American Mineralogist, Volume 70, pages 845–848, 1985

Freedite and thorikosite from Långban, Sweden, and Laurion, Greece: two new species related to the synthetic bismuth oxyhalides

PETE J. DUNN

Department of Mineral Sciences
Smithsonian Institution, Washington, D.C. 20560

AND ROLAND C. ROUSE

Department of Geological Sciences
University of Michigan, Ann Arbor, Michigan 48109

Abstract

Freedite and thorikosite are new mineral species, which are closely related structurally and chemically to one another and to the synthetic bismuth oxyhalides.

Freedite, $Pb_{15}(Cu,Fe)_3^{2+}As_4^{3+}O_{19}Cl_{10}$, is monoclinic, space group *C*2, *Cm*, or *C*2/*m*, with $a = 13.569(5)$, $b = 20.085(4)$, $c = 7.463(4)$Å, $\beta = 105.75(5)°$, $V = 1958(2)$Å^3, and Z = 2. Freedite is greenish-yellow, with vitreous luster, {100} cleavage, and a specific gravity of 7.0 g/cm^3 (obs). It is found associated with ecdemite, lead, copper, finnemanite, and calcite at the Långban Mine, Värmland, Sweden. The species is named in honor of Dr. Robert L. Freed of Trinity University.

Thorikosite, $(Pb_3Sb_{0.6}As_{0.4})(O_3OH)Cl_2$, is tetragonal, space group *I*4/*mmm*, with $a = 3.919(1)$, $c = 12.854(5)$Å, $V = 197.4(1)$Å^3, and Z = 1. Thorikosite forms light yellow prismatic crystals, tabular on {001}, with perfect {001} cleavage, vitreous luster, and density of 7.24 g/cm^3 (calc). Thorikosite occurs associated with hydrocerussite, paralaurionite, sphalerite, and calcite in the slags of Laurion, Greece.

Introduction

In early 1983, Roland Eriksson of Långban, Sweden, sent an unknown mineral to one of the authors (PJD). Our initial investigation suggested it was a new species related to the synthetic bismuth oxyhalide group (Sillén, 1942; Structure Reports, 1947–1948). Subsequent chemical and structural studies have confirmed this hypothesis. We have named this new species *freedite* in honor of Dr. Robert L. Freed of Trinity University in San Antonio, Texas, in recognition of his contributions to the science of mineralogy.

While this mineral was under investigation, another closely related compound from Laurion, Attike, Greece, was called to our attention by Robert and Norma Jaxel of Camp Springs, Maryland. This mineral has been named *thorikosite* after the ancient town of Thorikos, near which the Laurion Mines are located. Once the relationship between these phases was clear, they were investigated simultaneously and, because of their close chemical and structural relationships, we have chosen to publish them together.

Both the minerals and their names were approved by the Commission on New Minerals and Mineral Names, IMA. Type material is preserved at the Smithsonian Institution under catalogue numbers NMNH 160352 and 160353 (freedite) and NMNH 161928 (thorikosite).

Experimental methods

Single-crystals of both freedite and thorikosite were studied using the Weissenberg, precession, and oscillating crystal X-ray methods. Refined unit cell parameters were calculated by least-squares refinement of powder diffraction data, which were obtained with a 114.6 mm diameter Gandolfi camera, a polycrystalline sample, Cu*K*α X-radiation and NBS silicon (a = 5.43088Å) as an internal standard. The powder diffraction data for both species are compared in Table 1.

The samples were chemically analyzed using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μA, measured on brass. Wavelength-dispersive microprobe scans indicated the absence of any elements with atomic number greater than 9, except those reported herein. The standards used were PbO (Pb), olivenite (As), Cu_2O (Cu), NaCl (Cl), Sb_2O_3 (Sb), and hornblende (Fe). The data were corrected using a modified version of the *MAGIC*-4 computer program. Paucity of material precluded a water determination for thorikosite, but a TGA-EGA study of freedite was obtained using a Mettler TA-1 thermoanalyzer/Inficon IQ200 mass spectrometer system (R. A. Ramik, pers. comm.). This indicated that CO_2 and H_2O together sum to 0.2 weight percent. We attribute the CO_2 to calcite impurities and consider the H_2O to be negligible. In subsequent calculations of the unit cell contents and chemical formula, freedite has been assumed to be anhydrous. The question of water in thorikosite will be considered later.

