

THE ORE MINERALOGY OF THE OTISH MOUNTAINS URANIUM DEPOSIT, QUEBEC: SKIPPENITE, $\text{Bi}_2\text{Se}_2\text{Te}$, AND WATKINSONITE, $\text{Cu}_2\text{PbBi}_4(\text{Se},\text{S})_8$, TWO NEW MINERAL SPECIES

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ABSTRACT

Uranium vein-type deposits located in the Otish Mountains basin (Quebec) are associated with strongly albitized doleritic dykes and sills. Two periods of mineralization were recognized. The first, contemporaneous with the albitization, consists of brannerite and uraninite. The second, separated from the previous by tectonic movements, is characterized by carbonate gangue (dolomite), and a complex association of selenides, tellurides and sulfides including: skippenite, watkinsonite, poubaite, součekite, clausthalite, aikinite, wittichenite, molybdenite, pyrite, chalcopyrite, galena, digenite, covellite, electrum, native bismuth, and several unidentified bismuth selenides-tellurides. *Skippenite*, $\text{Bi}_2\text{Se}_2\text{Te}$, is rhombohedral, $R\bar{3}m$, a 4.183(4), c 29.12(8) Å, $V = 441.3$ Å³, $Z = 3$. The calculated density is 7.94 g/cm³. Strongest lines in the powder pattern: 4.85(6)(00.6), 3.584(6)(10.1), 3.074(10)(01.5), 2.267(7)(10.10), 2.090(8)(11.0); 1.422(5)(11.5). Aggregates of lamellar crystals with perfect {0001} cleavage. White in reflected light and moderately anisotropic. Reflectances (in air): 43.0–41.0(420), 50.3–49.0(540), 50.8–49.4(700 nm). $\text{VHN}_{25} = 63$. Microprobe analyses yield the empirical formula $(\text{Bi}_{2.05}\text{Cu}_{0.04}\text{Pb}_{0.01}\text{Se}_{2.00}\text{Te}_{0.87}\text{S}_{0.13})$. The mineral is named in honor of Prof. G. Skippen, Carleton University, Ottawa. Skippenite is associated with bismuth selenides whose composition is close to $\text{Bi}_2(\text{Se},\text{Te},\text{S})_2$ and $(\text{Bi},\text{Pb})_2(\text{Se},\text{Te},\text{S})_3$. *Watkinsonite*, $\text{Cu}_2\text{PbBi}_4(\text{Se},\text{S})_8$, is monoclinic, $P2/m$, Pm or $P2$, a 12.921(3), b 3.997(1), c 14.989(3) Å, β 109.2(2)°, $V = 731$ Å³, $Z = 2$, calculated density 7.82 g/cm³. The strongest lines in the powder pattern are: 3.573(9)(111), 2.976(10)(205), 2.929(10)(311), 2.407(7)(306), 2.140(7)(207,415), 2.065(7)(316,514), 1.484(7)(812,703). Forms aggregates of irregular grains. In reflected light, white with a bluish shade. Moderate anisotropy with blue grey to greyish brown polarization colors. $\text{VHN}_{25} = 166$. Neither cleavage nor twinning. Reflectances (in air): 46.6–43.2(420), 48.6–45.4(540), 49.0–45.8(700 nm). The empirical formula calculated from microprobe analyses is $\text{Cu}_{2.36}\text{Pb}_{1.26}\text{Bi}_{3.70}(\text{Se}_{6.21}\text{S}_{1.74}\text{Te}_{0.05})_8$. The ideal formula may be written $\text{Cu}_{2+x}\text{Pb}_{1+x}\text{Bi}_{4-x}(\text{Se},\text{S},\text{Te})_8$, with $x \approx 0.30$. The mineral is named in honor of Prof. D.H. Watkinson, Carleton University, Ottawa. The Otish Mountains deposit is the second occurrence of *poubaite* and *součekite*. Poubaite exhibits perfect {001}

cleavage; $\text{VHN}_{25} = 99$. Rhombohedral, $R\bar{3}m$, a 4.271(2), c 40.27(4) Å, $V = 635.8$ Å³, $Z = 3$. Strongest lines in the powder pattern: 3.638(6)(01.2), 3.105(10)(10.7), 2.270(8)(01.14), 2.135(9)(11.0), 1.764(7)(01.20), 1.557(6)(20.14), 1.359(7)(20.20). Microprobe analyses gave the empirical formula $\text{Pb}_{0.92}\text{Bi}_{2.08}(\text{Se}_{1.80}\text{Te}_{1.86}\text{S}_{0.34})$, suggesting Se and Te ordering within layers of semimetallic atoms; the ideal formula is $\text{PbBi}_2\text{Se}_2\text{Te}_2$. The composition of *součekite* is $\text{Cu}_{1.03}\text{Pb}_{1.00}\text{Bi}_{1.04}(\text{S}_{1.60}\text{Se}_{1.35}\text{Te}_{0.05})$. Microprobe analyses of aikinite revealed Se-content of 4.5 wt.%; the ideal formula is $\text{Cu}_{1-x}\text{Pb}_{1-x}\text{Bi}_{1+x}(\text{S}_{2.65}\text{Se}_{0.35})$, with $x \approx 0.08$. Wittichenite composition is close to stoichiometry, with a minor replacement of S by Se (up to 0.7 wt.%).

Keywords: Otish Mountains, Quebec, uranium mineralization, skippenite, watkinsonite, new minerals, poubaite, součekite, aikinite, wittichenite, selenides, tellurides.

SOMMAIRE

Les gisements uranifères du bassin des monts Otish (Québec) sont liés à des dykes et sills de dolérites, fortement albitisés. Deux épisodes minéralisants ont été reconnus. Le premier, contemporain de l'albitisation, comporte la brannerite et l'uraninite. Le second, séparé du précédent par des mouvements tectoniques, est caractérisé par une gangue carbonatée (dolomite) dans laquelle apparaît une association complexe de séléniures, tellurures et sulfures comprenant: skippenite, watkinsonite, poubaite, součekite, clausthalite, aikinite, wittichenite, molybdenite, pyrite, chalcopyrite, galena, digenite, covellite, electrum, bismuth natif, et plusieurs séléniures et tellurures de Bi non identifiés. La *skippenite*, $\text{Bi}_2\text{Se}_2\text{Te}$, est rhomboédrique, $R\bar{3}m$, a 4.183(4), c 29.12(8) Å, $V = 441.3$ Å³, $Z = 3$. La densité calculée est 7.94. Raies les plus intenses du diagramme de poudre: 4.85(6)(00.6), 3.584(6)(10.1), 3.074(10)(01.5), 2.267(7)(10.10), 2.090(8)(11.0), 1.422(5)(11.5). Agrégats de cristaux lamellaires avec un clivage parfait suivant {0001}. De couleur blanche en lumière réfléchie, anisotropie moyennement forte. Pouvoir réflecteur (air): 43.0–41.0(420), 50.3–49.0(540), 50.8–49.4(700 nm). $\text{VHN}_{25} = 63$. Les analyses à la microsonde électronique ont donné une for-

