carbonate-cyanotrichite, chalcocalumite, chalcophyllite, chlorargyrite, devilline, olivenite, osarizawaite, pseudobolélite, pyromorphite, serpierite, smithsonite, spangolite, native sulfur, vanadinite and wulfenite. In addition, there is a local concentration of selenites, especially chalcomenite; a detailed illustration of these minerals is given in Gramaccioli *et al.* (1997).

Orlandiite occurs in these chalcomenite-rich concentrations as very small elongate tabular crystals (up to 0.1 mm in length), which are colorless to white, and in places associated with lemon-yellow aggregates (up to 0.1 mm in diameter) of platy crystals of the other new phase (hereafter referred to as the "second phase"). These are generally found together with chlorides, such as green atacamite or very small small dark blue cubes of pseudobolélite or, much more rarely, with chlorargyrite of an unusual pale pink color. In the same association, there are several other selenium oxysalts, all of them in very minor amounts with respect to chalcomenite, which is by far the most abundant selenium-rich mineral.

Among these oxidized selenium-bearing minerals, there are elongate bundles of olsacherite or, much more rarely, mandarinioite, in small spherical aggregates of prismatic yellowish green crystals. At the outermost part

of the selenium-rich concentrations, we found attractive blue crystals of schmiederite, in cases closely resembling linarite, or francisite in earthy green masses. A detailed study of all these secondary minerals is in progress. In some aspects, the assemblage of selenium minerals at Baccu Locci appears to be rather selective, since some of the most widespread selenium oxysalts are altogether absent. For instance, notwithstanding a persistent and systematic search, no clinochalcomenite has ever been found at the locality, and in spite of the presence of lead and the selenite ion, no molybdomenite or kerstenite has yet been identified in this association.

Similarly, with the exception of a single nodule (1 cm in diameter) consisting of a solid solution of clausthalite (PbSe) and galena in almost equal proportions (PbS = 57 mol%), no pure selenides have been discovered yet in the locality; most of the unoxidized ore in the assemblage consists of galena, covellite, and arsenopyrite.

PHYSICAL AND OPTICAL PROPERTIES

Orlandiite forms elongate tabular crystals (Figs. 1A, B), invariably twinned on {010}; they are brittle, white to colorless, with a vitreous to silky luster and a perfect cleavage on {010}. The second phase appears as very small aggregates (100 μm in diameter) of lemon-yellow platy crystals, up to 10 μm long and 2 μm thick. Neither mineral is fluorescent in either short-wave (254 nm) or long-wave (366 nm) ultraviolet light. They can be easily distinguished from each other using the stereo-microscope, and with some experience, also from olsacherite, and from much more common minerals such as pyromorphite, gypsum, or vanadinite.

The measurement of the optical properties of these lead selenites is very difficult, owing not only to the very small size of the crystals, but also to their strong reactions with all available liquids of high index of refraction. These readily attack the minerals, turning them into a black opaque residue, thereby preventing any useful observation with a petrographic microscope. The only possibility in this respect was to measure the Brewster angle with the optical goniometer; in this way, in spite of the extremely small size of the grains in polished mounts, we obtained approximate values of the mean index of refraction $n = 1.96 (\pm 0.05)$ and $1.83 (\pm 0.05)$, respectively, for orlandiite and the other new phase. If the values of the calculated densities from the unit cell and the chemical composition are considered for the two minerals ($D_{\text{calc}} = 5.66$ and 5.25 g/cm^3 , respectively), the corresponding estimates of the mean indices of refraction using the Gladstone-Dale rule and Mandarino's (1981) constants and criteria are 1.96 and 1.87, respectively. These are in excellent to good agreement with observed values.

For orlandiite, the infrared spectrum recorded in transmission on a very small crystal using an FT-IR infrared microprobe shows sharp absorptions due to

H_2O and the OH group (3410–3160 and 1586 cm^{-1}), and absorptions at 788 and 724 cm^{-1} due to the selenite group (Ross 1974). For the other new phase, the IR spectrum recorded from a very small grain using the same instrument and conditions shows sharp absorptions in the OH region ($3700\text{--}2900 \text{ cm}^{-1}$) and absorptions at 810 and 738 cm^{-1} due to the selenite group.