0003–004X/85/0708–0845$02.00

Table 1. X-ray powder diffraction data for freedite and thorikosite

Freedite				Thorikosite			
I	d_{obsd}	d_{calc}	hkl	I	d_{obsd}	d_{calc}	hkl
4	6.51	6.53	200	3	6.39	6.43	002
<1	4.97	5.02	040				
<1	4.244	4.254	310				
5	3.832	3.839	150	7	3.754	3.749	101
4	3.581	3.591 3.584	002 -202				
2	3.254	3.265	400	3	3.203	3.213	004
<<1	3.040	3.034	061				
10	2.949	2.952	350	10	2.891	2.892	103
8	2.830	2.838 2.828	202 -402				
8	2.734	2.734	-152	5	2.775	2.771	110
<<1	2.568	2.569	351				
<<1	2.445	2.446 2.443	-262 212				
<<1	2.367	2.373	-313				
2	2.177	2.177	600	1	2.141	2.142	006
5	2.096	2.099 2.093	352 -552	3	2.099	2.099	114
2	2.009	2.009	0·10·0	2	1.959	1.960	200
<<1	1.935	1.942 1.934	601 0·10·1				
<<1	1.914	1.920	2·10·0				
2	1.867	1.866	-204				
1	1.753	1.753 1.752	0·10·2 -2·10·2	1	1.737	1.737	211
4	1.704	1.705 1.701	552 -752	2	1.695	1.695	116
2	1.692	1.692	750	2	1.664	1.663	107
2	1.671	1.671 1.666	602 -802				
4	1.639	1.639 1.638	2·10·2 -4·10·2	3	1.621	1.622	213
<1	1.620	1.622 1.617	204 -604				
4	1.577	1.579 1.575	154 -554				
<1	1.476	1.476	6·10·0	1	1.445	1.446	206
<1	1.416	1.418 1.414	-754 -804				
<<1	1.401	1.403 1.400	752 -952				
2	1.366	1.367 1.365	-2·10·4 950	<1 <<1	1.387 1.342	1.386 1.342	220 109
<<1	1.353	1.354 1.351	802 -10·0·2				
<<1	1.332	1.332	1·15·0				
<<1	1.304	1.306	10·0·0				
3b	1.282	1.285 1.282 1.280	6·10·2 -8·10·2 3·15·0	2	1.268	1.268	217
2	1.261	1.262 1.260	2·10·4 -6·10·4				
2	1.254	1.255 1.251	554 -954				
<<1	1.226	1.226	-10·0·4				
<1	1.197	1.197 1.195	006 -606				
<1	1.188	1.188	-356				
1b	1.178	1.180 1.176 1.175	952 3·15·2 -5·15·2				
<1	1.158	1.159 1.156	4·10·4 -8·10·4				
<<1	1.139	1.139	11·5·0				

114.6 mm Gandolfi camera, polycrystalline specimens, CuKα radiation, Ni filter, visually estimated intensities, b = broadened line. Indexed with the aid of single-crystal photographs.

Freedite

The interpretation of the crystallography of freedite (and thorikosite) was difficult due to the poor quality of the available crystals, all of which are composites of several individuals. However, it was possible to determine that freedite is monoclinic, space group *C*2, *Cm*, or *C*2/*m*, with unit cell parameters $a = 13.569(5)$, $b = 20.085(4)$, $c = 7.463(4)$Å, $\beta = 105.75(5)°$, $V = 1958(2)$Å^3, and Z = 2. Two additional cells can be recognized on the single-crystal photographs. The first is a *C*-centered, monoclinic subcell for which $A = a = 13.569$, $B = b/5 = 4.017$, $C = c/2 = 3.732$Å, and $\beta = 105.75°$. The second is a body-centered, orthogonal pseudocell having parameters $A' = b/5 = 4.017$, $B' = d(001)/2 = 3.591$, and $C' = a = 13.569$Å. This orthogonal cell corresponds to the body-centered tetragonal cell of thorikosite.