mule empirique ($\text{Bi}_{2.05}\text{Cu}_{0.04}\text{Pb}_{0.01}\text{Se}_{2.00}(\text{Te}_{0.87}\text{S}_{0.13})$). Nommé en l'honneur du Prof. G. Skippen, Université de Carleton, Ottawa. La skippenite est parfois associée à des séléniures de Bi dont la composition est proche de $\text{Bi}_2(\text{Se},\text{Te},\text{S})_2$ et de $(\text{Bi},\text{Pb})_2(\text{Se},\text{Te},\text{S})_3$. La *watkinsonite*, $\text{Cu}_2\text{PbBi}_4(\text{Se},\text{S})_8$, est monoclinique, $P2/m$, Pm ou $P2$, avec a 12,921(3), b 3.997(1), c 14.989(3) Å, β 109.2(2)°, $V = 731 \text{ \AA}^3$, $Z = 2$, densité calculée 7.82. Les raies les plus intenses du diagramme de poudre sont: 3.573(9)(111), 2.976(10)(205), 2.929(10)(311), 2.407(7)(306), 2.140(7)(207,415), 2.065(7)(316,514), 1.484(7)(812,703). En agrégats de plages irrégulières. En lumière réfléchie, elle est blanche avec une pointe de bleuâtre. L'anisotropie est modérément forte, avec les teintes de polarisation gris bleuâtre à brun grisâtre. $\text{VHN}_{25} = 166$. On n'a observé ni clivage, ni macles. Pouvoir réfracteur (air): 46.6–43.2(420), 48.6–45.4(540), 49.0–45.8(700 nm). La formule cristallochimique calculée à partir des analyses à la microsonde électronique est $\text{Cu}_{2.36}\text{Pb}_{1.26}\text{Bi}_{3.70}(\text{Se}_{6.21}\text{S}_{1.74}\text{Te}_{0.05})_8$. La formule idéale doit s'écrire $\text{Cu}_{2+x}\text{Pb}_{1+x}\text{Bi}_{4-x}(\text{Se},\text{S},\text{Te})_8$, avec $x \approx 0.30$. Nommé en l'honneur du Prof. D.H. Watkinson, Université de Carleton, Ottawa. Le gisement des monts Otish est le deuxième gisement connu de la poubaïte et de la součekite. La *poubaïte* présente un clivage parfait suivant (0001); $\text{VHN}_{25} = 99$. Rhomboédrique, $R\bar{3}m$, a 4.271(2), c 40.27(4) Å, $V = 635.8 \text{ \AA}^3$, $Z = 3$. Les raies les plus intenses du diagramme de poudre sont: 3.638(6)(01.2), 3.105(10)(10.7), 2.270(8)(01.14), 2.135(9)(11.0), 1.764(7)(01.20), 1.557(6)(20.14), 1.359(7)(20.20). Les analyses à la microsonde électronique conduisent à la formule $\text{Pb}_{0.92}\text{Bi}_{2.08}(\text{Se}_{1.80}\text{Te}_{1.86}\text{S}_{0.34})$, faisant entrevoir une distribution ordonnée de Se et Te dans les couches d'atomes semi-métalliques et une formule idéale $\text{PbBi}_2\text{Se}_2\text{Te}_2$. La composition de la součekite correspond à $\text{Cu}_{1.03}\text{Pb}_{1.00}\text{Bi}_{1.04}(\text{S}_{1.60}\text{Se}_{1.35}\text{Te}_{0.05})$. Les analyses de l'aïkinite ont révélé une teneur en Se de 4.5%; sa formule idéale s'écrit $\text{Cu}_{1-x}\text{Pb}_{1-x}\text{Bi}_{1+x}(\text{S}_{2.65}\text{Se}_{0.35})$, avec $x \approx 0.08$. La composition de la wittichenite est proche de la stoechiométrie, avec un remplacement restreint de S par Se (jusqu'à 0.7% en poids).

Mots-clés: monts Otish, Québec, minéralisation uranifère, skippenite, watkinsonite, nouveaux minéraux, poubaïte součekite, aïkinite, wittichenite, séléniures, tellurures.

INTRODUCTION

Selenide-bearing uranium mineralization is relatively common, and its mineralogy has been extensively studied during the last thirty years. This is the case of deposits in the Athabasca basin, Saskatchewan (Robinson 1955, Harris *et al.* 1970, Harris & Burke 1971), of deposits in the Bohemian Massif (Kvaček 1965, 1973), the Chaméane deposit in the French Massif Central (Agrinier *et al.* 1967, Johan *et al.* 1982), and of several occurrences in the Clausthal district, Germany (Tischendorf 1959, 1960). In all these deposits, selenium is associated with Cu, Fe, Pb, Ag, Zn, Hg and Tl, and more rarely with Au, Sb and As; the parageneses are con-

siderably deficient in sulfur. Base-metal sulfides, where present, belong to distinct periods of mineralization that may be selenium-free. The Chaméane deposit must be considered an exception because of the extensive replacement of Se by S in some sulfides (chalcopyrite–eskebornite series), as documented by Johan *et al.* (1982). Rarely, nickel selenides (Kuusamo, Finland; Vuorelainen *et al.* 1964) and molybdenum selenides (Kapijimpanga, Zambia; Čech *et al.* 1973) have been observed.

Mineralization with bismuth selenides is less common. Besides the classical occurrence of guanajuatite and paraguanaujatite at Guanajuato, Mexico (Ramdohr 1948), bismuth selenides and lead–bismuth seleniferous sulfosalts were described from: Falun, Sweden (Karup-Møller 1970, Johan & Picot 1976, Mumme 1976), Orijärvi, Finland (Vorma 1960), and the Ikuno mine, Japan (Kato 1959). More recently, Large & Mumme (1975) discovered seleniferous bismuth sulfosalts in the Juno deposit, Tennant Creek, Northern Territory, Australia, where Mumme (1975, 1976) and Mumme & Watts (1976) identified three new copper–lead–bismuth seleniferous sulfosalts (junoite, proudite and pekoite). This type of mineralization is characterized by an intimate association of sulfides and selenides, by replacement of S by Se giving rise to selenium-bearing sulfides, and by the presence of gold (Falun, Juno mine), which seems to be typical.

The association of Cu-, Pb-, Bi-sulfides, selenides and tellurides with uranium is rather exceptional. Until now, only three occurrences, Oldřichov, Czechoslovakia (Čech & Vavřín 1978, 1979), Mazenod Lake, Northwest Territories (Miller 1981) and Cluff Lake, Saskatchewan (Ruhlmann 1985) were known. The Otish Mountains deposit described in this paper is the fourth example of this very rare mineral paragenesis. Our study of this deposit has led to the characterization of two new mineral species, skippenite and watkinsonite, approved by the Commission on New Minerals and Mineral Names, I.M.A. Type material of skippenite and watkinsonite has been deposited at École des Mines in Paris.

GEOLOGICAL SETTING AND PARAGENESES

The Otish Mountains uranium deposit, located in the central part of Quebec (71°03'00" W, 52°12'30" N), is situated in the Proterozoic Otish basin, which belongs to a pericratonic belt at the border of the Grenville Front (Wynne-Edwards 1972). The sedimentary rocks that occur in this basin (Otish Group) are essentially of volcano–detrital origin and lie discordantly either on the Archean basement made up of granites and greenstones, or on the Lower Aphebian Chibougamau Group. All these units were intruded by thick doleritic dykes and sills during the Hudsonian tectonic event.

The different types of mineralization discovered in the Otish basin are mainly associated with these doleritic bodies. A large diversity of ore parageneses and their depositional sequence suggest the existence of several metallogenic phases (Ruhlmann *et al.* 1986).

Two major hydrothermal metallogenic cycles of uranium are inferred. The first, associated with the Late Hudsonian tectonic activity, led to the deposition of two distinct mineral assemblages: albite with uranium minerals, and Cu-, Pb-, Bi-selenides, tellurides and sulfides in a carbonate gangue (dolomite and calcite), with chlorite as product of hydrothermal alteration of amphibole and biotite (Ruhlmann *et al.* 1986). The second cycle, which is weaker,

produced pitchblende and coffinite mineralization in a calcite gangue. Its age is approximately 306 Ma and seems to correspond to the mineralization event well known in other areas, as for example in the Athabasca basin (Ruhlmann *et al.* 1986).

Sulfides associated with a quartz gangue were rarely observed. They were emplaced between the two major metallogenic cycles mentioned above. The uranium mineralization associated with albitization was generated by a large-scale metallogenic process affecting the Archean basement, the Proterozoic cover, and doleritic bodies intruding both of these major geological units.

Mineralized zones are developed along fractures in the dolerite dykes and sills, and are surrounded