CHEMICAL COMPOSITION

Electron-microprobe analyses (wavelength dispersion) of the two phases were performed on polished grain-mounts using an ARL-SEMQ instrument of the Italian National Research Council (C.N.R.) at Centro di studio per la Geodinamica Alpina e Quaternaria, Milan. The standards and operating conditions are reported in the footnote of Table 1. Because of the very small amount of material available, no direct determination of the H_2O content has been carried out. For orlandiite, the amount of H_2O present in the mineral has been deduced from the results of crystal-structure refinement, and for the other new phase, the corresponding amount has been deduced from the OH content based on charge balance. In both cases, the total is very reasonable. In order to overcome volatilization of water and possibly of lead chloride, the electron beam was set at a diameter of 15 μm during the analysis of both minerals. The resulting chemical formula for orlandiite is in good agreement with that obtained from crystal-structure data. The only possible check for the other phase, for which the crystal structure is unknown, was to consider mass and charge balance (which needs some OH); the total is close to 100%.

TABLE 1. CHEMICAL COMPOSITION OF THE NEW LEAD SELENITES FROM BACCU LOCCI, SARDINIA, ITALY

Wt%	Orlandiite	Range	Theoretical	Second new phase	Range	Theoretical
Cl	14.35	13.28–15.33	13.73	8.41	8.29–8.49	8.35
PbO	74.18	71.73–75.49	75.50	61.26	59.97–62.11	60.80
SeO ₂	12.31	11.91–12.52	11.67	24.84	23.90–25.91	24.67
SO ₂	0.20	0.12–0.37		0.14	0.12–0.16	0.14
ZnO	0.35	0.15–0.80		1.75	1.69–1.91	1.74
CdO	0.11	0.07–0.17		1.44	1.24–1.55	1.43
CuO	0.39	0.20–0.81		4.29	4.01–4.41	4.24
FeO	0.42	0.40–0.43		0.40	0.38–0.41	0.40
H ₂ O*	2.34		2.20	0.11		0.11
Less O=Cl	3.24		3.10	1.88		1.88
Total	101.41		100.00	100.76		100.00

* From the structure determination and charge balance (relative to OH). Number of analyses at the electron microprobe: eight for orlandiite, six for the second new phase. Accelerating voltage 20 kV, sample current on brass 15 nA. Standards: phosgenite (Cl), anglesite (Pb, S), pure metals (Se, Zn, Cd, Cu, Fe). Theoretical composition for orlandiite and for the second new phase, from the empirical chemical formulae $\text{Pb}_3(\text{Cl}_{1.54}\text{OH}_{0.32})_{24}(\text{SeO}_3)_4\text{H}_2\text{O}$ and $(\text{Pb}_{3.74}\text{Cd}_{0.15})_{23.89}(\text{Cu}_{0.71}\text{Zn}_{0.25}\text{Fe}_{0.08})_{21.16}\text{Cl}_3[(\text{Se}_{1.02}\text{S}_{0.01})_{21.03}\text{O}_3]_3(\text{OH}_{0.77}\text{Cl}_{0.23})$, respectively.