The results of an electron microprobe analysis of freedite are given in Table 2. Unit cell contents, calculated using the refined cell parameters and observed specific gravity are $Pb_{29.4}(Cu,Fe)_{5.5}As^{3+}_{7.6}Cl_{18.4}O_{37.1}$, which we interpret as $Pb_{15}(Cu,Fe)^{2+}_{3}As^{3+}_{4}O_{19}Cl_{10}$ with Z = 2, using the fact that the possible space groups have equipoint ranks of 2, 4, and 8. We have assumed As to be trivalent because of the intimately associated ecdemite and because a crystal structure analysis of the closely related phase, thorikosite, is consistent with arsenic and antimony in this valence state. The true formula of freedite is not yet firmly established, but the provisional formula given above represents a good approximation. The uncertainties can only be resolved by a crystal structure analysis, a rather formidable task considering the size of the supercell and the quality of the crystals. Freedite is bright greenish-yellow with a yellow streak. The luster is greasy to vitreous. Most material is slightly turbid. The hardness (Mohs) is approximately 3 and the mineral is brittle. The cleavage is perfect on {100} and the fracture is irregular. The specific gravity, measured using a Berman balance, is 7.0±0.5 g/cm^3, compared with the calculated value of 7.22 g/cm^3. Freedite is biaxial and all indices of refraction are greater than 1.90. Pleochroism is weak to indiscernible. There is no fluorescence in ultraviolet radiation.

Freedite occurs at the Långban Mine, Värmland, Sweden, where it forms aggregates with a slightly radial texture. It is intimately associated with calcite, ecdemite, lead, copper, and finnemanite on andradite/magnetite ore.

Table 2. Microprobe analyses of freedite and thorikosite

	Freedite			Thorikosite		
	Analysis	Theory*	Atoms per cell†	Analysis	Theory**	Atoms per cell†
PbO	80.2%	78.68%	29.4	77.6%	77.81%	2.9
CuO	4.9	5.23	5.1	---	---	---
FeO	0.4	0.35	0.5	---	---	---
Sb_2O_3	---	---	---	9.8	10.16	0.6
As_2O_3	9.2	9.29	7.6	4.4	4.59	0.4
H_2O	---	---	---	2.2***	1.06	2.0
Cl	8.0	8.33	18.4	7.7	8.24	1.8
O = Cl	1.8	1.88		1.7	1.86	
Total	100.9%	100.00%		100.0%	100.00%	

*For $Pb_{30}(Cu_{5.6}Fe_{0.4})As_8O_{38}Cl_{20}$

**For $(Pb_3Sb_{0.6}As_{0.4})(O_3OH)Cl_2$

***H_2O by difference

†Calculated from the analyses using a density of 7.0 g/cm^3.

It is among the last phases to form and may have been abundant locally. The samples seen by us suggest it is not an exceedingly rare species.

Thorikosite

Diffraction photographs established that thorikosite is tetragonal with space group *I*422, *I*$\bar{4}$2*m*, *I*4*mm*, or *I*4/*mmm*. Unit cell parameters are $a = 3.919(1)$ and $c = 12.854(5)$Å, the cell volume is 197.4(1)Å^3, and Z = 1. Subsequent to the Weissenberg and precession studies, a crystal structure analysis was performed; this established the chemical formula of thorikosite (see below) and fixed its space group as *I*4/*mmm* (Rouse and Dunn, in press).

An electron microprobe analysis of thorikosite is given in Table 2. Since the specific gravity could not be determined experimentally, a value of 7.0 g/cm^3 was assumed by analogy to freedite for the purpose of calculating the unit cell contents. The calculation yielded $Pb_{2.9}Sb_{0.6}As_{0.4}H_{2.0}O_{4.5}Cl_{1.8}$, assuming the presence of water, as H_2O or (OH). This assumption could not be verified analytically due to lack of sufficient material for a water determination. It is, however, supported by the crystal structure analysis, which revealed four (Pb, Sb, As) atoms disordered over a single four-fold equipoint plus four oxygen and two chlorine atoms. The resulting formula is $Pb_3Sb_{0.6}As_{0.4}O_4Cl_2$, which is out of charge balance by one excess negative charge. Since the structure refinement indicated full occupancy of both anion sites, there must be one $(OH)^-$ disordered over the oxygen site. The formula of thorikosite is therefore fixed at $(Pb_3Sb_{0.6}As_{0.4})(O_3OH)Cl_2$.