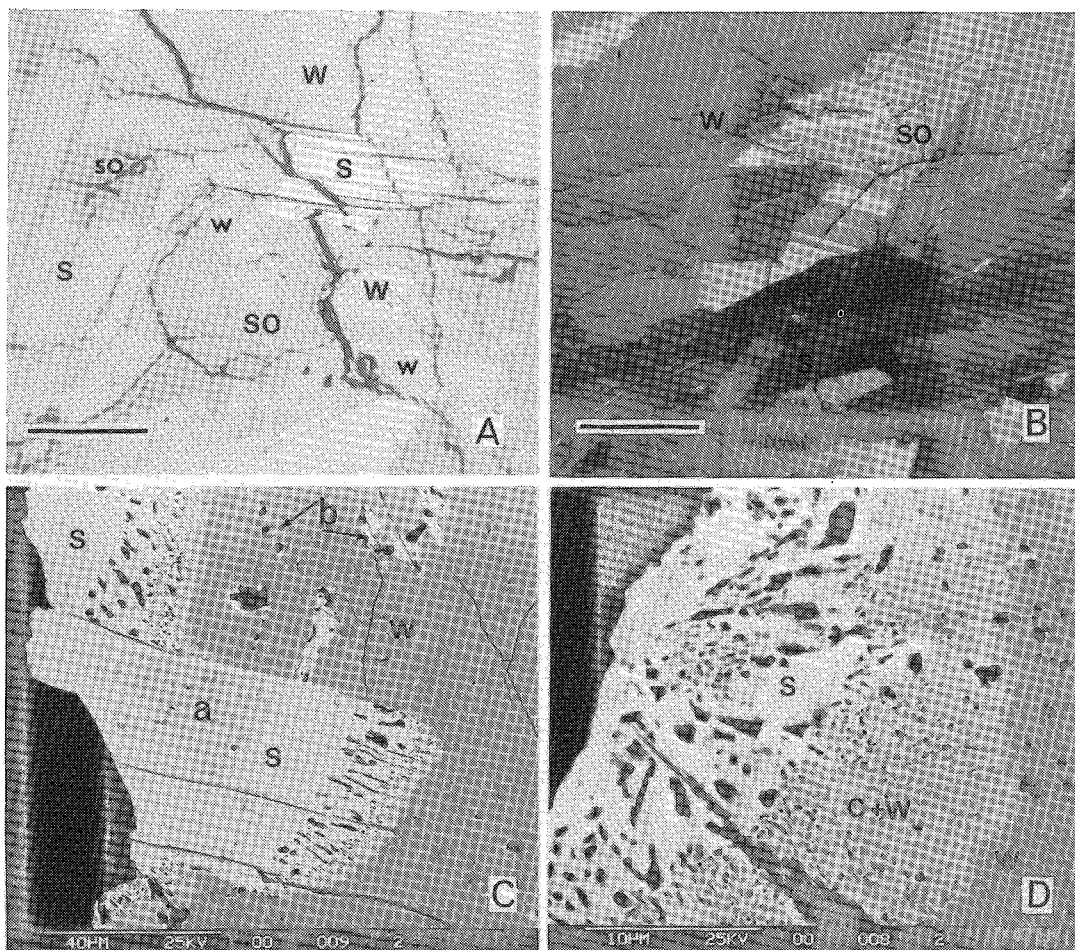


FIG. 1. A. Součekite (so) and watkinsonite (w) replace skippenite (s) with perfect {0001} cleavage, along grain boundaries. Watkinsonite is replaced by součekite. Reflected plane-polarized light, oil immersion. Scale bar represents 100 μm . B. Watkinsonite (w) is replaced by polysynthetically twinned součekite (so); (s) skippenite. Reflected light, crossed polarizers, oil immersion. Scale bar represents 100 μm . C. SEM photograph of skippenite (s) crystal containing an inclusion of $\text{Bi}_2(\text{Se},\text{Te},\text{S})_2$ (a). $\text{Bi}_2(\text{Se},\text{S})_2$ (b) associated with clausthalite and chalcopyrite penetrates along watkinsonite (w) grain boundaries. D. SEM photograph of skippenite (s) rimmed by a symplectitic intergrowth of Cu-bearing clausthalite and watkinsonite (c + w).

by zones of hydrothermal alteration, symmetrically disposed with respect to the fractures. The most external zone of alteration is rich in epidote in microfractures subparallel to dyke walls. Toward the centre, chloritization of amphibole and biotite is evident. The central zone exhibits extensive albitization. The main uranium minerals are uraninite and brannerite.

This mineralization was followed by important tectonic movements that were responsible for the intense brecciation of all earlier minerals. Fractures are filled by dolomite that belongs to the later carbonate-bearing period, and a complex assemblage of Bi, Pb, Cu, Fe, Mo-tellurides, selenides and sulfides.

The second metallogenic cycle carrying uranium in the Otish basin is of lesser importance. Pitchblende, associated with coffinite, occurs in a calcite gangue, rich in hematite inclusions. Pyrite, marcasite and galena rarely occur in this type of mineralization.

Se-, Te-, and S-bearing assemblages of the first metallogenic cycle appear to be later with respect to the carbonate gangue, penetrating between carbonate grains and partly replacing them. Thus the development of ore is very irregular and, consequently, the establishment of a general sequence of crystallization is difficult. The following mineral associations were observed (arrow indicates proposed sequence of crystallization): 1. $\text{Bi}_2(\text{Se, Te, S})_2 \rightarrow$ skippenite \rightarrow watkinsonite \rightarrow clausenthalite \rightarrow chalcopyrite \rightarrow electrum, 2. poubaitite \rightarrow watkinsonite \rightarrow součekite, 3. součekite \rightarrow wittichenite, and 4. aikinite \rightarrow clausenthalite-galena solid solution. Taking into account these relationships, together with other observations on polished sections, the most plausible order of deposition of ore minerals is the following: for the first period of mineralization $\text{Bi}_2(\text{Se, Te, S})_2 \rightarrow \text{Bi}_2(\text{Se, Te, S})_3 \rightarrow \text{Bi}_2\text{Se}_2(\text{Te, S})$ (skippenite) $\rightarrow (\text{Bi, Pb})_2(\text{Se, Te, S})_3 \rightarrow \text{PbBi}_2\text{Se}_2\text{Te}_2$ (poubaitite) $\rightarrow \text{Cu}_2\text{PbBi}_4(\text{Se, S, Te})_8$ (watkinsonite) $\rightarrow \text{CuPbBi}(\text{S, Se})_3$ (součekite) $\rightarrow \text{Cu}_3\text{BiS}_3$ (wittichenite), and for the second period of mineralization: $\text{CuPbBi}(\text{S, Se})_3$ (aikinite) $\rightarrow \text{Pb}(\text{Se, S}) \rightarrow \text{PbSe} \rightarrow \text{Bi}_2(\text{Se, S})_2 \rightarrow \text{CuFeS}_2 \rightarrow (\text{Au, Ag})$. The paragenetic position of Se-bearing molybdenite (up to 5.2 Se, 0.5 Fe, 1.1 Pb, in wt. %), could not be determined. This molybdenite probably represents one of the earliest phases of the sulfide association, to which also belong chalcopyrite, pyrite, digenite and covellite. Kish & Cuney (1981) reported early molybdenite in uraninite-albite veins from the Mistamisk Valley, Quebec. Native elements and alloys (bismuth, gold, electrum) are very late, filling fractures in uraninite or associated (in the case of electrum) with sulfides and selenides. Electrum occurs as veinlets in the clausenthalite-chalcopyrite assemblage, and contains 16.7 Ag, 1.3 Cu and 1.4 Se (wt. %).

The most striking relationship is the interstitial

position of watkinsonite and součekite with respect to aggregates of tabular crystals of Pb-Bi-Se-Te-(S) minerals (Figs. 1a,b), thus showing a distinct compositional evolution with decreasing temperature that is characterized by an increase in $\text{Bi}/(\text{Se} + \text{Te} + \text{S})$ and $\text{Pb}/(\text{Pb} + \text{Bi})$ values. Phases of the Bi-Se-Te-S system that have disordered layers of semimetallic elements precipitated before those whose composition suggests an ordering of Se and (Te + S) atoms. This is also the case if Pb is considered. The $\text{Se}/(\text{Se} + \text{Te} + \text{S})$ ratio varies only slightly (0.78–0.70) from $\text{Bi}_2(\text{Se, Te, S})_2$ to lead-bearing paraganajuaite, but decreases suddenly to 0.45 with the crystallization of poubaitite. Thus, the late stages of crystallization of bismuth- and lead-bismuth selenides are characterized by a sharp increase in the activities of Pb and Te in the hydrothermal system.

Cu-, Pb-, and Bi-bearing phases appear after Bi- and Pb-Bi selenides. Again, the crystallization progressed with increasing $\text{Pb}/(\text{Pb} + \text{Bi})$ and decreasing $\text{Se}/(\text{Se} + \text{Te} + \text{S})$, but unlike the preceding case, the variation of $\text{Se}/(\text{Se} + \text{Te} + \text{S})$ is due to an abrupt increase in concentration of S. The system then became strongly depleted in Se, as shown by very low concentrations of Se in wittichenite, closing the first mineralization period.

The second period started with the precipitation of aikinite, which was followed, firstly by clausenthalite-galena solid solution, evolving progressively toward the PbSe end-member and, finally, by $\text{Bi}_2(\text{Se, S})_2$. All these phases are almost tellurium-free. An interesting relationship was observed between clausenthalite on one hand and watkinsonite and skippenite on the other. Clausenthalite penetrates along a watkinsonite-skippenite contact or along interstices between grains of watkinsonite, and replaces both older phases, giving rise to a sub-microscopic symplectitic intergrowth (Fig. 1d). Microprobe analyses show that clausenthalite in the symplectite is Cu-, Fe-, and Bi-bearing (3.0 Cu, 1.8 Fe, 3.2 Bi, wt. %) and contains up to 20 mol. % PbS in solid solution, whereas clausenthalite associated with chalcopyrite is sulfur-free. The average empirical formula of clausenthalite may be written $(\text{Pb}_{0.76}\text{Cu}_{0.12}\text{Fe}_{0.08}\text{Bi}_{0.04})(\text{Se}_{0.80}\text{S}_{0.20})$. Cuprian galena solid solution was described by Clark & Sillitoe (1971), Frenzel *et al.* (1973) and Burke (1980), but no data are available for copper solubility in PbSe. Clausenthalite-galena solid solution and clausenthalite are, together with a mineral whose composition is close to $\text{Bi}_2(\text{Se, S})_2$, the latest selenides of the Otish Mountains suite. Similarly, in the Chaméane uranium deposit, a late generation of clausenthalite closed the precipitation of selenides and preceded the deposition of the sulfides at the close of the ore formation (Johan *et al.* 1982).