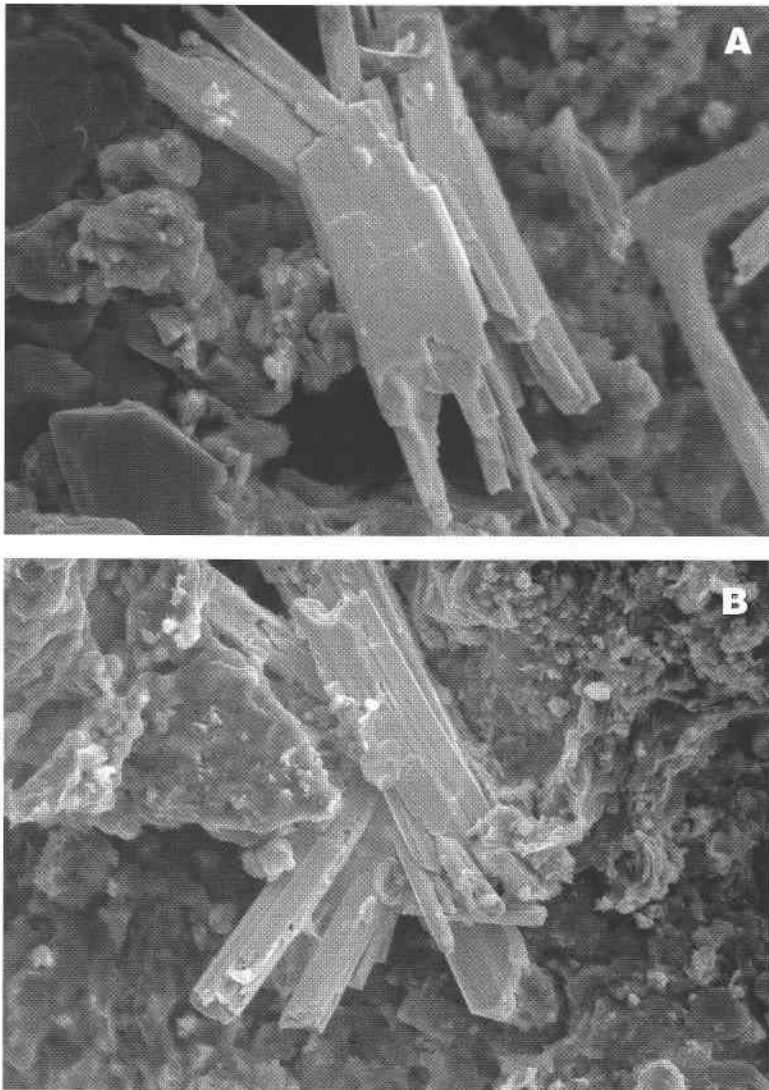


FIG. 1. Orlandiite, tabular elongate crystals on matrix. Photos taken with a Hitachi scanning electron microscope. The maximum length of the crystal aggregates is 150 μm .

Whereas in orlandiite lead is the only cation present as an essential constituent, other cations, such as copper as well as lead, seem to be essential in the second phase. On crystal-chemical grounds, zinc and cadmium are very likely substituents for copper, and probably also iron. For this reason, all these elements have been grouped in the proposed chemical formula. For orlandiite, minor amounts of these same elements have also been found; with the possible exception of Cd, they are not considered to be likely replacements for Pb in the structure and have been omitted from the chemical formula.

X-RAY DATA

The determination of accurate X-ray crystallographic data of orlandiite was particularly difficult, owing to the scarcity of suitable material. Single-crystal data show the mineral to be triclinic $P\bar{1}$ (no. 2), with a 8.136(3), b 8.430(6), c 9.233(7) Å, α 62.58(7)°, β 71.84(4)°, γ 75.13(4)°, and $Z = 2$. Powder-diffraction data obtained using a Gandolfi camera are reported in Table 2. From these data, a unit cell with a 8.146(12), b 8.428(22), c 9.241(22) Å, α 62.32(21), β 71.64(17), γ 75.22(19)° can be deduced, in good agreement with the results obtained

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR ORLANDIITE*

<i>hkl</i>	d_{obs} (Å)	d_{cal} (47 Å)	<i>I</i> / <i>I</i> ₀	<i>hkl</i>	d_{obs} (Å)	d_{cal} (Å)	<i>I</i> / <i>I</i> ₀
0 0 1	8.090	7.965	36	1 2 3	2.365	2.368	37
1 0 1	5.010	4.982	21	1 2 4	2.298	2.298	23
0 0 2	4.000	3.983	100	0 2 4	2.173	2.174	7
2 0 1	3.818	3.813	55	1 4 2	2.103	2.107	40
1 2 2	3.731	3.723	44	3 2 0	1.989	1.986	11
0 2 2	3.548	3.552	32	2 2 3	1.953	1.957	3
1 2 1	3.258	3.261	75	1 4 4	1.875	1.871	11
2 0 1	3.188	3.181	75	1 4 1	1.847	1.845	8
1 1 3	3.046	3.051	4	3 2 2	1.812	1.811	10
1 2 2	2.889	2.881	6	1 4 3	1.760	1.764	9
2 2 3	2.728	2.728	38	2 0 5	1.606	1.608	6
0 0 3	2.666	2.655	23	5 0 1	1.444	1.445	4
3 0 0	2.564	2.555	28	3 2 4	1.441	1.440	7
2 2 1	2.484	2.487	12				

* Gandolfi camera (diameter 114.6 mm), Ni-filtered CuK α radiation. Intensities calculated on the basis of the crystal structure.