Thorikosite occurs as light yellow prismatic crystals, which are tabular on {001}. Curved faces are common. The extremely small size precluded the measurement of most physical and optical properties. The calculated density is 7.24 g/cm^3. The crystals are very brittle, have a perfect {001} cleavage, vitreous luster, and are usually turbid. The cleavage can be explained by noting that the structure contains layers of anions and cations parallel to (001). Each cation is bonded strongly to four close oxygen atoms and weakly to four distant chlorine atoms. Breakage should occur preferentially through these weak Pb–Cl linkages.

Thorikosite occurs in vugs in the ancient slags of Laurion, Attike, Greece, associated with paralaurionite, hydrocerussite, sphalerite and calcite in the type specimen. Little can be said about the order of crystallization. We found many mineral specimens from Laurion which yielded powder diffraction data similar to those of thorikosite. The differences between thorikosite patterns and those of the other specimens were principally in the *d*-values less than 1.75. Such differences are in some cases quite subtle. In view of the solid solutions possible, we recommend that identification of thorikosite by X-ray powder pattern be exercised with utmost caution. We have not studied these other phases.

Discussion

Three lines of evidence indicate a close chemical and structural relationship among freedite, thorikosite, and certain members of the bismuth oxyhalide family (Sillén, 1942; Structure Reports, 1947–1948). Comparison of the crystallographic data in Table 3 shows that the unit cell and space group of thorikosite are similar to those of the synthetic compounds $Pb_{3.6}O_4Cl_{1.8}$ (Gasperin, 1964), $LiBi_3O_4Cl_2$ and its isotypes (Sillén, 1939), and the tetragonal polymorph of nadorite, $PbSbO_2Cl$ (Sillén and Melander, 1941). All of these compounds belong to the bismuth oxyhalide family, even though some contain Pb^{2+} rather than Bi^{3+} as their characteristic large cation. The basic structural unit of the bismuth oxyhalides is a body-centered tetragonal cell having $a \approx 4$Å and *c* commonly *ca.* 12 or 24Å. Some members of the group show an orthorhombic distortion such that $a \approx b \approx 4\sqrt{2} \approx 5.7$Å, examples being nadorite and its congeners perite ($PbBiO_2Cl$) and blixite ($Pb_2(O,OH)_{<2}Cl$). A second and previously unreported kind of distortion occurs in freedite, which has a monoclinic superstructure and an orthogonal, body-centered pseudocell, which corresponds to the basic unit cell of the bismuth oxyhalides.

Chemically, it can be seen from Table 3 that freedite and thorikosite have an especially close relationship to $LiBi_3O_4Cl_2$ and, indeed, thorikosite has proven to be isostructural with that compound. (Here we are considering only the orthogonal pseudocell of freedite, which has 1/10 the volume of the true cell). The ratio of large cations (Pb or Bi) to total small cations (Cu, Fe, As, Sb, or Li) to oxygen to chlorine is approximately 3 :1 :4 :2. Tetragonal nadorite and $Pb_{3.6}O_4Cl_{1.8}$ would seem to be exceptions; however, both they and the other phases in Table 3 all obey the more general rule that the cation to oxygen to chlorine ratio be approximately 2 :2 :1. There is complete solid solution between lead and antimony in the tetragonal polymorph of nadorite, the two elements being disordered over the same 4-fold equipoint (Sillén and Melander, 1941). The same solid solution also applies to lithium and bismuth in the $LiBi_3O_4Cl_2$ structure (Sillén, 1939), and to lead, antimony, and arsenic in the thorikosite structure. It is remarkable that these structures are able to tolerate solid solution among atoms of such diverse size. The results of