In the Otish Mountains deposit, besides the Se-bearing molybdenite mentioned above, the late sul-

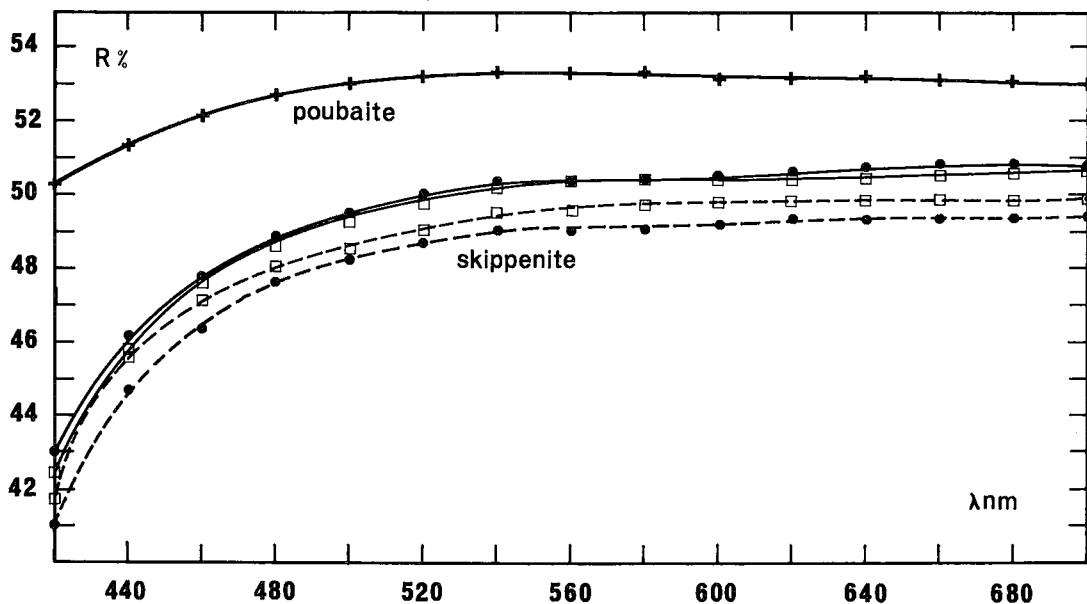


FIG. 2. Reflectances of skippenite and poubaite. For poubaite, only R_{max} is indicated.

fide association is characterized by a predominance of Se-free chalcopyrite. An SEM study revealed the presence of a clausthalite-chalcopyrite symplectitic intergrowth where these minerals are in contact. The final hydrothermal stages led to the extensive transformation of some selenides (mainly součekite), to the removal of Pb and Bi, and to the production of covellite, which invariably has a low Se-content (0.4 wt. %).

MINERALOGY

Skippenite: Bi_2Se_2Te

This new mineral species, named in honor of Professor George Skippen of Carleton University,

Ottawa, is the most abundant selenide in the Otish Mountains deposit. It occurs as massive aggregates of lamellar crystals (0.2 to 1 mm in length) flattened along [0001], and exhibiting perfect {0001} cleavage. The crystals are strongly deformed and show deformation lamellae. Skippenite is intimately associated with watkinsonite, which prevents the measurement of its density.

Aggregates of skippenite are megascopically steel-grey, with a high metallic lustre and black streak; it strongly resembles tetradymite or tellurobismuthite. In polished section, the color is white with a yellow tint; bireflectance is weak, noticeable in oil (yellowish white to grey), but not perceptible in air. The anisotropy is moderate without any strong chromatic effects; polarization colors vary from grey

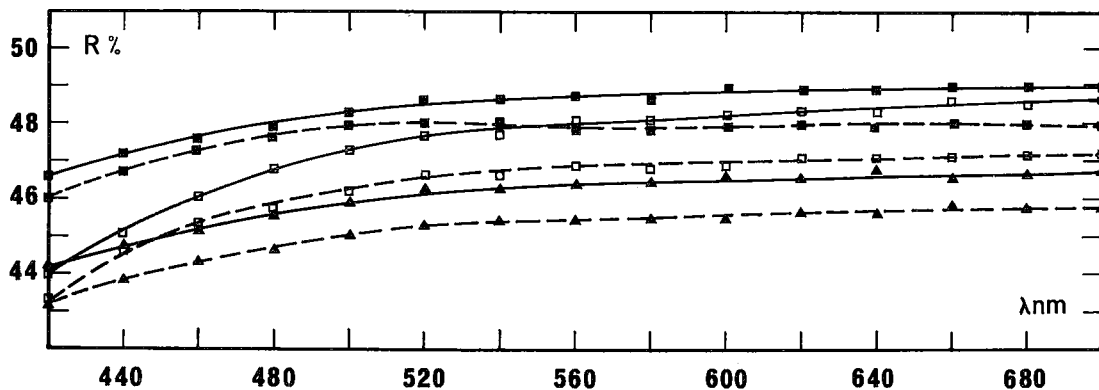


FIG. 3. Reflectances of watkinsonite. \blacktriangle grain 1; \square grain 2; \bullet grain 3; — R_{max} ; - - - R_{min} .

TABLE 1. REFLECTANCES OF SKIPPENITE, POUBAITE AND WATKINSONITE

λ nm	SKIPPENITE				POUBAITE		WATKINSONITE					
	Grain 1		Grain 2		Grain 1		Grain 1		Grain 2		Grain 3	
	R_{\max}	R_{\min}	R_{\max}	R_{\min}	R_{\max}	R_{\min}	R_{\max}	R_{\min}	R_{\max}	R_{\min}	R_{\max}	R_{\min}
420	43.0	41.0	42.4	41.7	50.3	46.0	44.2	43.2	44.0	43.3	46.6	46.0
440	46.1	44.6	45.7	45.7	51.4	46.6	44.7	43.8	45.1	44.6	47.2	46.7
460	47.8	46.5	47.7	47.2	52.2	47.2	45.2	44.3	46.1	45.3	47.6	47.3
480	48.8	47.7	48.5	48.0	52.7	47.6	45.6	44.7	46.8	45.8	48.0	47.7
500	49.5	48.3	49.3	48.5	53.0	48.0	45.9	45.0	47.3	46.3	48.3	47.9
520	50.0	48.7	49.8	49.0	53.2	48.3	46.2	45.2	47.6	46.6	48.5	48.1
540	50.3	49.0	50.2	49.4	53.3	48.5	46.3	45.4	47.8	46.7	48.6	48.0
560	50.4	49.1	50.3	49.7	53.3	48.6	46.4	45.4	48.0	46.8	48.7	47.8
580	50.4	49.1	50.4	49.8	53.3	48.8	46.4	45.5	48.1	46.9	48.8	47.8
600	50.5	49.2	50.5	49.8	53.3	48.8	46.5	45.6	48.2	47.0	48.8	47.9
620	50.6	49.3	50.5	49.8	53.2	48.9	46.6	45.6	48.3	47.0	48.9	47.9
640	50.8	49.4	50.5	49.9	53.2	49.0	46.6	45.7	48.4	47.1	48.9	48.0
660	50.8	49.4	50.6	49.9	53.1	49.0	46.6	45.7	48.5	47.1	49.0	48.0
680	50.8	49.4	50.7	49.9	53.1	49.1	46.7	45.8	48.5	47.1	49.0	47.9
700	50.8	49.4	50.8	49.9	53.0	49.1	46.7	45.8	48.6	47.2	49.0	47.9

Measurement conditions: plane polarized light, normal incidence, monochromator, photomultiplier with the cathode S_{20} , standard SiC, objective 44/0.65, half-field prism illuminator, obliquity corrected through $(R_{\perp} + R_{\parallel})/2$.

to bluish grey. No internal reflections were observed. The reflectance (Table 1, Fig. 2) is relatively high, approaching values measured for laitakarite, but distinctly lower than R_{\max} of poubaite (Fig. 3), paraganajuatite, tetradymite, jositite or tellurobis-muthite (Picot & Johan 1982). The reflectance measurements performed on randomly oriented grains indicate that R_{\max} values can be attributed to R_{\circ} . This suggests that skippenite is optically negative. Vickers microhardness VHN (10 indentations, 25-g load) is 63.0(7.7) (range 52.2 - 74.2). Deformed indentations reveal microhardness anisotropy, reported also for rucklidgeite by Zavjalov & Begizov (1977).