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR THE SECOND PHASE*

<i>hkl</i>	d_{obs} (Å)	d_{cal} (Å)	<i>I</i> / <i>I</i> ₀	<i>hkl</i>	d_{obs} (Å)	d_{cal} (Å)	<i>I</i> / <i>I</i> ₀
0 0 1	11.100	11.104	76	2 2 5	2.545	2.548	20
0 1 0	8.279	8.255	100	2 2 2	2.520	2.519	20
1 0 0	7.344	7.338	70	3 0 1	2.462	2.458	20
1 1 0	6.674	6.665	80	3 2 4	2.440	2.445	20
1 1 2	6.036	6.064	60	0 3 1	2.418	2.411	20
1 0 1	5.788	5.782	65	0 3 5	2.388	2.389	20
0 2 2	4.568	4.537	45	2 2 2	2.361	2.365	20
1 1 3	4.335	4.309	40	1 4 5	2.331	2.330	20
1 0 2	4.182	4.171	40	3 3 3	2.297	2.298	25
1 1 1	4.105	4.100	44	3 4 4	2.274	2.272	20
0 2 3	3.840	3.839	40	3 3 5	2.257	2.252	20
2 2 1	3.742	3.769	30	1 0 5	2.208	2.208	20
2 0 0	3.685	3.669	30	2 2 6	2.154	2.154	20
2 0 1	3.635	3.630	35	1 3 1	2.133	2.134	20
0 2 1	3.373	3.369	40	1 2 3	2.106	2.104	15
1 1 2	3.314	3.311	30	0 3 6	2.079	2.074	15
1 2 2	3.247	3.243	25	0 4 0	2.065	2.064	15
1 1 4	3.224	3.215	25	4 2 3	2.043	2.040	15
1 0 3	3.144	3.142	35	4 2 1	2.028	2.025	20
2 2 4	3.034	3.032	30	0 4 6	1.921	1.919	15
2 0 3	2.803	2.797	23	4 3 6	1.760	1.759	10
2 1 2	2.728	2.726	30	1 0 6	1.742	1.741	10
3 2 3	2.664	2.659	20	2 3 5	1.700	1.699	10
2 3 5	2.565	2.559	20	1 4 6	1.686	1.685	15

* From a D-max Rigaku diffractometer, Ni-filtered CuK α radiation.

from single-crystal data. The larger values of the estimated standard deviation obtained in this way are due to the paucity of pure material available to record the spectrum.

For the second phase, of which no adequate single crystals could be found, only powder data are available (Table 3). From these data, a triclinic unit cell with *a*

8.290(8), *b* 10.588 (13), *c* 13.587(15) Å, α 124.47(8), β 110.60 (9), γ 63.26(9)°, and *Z* = 2 can be deduced, and the reflections are indexed on this basis.

The single-crystal data for orlandiite were obtained using a Enraf-Nonius CAD4 diffractometer; the crystal structure was solved by direct methods and refined using 1226 reflections with *I* > 3 σ (*I*); the final *R* index is 0.042. Full details of the crystal structure will be published in a separate paper (Demartin *et al.*, in prep.). The structure contains layers with idealized composition 2PbCl₂ and PbSeO₃•H₂O, respectively, alternatively stacked along [100]. Two independent Pb sites belong to the PbCl₂ layers and display tricapped-trigonal prismatic coordination, similarly to that observed in a number of other minerals containing lead and chlorine [laurionite group, barstowite Pb₄Cl₆(CO₃)•H₂O: Merlino *et al.* (1991, 1993, 1996)].

The PbSeO₃•H₂O layer displays extensive disorder due to the splitting of the Pb site into two different positions, having a population of about 0.75 and 0.25, respectively; a corresponding splitting also is observed for the selenite groups. Such a statistical disorder can be considered as a random stacking of the PbSeO₃•H₂O layers in the crystal, with the prevalence of one configuration.

DISCUSSION

The presence of a variety of secondary selenium minerals at Baccu Locci is notable because of the rarity of these minerals in nature. This locality seems to be the richest in selenium oxysalts in the world, after the celebrated El Dragon mine in Bolivia (Grundmann *et al.* 1990, Mandarin 1994). A particular characteristic of the Baccu Locci selenium-rich assemblage is the presence of a significant number of chloride minerals. This strongly suggests the essential presence of chlorine for such a paragenesis, and a requisite threshold concentration of the chloride ion in the depositing solutions.

In recent years, a number of chloride-containing selenites have been discovered in nature as minerals deposited by fumarolic activity around the crater of the Tolbachik volcano in Kamchatka, Russia (see, for instance, Vergasova *et al.* 1989, 1997, 1999, Semenova *et al.* 1992, Krivovichev *et al.* 1998). The presence of selenium compounds in the fumarolic deposits from Vesuvius was noted long ago (Zamboni & Coniglio 1925). However, none of the minerals deposited in fumaroles bears any chemical or crystallographic resemblance to the new phases discovered at Baccu Locci. Without entering into detailed geochemical discussions, it is not difficult to imagine that the conditions of formation are drastically different, the volcanic occurrences being the result of deposition from a vapor phase at higher temperature and a much lower pH than at Baccu Locci.

The presence of chlorides in the secondary minerals may possibly be due to the Eocene transgression event, at a stage when the deposit was covered by the sea.

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