Table 3. Crystal-chemical data for freedite, thorikosite, and related compounds

Name	Formula	Z	Space Group	Cell (Å)
Freedite				
supercell	$Pb_{15}(Cu,Fe)_3As_4O_{19}Cl_{10}$	2	C2, Cm, or C2/m	a = 13.569 b = 20.085 c = 7.463 β = 105.75°
pseudocell	$\sim Pb_3(Cu,Fe,As)O_4Cl_2$	1	Orthogonal I-centered	A = 4.017 B = 3.591 C = 13.569
Thorikosite	$(Pb_3Sb_{0.6}As_{0.4})(O_3OH)Cl_2$	1	I4/mmm	a = 3.919 c = 12.854
---	$Pb_{3.6}O_4Cl_{1.8}$	1	I4/mmm	a = 3.91 c = 13.00
---	$LiBi_3O_4Cl_2$	1	I4/mmm	a = 3.848 c = 12.05
Tetragonal nadorite	$PbSbO_2Cl$	2	I4/mmm	a = 3.895 c = 12.29

the thorikosite structure analysis suggest that this is accomplished by small positional shifts of the oxygens and chlorines to accommodate the range of cation sizes; i.e., the structure is characterized by a modest, but pervasive, degree of positional disorder (Rouse and Dunn, in press).

Comparison of the powder diffraction data of freedite and thorikosite (Table 1) with those of $Pb_{3.6}O_4Cl_{1.8}$ (JCPDS 21-473) and the bromine analogue of $LiBi_3O_4Cl_2$ (JCPDS 16-669) reveals two salient features. Firstly, the data for the latter three phases are strikingly similar and, in fact, contain the same reflections with the same indices except for three weak lines not observed from thorikosite. Secondly, the data sets for the three simple tetragonal phases are virtually subsets of that of freedite, which is consistent with the supercell-pseudocell relationship deduced from single-crystal data for that mineral. With four exceptions, all freedite reflections with intensities of 1 or greater (on a scale of 10) correspond to reflections in the patterns of the simple tetragonal phases.

Freedite and thorikosite are thus established as the newest of the naturally occurring members of the bismuth oxyhalide family, the others being the aforementioned nadorite, perite, and blixite, plus bismutite ($Bi_2O_2CO_3$), beyerite ($CaBi_2O_2(CO_3)_2$, kettnerite ($CaBiOFCO_3$), and possibly ecdemite and heliophyllite (both *ca.* $Pb_3AsO_{<4}Cl_{<2}$). These minerals are not all isostructural, as they represent several different structure types within the bismuth oxyhalide family. In bismutite and beyerite, the carbonate ion plays the same structural role as a halide (Lagercrantz and Sillén, 1948). It has also been suggested that sundiusite ($Pb_{10}(SO_4)Cl_2O_8$) belongs in this family, with the sulfate ion playing the role of a halide, but the evidence for such a relationship is ambiguous and incomplete (Dunn and Rouse, 1980).

Acknowledgments

We thank Robert and Norma Jaxel for providing samples for study and calling our attention to thorikosite. We are indebted to Mr. Robert A. Ramik for TGA-EGA analysis of freedite. We thank Drs. Malcolm Ross and Joan Fitzpatrick for critical readings of the manuscript.

References

Dunn, P. J. and Rouse, R. C. (1980) Sundiusite, a new lead sulfate oxychloride from Långban, Sweden. American Mineralogist, 65, 506–508.

Gasperin, M. (1964) Sur la synthèse d'un oxychlorure de plomb. Bulletin Société francaise de Minéralogie et de Cristallographie, 87, 278–280.

Lagercrantz, A. and Sillén, L. G. (1948) On the crystal structure of $Bi_2O_2CO_3$ (bismutite) and $CaBi_2(CO_3)_2$ (beyerite). Arkiv för Kemi, Mineralogi och Geologi, 25A, No. 20, 1–21.

Rouse, R. C. and Dunn, P. J. (1985) The structure of thorikosite, a naturally occurring member of the bismuth oxyhalide group. Journal of Solid State Chemistry. (in press).

Sillén, L. G. (1939) Röntgenuntersuchungen von $LiBi_3O_4Cl_2$ und verwandten Stoffen. Zeitschrift für anorganische und allgemeine Chemie, 242, 41–46.

Sillén, L. G. (1942) Über eine Familie von Oxyhalogeniden. Die Naturwissenschaften, 30, 318–324.

Sillén, L. G. and Melander, L. (1941) X-ray studies on the oxyhalide minerals nadorite (ochrolite) $PbSbO_2Cl$ and ekdemite. Zeitschrift für Kristallographie, 103, 420–430.

Structure Reports (1947–1948) Bismuth oxyhalides, 11, 305–320.

Manuscript received, August 6, 1984;
accepted for publication, March 8, 1985.