A single-crystal study (Weissenberg photographs, Ni-filtered Cu radiation) showed skippenite to be rhombohedral, $R\bar{3}m$, $R3m$, or $R32$, with the following unit-cell parameters, refined by least squares from the powder pattern: a 4.183(4), c 29.12(8) Å; $V = 441.3$ Å³; $Z = 3$; $c/a = 6.961$. The unit-cell dimensions, as well as the powder pattern (Table 2), are very close to data published for synthetic Bi_2Se_3 (Dönges 1951, Schubert *et al.* 1953, Berry & Thompson 1962). An X-ray study of skippenite shows that it belongs to the group of selenides and tellurides with a layered, tetradymite-like structure (Harker 1934), possessing a unit-cell that contains 15 layers (Strunz 1963). By analogy with these compounds, we attribute space group $R\bar{3}m$ to skippenite. According to Semiletov (in Strunz 1963), the layers in Bi_2Se_3 are placed in the following order: AcBAC - BaCBa - CbACb, where A,B,C = Se and a,b,c = Bi. By analogy with tetradymite, the most probable sequence of stacking for the skippenite structure might be: A'cBAC - B'aCBa - C'bACb, where A'B'C' = Te,S; A,B,C = Se and a,b,c = Bi. Skippenite is isostructural with kawazulite Bi_2SeTe_2 (Kato 1970). The calculated density is 7.80 g/cm³ for $Bi_2Se_2(Te_{0.87}S_{0.13})$ and 7.94 g/cm³ for Bi_2Se_2Te .

Microprobe analyses performed on various grains reveal a rather constant chemical composition (Table 3). The average empirical formula calculated on the basis of 3(Se + Te + S) is $(Bi_{2.05}Cu_{0.04}Pb_{0.01})Se_{2.00}(Te_{0.87}S_{0.13})$, which is very close to the ideal composition Bi_2Se_2Te . Cu, and Pb concentrations are very low and highly variable. Except for one composition (3, Table 3), no concomitant increase in concentration of these two elements was observed, which precludes the explanation that these concentrations could be due to submicroscopic inclusions of watskinsonite. For this reason, we have incorporated these elements into the empirical formula of skippenite, but we are unable to propose a suitable

TABLE 2. X-RAY POWDER DATA FOR SKIPPENITE AND POUBAITE

SKIPPENITE				POUBAITE			
I	d_{obs}	d_{calc}	hk.l	I	d_{obs}	d_{calc}	hk.l
5	9.71	9.704	00.3	4	6.70	6.712	00.6
6	4.85	4.852	00.6	5	4.472	4.475	00.9
6	3.584	3.595	10.1	6	3.638	3.638	01.2
2	3.237	3.243	10.4	4	3.364	3.361	01.5
10	3.074	3.076	01.5	10	3.105	3.111	10.7
1	2.562	2.567	01.8	3	2.727	2.724	10.10
7	2.267	2.269	10.10	2	2.606	2.602	01.11
5	2.133	2.137	01.11	1	2.376	2.375	10.13
8	2.090	2.091	11.0	8	2.270	2.271	01.14
3	1.944	1.941	00.15	9	2.135	2.135	11.0
3	1.916	1.921	11.6	1	2.077	2.081	10.16
2 B	1.808	1.808	02.1	3	1.992	1.995	01.17
		1.803	01.14	4 B	1.923	1.927	11.9
4	1.730	1.729	20.5	2	1.842	1.839	01.19
3	1.622	1.621	20.8	2	1.802	1.802	11.12
4	1.537	1.538	02.10			1.802	20.5
5 B	1.422	1.423	11.15	7	1.764	1.768	01.20
3	1.350	1.351	01.20	2	1.678	1.681	02.10
4 B	1.332	1.333	12.5			1.678	00.24
2	1.283	1.284	02.16	1	1.586	1.588	02.13
		1.281	12.8	6	1.557	1.556	20.14
4	1.239	1.239	21.10	1	1.461	1.458	20.17
				5	1.427	1.428	10.26
				7	1.359	1.362	20.20
				5	1.322	1.321	21.10
						1.319	11.24
				5	1.259	1.257	12.14
				4 B	1.226	1.226	10.31

B broad line; 76.4 mm Debye-Scherrer camera, Ni-filtered Cu radiation, intensities estimated visually

TABLE 3. CHEMICAL COMPOSITION OF SKIPPENITE AND POUBAITE

	SKIPPENITE						POUBAITE					
	1	2	3	4	5	6	1	2	3	4	5	6
Cu wt. %	0.47	0.08	0.17	0.00	0.06	0.38	0.00	0.00	0.00	0.00	0.00	0.00
Pb	0.00	0.20	0.22	0.44	0.00	0.00	18.80	19.07	18.22	18.68	18.88	18.76
Bi	61.61	61.62	60.41	59.67	60.63	61.17	42.53	43.21	42.34	42.91	42.26	42.23
Se	21.79	22.77	22.62	22.76	22.39	22.40	13.94	13.39	13.85	14.00	14.04	14.17
S	0.55	0.56	0.60	0.51	0.51	0.75	1.15	1.21	1.10	0.74	1.15	1.14
Te	15.55	15.66	15.87	16.02	15.41	15.57	23.13	22.95	23.42	23.55	22.71	23.13
Total	99.52	100.89	99.89	99.40	99.00	100.27	99.55	99.83	98.93	99.88	99.04	99.43
Cu at.	0.05	0.08	0.02	0.00	0.07	0.04	0.00	0.00	0.00	0.00	0.00	0.00
Pb	0.00	0.06	0.01	0.01	0.00	0.00	0.92	0.95	0.89	0.94	0.93	0.91
Bi	2.12	2.06	2.02	1.99	2.07	2.05	2.14	2.07	2.06	2.13	2.06	2.04
Se	2.02	2.02	2.00	2.01	2.02	1.98	1.79	1.75	1.78	1.84	1.82	1.81
S	0.12	0.12	0.13	0.11	0.11	0.16	0.37	0.39	0.35	0.24	0.36	0.36
Te	0.88	0.86	0.87	0.88	0.87	0.86	1.84	1.86	1.87	1.92	1.82	1.83

CAMEBAX electron microprobe (BRGM-CNRS microprobe laboratory, Orléans); standards: Cu, Bi, Se, Te metals, PbS, FeS₂; atomic proportions calculated on the basis of 3(Se+S+Te) for skippenite and of 4(Se+S+Te) for poubaite.

mechanism of substitution. Miller (1981) reported an unidentified bismuth mineral (mineral B), whose composition is close to Bi₂Se₂Te, from the Mazenod Lake deposit, Northwest Territories.

Watkinsonite: Cu₂PbBi₄(Se,S,Te)₈

Aggregates of skippenite commonly enclose irregular grains of a new selenide that belongs to the system Pb-Cu-Bi-Se; it was named *watkinsonite* in honor of Professor David H. Watkinson of Carleton University, Ottawa. Watkinsonite partly replaces skippenite crystals, penetrating along their interstices (Figs. 1a,b). Locally, clausthalite associated with Bi₂(Se,S)₂ outlines interstices of watkinsonite grains and generates a symplectitic intergrowth at skippenite-watkinsonite contacts (Figs. 1c,d).

On a fresh fracture, the aggregates of watkinsonite are black, and exhibit a moderate metallic lustre and conchoidal fracture. No cleavage was observed, even in polished section, after etching with HNO₃. The size of individual watkinsonite grains varies from 0.01 to about 3 mm, usually smaller than 1 mm. Because of its intergrowth with skippenite, the density of watkinsonite could not be measured. VHN₂₅ (average of 10 indentations) is 166 (range 186 - 155).

In reflected light, the mineral is white in color with a bluish tint, compared to the associated skippenite.

Bireflectance is not discernible in air, is very weak in oil, and varies from greyish white to bluish white. Internal reflections and twinning were not observed. Watkinsonite shows a moderate anisotropy with blue-grey to dark greyish brown polarization colors.

Reflectance measurements were performed on three randomly oriented grains (Table 1, Fig. 2). The results indicate that the reflectance of watkinsonite is very close to that of součekite (Čech & Vavříň 1979), only slightly lower than that of aikinite (Picot & Johan 1982), and distinctly lower than that of skippenite (Table 1).

Selected compositions of watkinsonite are given in Table 4. The selection was made by allowing a maximum of 1% in the deviation of cation charge from electroneutrality. The empirical formula calculated from the average composition (Table 4) on the basis of 8(Se+S+Te) is Cu_{2.36}Pb_{1.26}Bi_{3.70}(Se_{6.21}S_{1.74}Te_{0.05}). Silver was detected in some grains, but its concentration does not exceed 0.06 atoms per formula unit. The Se/(Se+S) value is close to 0.80. All the analyses reveal a deficit in Bi atoms and a corresponding excess in Pb and Cu with respect to the ideal formula, which may be written Cu₂PbBi₄(Se,S)₈. Taking into account the empirical composition given in Table 4, these deviations may be interpreted in terms of the substitution scheme Cu⁺ + Pb²⁺ = Bi³⁺ + □, well known in the

TABLE 4. SELECTED PROBE DATA FOR WATKINSONITE

	1	2	3	4	5	6	7	8	9	10	11
Cu wt. %	9.04	8.06	8.36	8.42	9.78	8.09	9.16	8.75	8.22	8.40	8.52
Pb	15.83	14.03	14.69	14.58	15.47	14.34	15.44	15.74	14.54	14.84	16.39
Bi	43.90	46.44	45.35	45.39	43.15	45.63	43.37	43.71	45.04	45.01	42.69
Se	27.98	28.22	27.87	28.25	27.44	28.50	27.83	27.95	28.73	28.39	28.41
S	3.24	3.20	3.17	3.26	3.47	3.24	3.25	3.21	3.10	3.16	3.03
Te	0.46	0.34	0.50	0.53	0.19	0.33	0.25	0.22	0.20	0.47	0.29
Total	100.45	100.29	99.94	100.43	99.50	100.13	99.30	99.58	99.83	100.27	99.33
Cu at.	2.48	2.21	2.30	2.29	2.70	2.42	2.53	2.42	2.24	2.29	2.35
Pb	1.33	1.18	1.24	1.22	1.30	1.19	1.30	1.34	1.22	1.24	1.38
Bi	3.66	3.86	3.81	3.74	3.61	3.76	3.64	3.67	3.73	3.73	3.58
Se	6.18	6.22	6.19	6.18	6.08	6.22	6.18	6.22	6.30	6.22	6.30
S	1.76	1.74	1.74	1.75	1.90	1.74	1.78	1.76	1.67	1.70	1.66
Te	0.06	0.04	0.07	0.07	0.02	0.04	0.04	0.02	0.03	0.08	0.04

CAMEBAX electron microprobe (BRGM-CNRS microprobe laboratory, Orléans); standards: FeS₂, PbS, Cu, Bi, Te, Se metals; atomic proportions calculated for 8(Se+S+Te).

TABLE 5. X-RAY POWDER DATA FOR WATKINSONITE

I	d _{obs}	d _{calc}	hkl	I	d _{obs}	d _{calc}	hkl
1	7.23	7.243	102				
1	4.71	4.718	003	7 B	2.140	2.141	207
4	4.514	4.521	203			2.139	415
3	4.303	4.303	301	7 B	2.065	2.067	316
2	3.981	3.981	101			2.067	514
3	3.744	3.744	104	2	2.024	2.022	007
9 B	3.573	3.578	111			2.019	407
1	3.407	3.394	211	1	1.975	1.972	120
3	3.250	3.252	304	1	1.935	1.925	601
		3.250	203	2	1.899	1.897	107
5	3.133	3.133	104	5	1.873	1.876	606
10	2.976	2.968	205			1.872	208
10	2.929	2.929	311	3	1.801	1.803	602
5	2.831	2.832	212			1.799	306
		2.831	005	3	1.789	1.789	222
2	2.767	2.794	305	2	1.744	1.743	700
		2.735	313	4	1.722	1.728	508
2	2.554	2.549	501	5 B	1.667	1.674	108
1	2.493	2.494	206			1.665	701
7	2.407	2.415	306	1	1.522	1.525	800
1	2.325	2.318	304			1.516	708
6	2.245	2.251	505	7	1.484	1.488	812
		2.246	403			1.484	703
		2.237	214				

B: broad line; 76.4-mm Debye-Scherrer camera, Ni-filtered Cu radiation. Intensities estimated visually.

bismuthinite-aikinite series. However, the existence of a partial Bi, Pb disorder on octahedral sites cannot be excluded at this stage of the study. Assuming a full occupancy of Se sites, microprobe analyses (Table 4) yield the following formula: $\text{Cu}_{2+x}\text{Pb}_{1+x}\text{Bi}_{4-x}(\text{Se}_{6.21}\text{S}_{1.74}\text{Te}_{0.05})$, with $x \approx 0.30$.

A fragment of watkinsonite scraped off a polished section was studied by the Weissenberg method (Ni-filtered Cu radiation). The photographs show evidence of monoclinic symmetry, $P2/m$, $P2$ or Pm . Unit-cell parameters refined by least-squares from the powder pattern are: a 12.921(3), b 3.997(1), c 14.989(3) Å, $\beta = 109.2(2)^\circ$, $V = 731$ Å³, $Z = 2$, $a:b:c = 3.233/1/3.750$. The density calculated for the composition $\text{Cu}_2\text{PbBi}_4(\text{Se}_{6.21}\text{S}_{1.74}\text{Te}_{0.05})$ is 7.82 g/cm³. An X-ray powder pattern of watkinsonite is given in Table 5.

The composition of watkinsonite, projected onto the plane $\text{Cu}_2\text{Se}-\text{PbSe}-\text{Bi}_2\text{Se}_3$, falls on the tie-line $\text{PbBi}_2\text{Se}_4 - \text{CuBiSe}_2$. The compound PbBi_2Se_4 possesses a layered, Bi_2Se_3 -like structure (Agaev & Semiletov 1968); the natural analogue, poubaite, was described by Čech & Vavřín (1978) (see below). The Se-analogues of galenobismuthite and cuprobismuthite are not known. AgBiSe_2 (bohdanowiczite) has a hexagonal structure close to that of matildite.

In the plane $\text{Cu}_2\text{S}-\text{PbS}-\text{Bi}_2\text{S}_3$, the composition of a sulfur analogue of watkinsonite falls at the limit of the CuBi_3S_5 solid-solution field at 500°C and on the tie-line limiting the Cu-rich side of the field aikinite-bismuthinite solid solution - CuBi_3S_5 at 400°C (Chang & Hoda 1977). It seems, then, that the stability fields of Se-equivalents of cuprobismuthite and of galenobismuthite, as well as that of watkinsonite, are restricted to temperatures lower than 400°C.

The unit-cell parameters of watkinsonite are close to those determined by Ohmasa & Nowacki (1973)

for synthetic CuBi_3S_5 , but the space group differs from the C -centered cell reported by previous authors. However, the composition CuBi_3S_5 results from structure determinations, which disagree with the attribution of the formula CuBi_3S_5 to this compound. This indicates that the stability field of CuBi_3S_5 solid solution may be enlarged toward Bi_2S_3 relative to that reported by Chang & Hoda (1977). Assuming the substitution $\text{Cu}^+ + \text{Pb}^{2+} \rightleftharpoons \text{Bi}^{3+} + \square$, $\text{Cu}_2\text{PbBi}_4\text{Se}_8$ may be a homologue of CuBi_5Se_8 or $\text{Cu}_6\text{Pb}_5\text{Se}_8$, even though these compounds remain unknown in the Cu-Pb-Bi-Se system.

Poubaite: $\text{PbBi}_2\text{Se}_2\text{Te}_2$

Lath-shaped crystals with perfect $\{0001\}$ cleavage, similar in composition to poubaite (Čech & Vavřín 1978) occur associated with součekite and wittichenite. This is the second known occurrence of this very rare mineral. It is very difficult to distinguish poubaite from skippenite only by its optical properties. Reflectance values are quite similar (Table 1), as are color and anisotropy. However, poubaite seems to exhibit more intense bireflectance. $\text{VHN}_{25} = 99$ (average of 10 indentations, range 74.2–121.9). A weak hardness anisotropy was observed; for sections approximately perpendicular to $[0001]$, $\text{VHN}_{25} = 91(15)$ was measured, whereas strongly anisotropic sections (approximately parallel to $[0001]$) yielded $\text{VHN}_{25} = 107(11)$.

Microprobe analyses (Table 3) are compatible with the formula $\text{PbBi}_2(\text{Te}, \text{Se}, \text{S})_4$, and reveal an average $(\text{Te}/\text{Se})_{\text{at}}$ value 1.03. X-ray powder-diffraction data (Table 2) correspond well to those of Čech & Vavřín (1978). Taking into account the structure determination of PbBi_2Se_4 by Agaev & Semiletov (1968), the powder diagram was indexed on a hexagonal unit-cell belonging to space group $R\bar{3}m$, with a 4.271(2), c 40.27(4) Å, $V = 635.8$ Å³. The values of these parameters are close to those obtained by Čech & Vavřín (1978) (a 4.25, c 39.77 Å) for poubaite from Oldřichov, Czechoslovakia.

Taking into account the fact that for poubaite from Otish Mountains, the $(\text{Te}/\text{Se})_{\text{at}}$ value is close to 1, sulfur atoms might be equally distributed among Te and Se structural sites, and the empirical formula may be written $\text{PbBi}_2(\text{Se}, \text{S})_2(\text{Te}, \text{S})_2$. It is noteworthy that the composition of poubaite given by Čech & Vavřín (1978) corresponds to the formula $\text{PbBi}_2\text{Se}_2(\text{Te}_{1.4}\text{S}_{0.6})$, half of the sites within the semimetallic layers being occupied by Se atoms, which suggests an ordered, rather than a random, distribution of Se and Te.

Čech & Vavřín (1978) ascribed the formula $\text{PbBi}_2(\text{Se}, \text{Te}, \text{S})_4$ to poubaite, with $\text{Se} > \text{Te}$ and $\text{Se} > \text{S}$. Consequently, they considered the material to be a sulfurian-tellurian poubaite. Thus the ideal

formula for a Te- and S-free poubaite end-member must be $PbBi_2Se_4$, corresponding to the synthetic compound whose structure was determined by Agaev & Semiletov (1968). Our results indicate, however, that the ideal composition of poubaite corresponds to the formula $PbBi_2Se_2Te_2$ and that poubaite may be a selenium equivalent of aleksite, $PbBi_2S_2Te_2$ (Lipovetskii *et al.* 1978).

This generates a nomenclature problem within the ternary system $PbBi_2S_4 - PbBi_2Se_4 - PbBi_2Te_4$. The compounds $PbBi_2Se_4$ and $PbBi_2Te_4$ were prepared by synthesis and extensively studied. They are isostructural, which suggests large miscibility (Agaev & Semiletov 1968, Zhukova & Zaslavskii 1972). The mineral rucklidgeite, described as $(Bi,Pb)_3Te_4$ (Zavjalov & Begizov 1977), has a composition corresponding to $PbBi_2Te_4$ and is identical to synthetic $PbBi_2Te_4$. On the other hand, the rhombohedral form of $PbBi_2S_4$ with a tetradyomite-like structure remains unknown.

Considering the statistical occupancy of layers of semimetallic atoms by Se, Te and S, the solid-solution fields (A, B, C; Fig. 4) for the three end-members are limited, respectively, by the following values: A: $Se/(Se + S) > 0.5$, $Se/(Se + Te) > 0.5$; B: $Te/(Te + Se) > 0.5$, $Te/(Te + S) > 0.5$; C: $S/(S + Se) > 0.5$, $S/(S + Te) > 0.5$. According to this defini-

tion, all compositions of poubaite from the Otish Mountains deposit fall near the limit, but inside the $PbBi_2Te_4$ solid-solution field (field B, Fig. 4), whereas the composition of poubaite from Oldřichov falls in the $PbBi_2Se_4$ solid-solution field (field A, Fig. 4). However, if the ordering of Se, Te and S is taken into consideration, the composition of poubaite from Oldřichov falls on the join $PbBi_2Se_2S_2 - PbBi_2Se_2Te_2$ (Fig. 4).

Součekite: $CuPbBi(S,Se,Te)_3$

Součekite was described as a new mineral by Čech & Vavřín (1979), from quartz-carbonate veins at Oldřichov, Czechoslovakia, where it occurs with poubaite (Čech & Vavřín 1978), clausthalite-galena solid solution, sulfur-bearing rucklidgeite and pitchblende. The Otish Mountains deposit is the second occurrence of součekite reported in the world.

Polysynthetically twinned součekite replaces watinsonite and poubaite (Figs. 1a,b). More rarely, součekite aggregates are surrounded by wittichenite. It is noteworthy that the assemblage součekite + aikinite never is observed in the Otish Mountains assemblages. This suggests an incompatibility of the $CuPbBiS_3$ dimorphs.

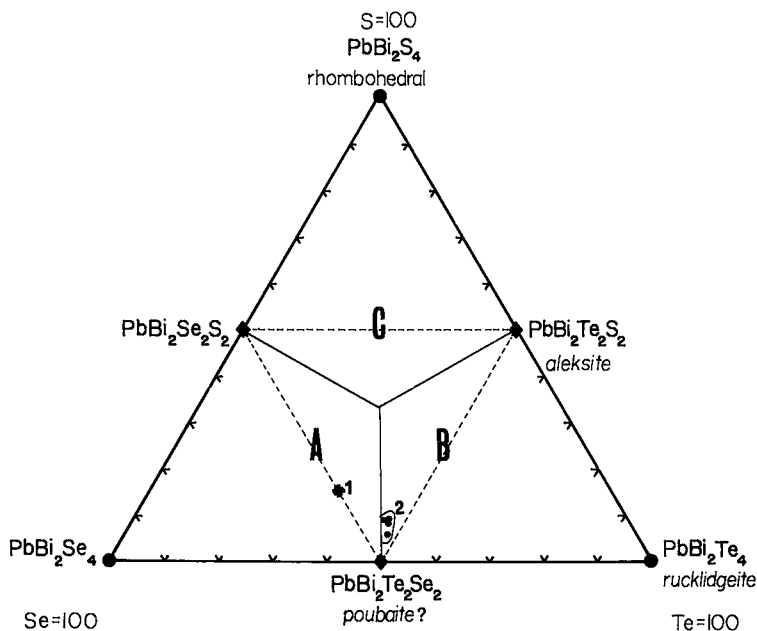


FIG. 4. Composition of poubaite projected onto the plane $PbBi_2Se_4 - PbBi_2S_4 - PbBi_2Te_4$; 1 Oldřichov (Cech & Vavřín 1978), 2 Otish Mountains. See text for other explanations.

TABLE 6. MICROPROBE DATA FOR SOUCEKITE, AIKINITE AND WITTICHENITE

	SOUCEKITE							AIKINITE		WITTICHENITE		
	1	2	3	4	5	6	7	1	2	1	2	3
Cu wt. %	9.91	10.13	9.93	10.19	9.91	9.68	10.06	9.96	10.04	38.64	39.18	38.56
Pb	31.87	31.64	31.06	32.30	32.26	31.67	31.95	32.42	32.40	0.49	0.78	0.88
Bi	33.25	33.29	33.84	33.40	32.79	33.34	33.11	38.38	38.39	40.65	40.32	40.21
Se	16.05	16.07	16.17	16.29	15.94	16.67	16.93	4.58	4.59	0.17	0.37	0.73
S	7.68	7.77	7.84	7.86	7.85	7.91	7.89	14.35	14.68	19.61	19.63	19.16
Te	1.07	1.11	1.01	0.92	0.94	1.05	1.25	0.12	0.12	0.04	0.00	0.03
Total	99.83	100.01	99.85	100.96	99.69	100.32	100.59	99.81	100.22	99.60	100.28	99.57
Cu at.	1.04	1.05	1.03	1.05	1.03	0.98	1.01	0.93	0.92	2.97	3.00	3.00
Pb	1.02	1.01	0.98	1.02	1.02	0.98	0.96	0.93	0.91	0.01	0.02	0.02
Bi	1.06	1.05	1.06	1.05	1.04	1.03	1.01	1.09	1.07	0.95	0.94	0.95
Se	1.35	1.34	1.35	1.35	1.33	1.36	1.37	0.35	0.34	0.01	0.02	0.05
S	1.59	1.60	1.60	1.60	1.62	1.59	1.57	2.65	2.66	2.99	2.98	2.95
Te	0.06	0.06	0.05	0.05	0.05	0.05	0.06	0.00	0.00	0.00	0.00	0.00

atomic proportions calculated for $3(\text{Se}+\text{S}+\text{Te})$; see Table 3 for analytical conditions.

Microprobe analyses (Table 6) led to the empirical formula $\text{Cu}_{1.03}\text{Pb}_{1.00}\text{Bi}_{1.04}(\text{S}_{1.60}\text{Se}_{1.35}\text{Te}_{0.05})$. Compared to data published by Čech & Vavřín (1979), součekite from the Otish Mountains is slightly richer in Se and Te. Actually, its composition approaches the formula $\text{CuPbBiS}_{1.5}(\text{Se},\text{Te})_{1.5}$ and, as is shown in Table 6, is very consistent from one grain to another. Only minor Ag (up to 0.1 wt. %) was detected. The substitution $\text{Pb}^{2+} + \text{Cu}^{+} \rightleftharpoons \text{Bi}^{3+} + \square$ reported for aikinite does not seem to exist in součekite.

As mentioned above, the $\text{S}/(\text{S} + \text{Se} + \text{Te})$ value is remarkably constant, and the extent of replacement of $(\text{Se} + \text{S})$ by Te appears to be very restricted. Despite the coexistence of součekite with poubaite and rucklidgeite at Oldřichov (Čech & Vavřín 1978) and with poubaite in the Otish Mountains deposit, its Te-content remains low and might indicate a saturation limit of Te in the structure. Compositions published by Čech & Vavřín (1979) and those given in Table 6 show that the number of S atoms calculated on the basis of $3(\text{S} + \text{Se} + \text{Te})$ is always lower than 2, approaching 1.5. This may indicate possible S and Se ordering, with $\text{Se} > (\text{Te} + \text{S})$ on half of the sulfur sites in the bournonite-like součekite structure, and suggests a formula unit $\text{Cu}_4\text{Pb}_4\text{Bi}_4\text{S}_6(\text{Se},\text{S},\text{Te})_6$. A single-crystal study,

which could not be performed on the material available, is required to confirm this hypothesis.

X-ray powder data agree perfectly with those published by Čech & Vavřín (1979). The unit-cell parameters, calculated using least-squares refinement, are: a 8.176(3), b 8.529(3), c 8.105(3) Å, leading to a slightly larger unit-cell volume (565.2 Å³), compatible with higher atomic proportions of Se and Te in součekite from the Otish Mountains deposit.

Aikinite: $\text{Cu}_{1-x}\text{Pb}_{1-x}\text{Bi}_{1+x}(\text{S},\text{Se})_3$

Only the association aikinite + clausthalite-galena solid solution was observed. Microprobe analyses (Table 6) reveal a rather limited substitution of Se for S, corresponding to about 1/10 of sulfur sites. The low Se-content of aikinite, despite its coexistence with a selenium-rich phase, contrasts with a relatively high Se-concentration in součekite, indicating the strong preference of this element for the bournonite-like structure. The Te-content is lower than that in součekite but significantly higher than that of wittichenite (Table 6).

If calculated on the basis of $3(\text{S} + \text{Se} + \text{Te})$, the chemical formula shows a deficit in Cu and Pb atoms, compensated by an excess of Bi (Table 6). This result confirms the observation of Harris & Chen (1976), who found a systematic deficiency in Cu and Pb. They concluded that the compositional range for aikinite may be expressed by the general formula $\text{Cu}_{1-x}\text{Pb}_{1-x}\text{Bi}_{3-1.5x}$, with $0 < x < 0.29$, implying an ordering of the Pb and Bi atoms. However, Springer's (1971) study of synthetic intermediate members of the aikinite-bismuthinite series revealed that at a higher temperature ($> 300^\circ\text{C}$), the disorder of Pb and Bi atoms prevents the formation of superstructures. This conclusion was confirmed by Mumme & Watts (1976). Makovicky & Makovicky (1978) and Makovicky (1981) summarized the structural data of previous investigators on the aikinite-bismuthinite series and proposed the general formula $\text{Cu}_x\text{Pb}_x\text{Bi}_{8-x}\text{S}_{12}$ ($x_{\text{max}} = 4$), which is to be compared with $\text{Cu}_x\text{Pb}_x\text{Bi}_{12-x}\text{S}_{18}$ ($x_{\text{max}} = 6$) deduced by Mumme & Watts (1976).

TABLE 7. MICROPROBE DATA FOR $\text{Bi}_2(\text{Se},\text{Te},\text{S})_2$ AND $(\text{Bi},\text{Pb})_2(\text{Se},\text{Te},\text{S})_3$

	$\text{Bi}_2(\text{Se},\text{Te},\text{S})_2$		$(\text{Bi},\text{Pb})_2(\text{Se},\text{Te},\text{S})_3$				
	1	2	1	2	3	4	5
Cu wt. %	0.36	0.55	0.00	0.00	0.00	0.06	0.00
Pb	0.27	0.14	0.68	0.90	0.82	9.43	9.64
Bi	67.13	67.22	60.43	60.60	60.07	53.03	52.74
Se	19.77	22.07	25.40	26.14	26.65	27.57	27.46
S	0.41	0.49	0.66	0.67	0.62	0.72	0.70
Te	10.85	9.37	12.23	11.92	11.02	9.59	9.41
Total	98.79	99.84	99.40	100.23	99.23	100.40	99.95
Cu at.	0.03	0.05	0.00	0.00	0.00	0.01	0.00
Pb	0.01	0.00	0.02	0.03	0.03	0.31	0.32
Bi	1.85	1.85	1.98	1.95	1.95	1.70	1.71
Se	1.44	1.52	2.20	2.23	2.28	2.35	2.35
S	0.07	0.08	0.14	0.14	0.13	0.15	0.15
Te	0.49	0.40	0.66	0.63	0.59	0.50	0.50

atomic proportions calculated on the basis of $2(\text{Se}+\text{S}+\text{Te})$ for $\text{Bi}_2(\text{Se},\text{Te},\text{S})_2$, and of $3(\text{Se}+\text{S}+\text{Te})$ for $(\text{Bi},\text{Pb})_2(\text{Se},\text{Te},\text{S})_3$; see Table 3 for analytical conditions.

Considering disorder of the Pb and Bi atoms in the aikinite–bismuthinite solid-solution derivatives close to the aikinite end-member, the composition of aikinite from the Otish Mountains deposit may be written as $\text{Cu}_{1-x}\text{Pb}_{1-x}\text{Bi}_{1+x}(\text{S}_{2.65}\text{Se}_{0.35}\text{Te}_0)$, with $x \approx 0.08$ (Table 6).

Our single-crystal study (Weissenberg photographs, Ni-filtered Cu radiation) confirms the data of Moore (1967), Ohmasa & Nowacki (1970), Kohatsu & Wuensch (1971) and Mumme & Watts (1976). The orthorhombic unit-cell belongs to the space group *Pbmn* and has the following parameters, refined by least squares from the X-ray powder pattern: a 11.296(5), b 11.716(5), c 4.039(2) Å; $V = 534.5$ Å³. No signs of a superstructure have been found from the Weissenberg photographs. The replacement of S by Se leads to about a 1% increase in the b parameter.

Wittichenite: Cu_3BiS_3

Wittichenite forms a rim, partly transformed into covellite, around aggregates of součekite. Microprobe analyses (Table 6) reveal a nearly stoichiometric composition, with minor replacement of S by Se. Unlike wittichenite from other deposits (Burke 1980, McQueen & Larson 1985), it is iron-free, but contains lead in the bismuth position. The presence of Pb might be explained by the coexistence of wittichenite with a lead-rich phase (součekite). However, in the Långban deposit, in spite of the association with galena, wittichenite is lead-free (Burke 1980).

Among Cu-bearing sulfosalts in the Otish Mountains deposit, wittichenite is the poorest in selenium and tellurium. It appears to be one of the phases that crystallized late, followed and replaced by Se-bearing covellite (0.4 wt. % Se).

Clausthalite-galena solid solution: $\text{Pb}(\text{Se},\text{S})$

Associated with součekite and aikinite, clausthalite–galena solid solution shows a compositional range from 55 to 61 mol. % PbSe. Bismuth is consistently present, but its concentration does not exceed 1 at. %. Similarly, the Te-content is generally lower than 0.1 wt. %, rarely reaching 0.2 wt. %.

The unit-cell parameter a calculated from the X-ray powder pattern is 6.039(6) Å. This value agrees well with a linear increase of the cell parameter in the galena–clausthalite series. A similar compositional range for clausthalite–galena solid solution coexisting with součekite was reported by Čech & Vavřín (1979).

$\text{Bi}_2(\text{Se},\text{Te},\text{S})_2$

Microscopic and SEM examination of skippenite showed that the core of some crystals has a differ-

ent chemical composition and higher reflectance than the rest (Fig. 1c). Microprobe analyses (Table 7) reveal a significantly higher Bi-content compared to skippenite. The chemical formula is close to $\text{Bi}_2(\text{Se}_{1.5}\text{Te}_{0.5})$ with, however, a slight deficit in the number of Bi atoms.

On the other hand, a bismuth selenide that belongs to the second period of mineralization and that occurs as veinlets in aggregates of watkinsonite (Fig. 1c) is tellurium-free, and its composition approaches $\text{Bi}_2(\text{Se},\text{S})_2$. Only two analyses have been performed on this mineral, which is intimately associated with clausthalite and chalcopyrite. Unfortunately, an X-ray study of these phases could not be carried out owing to the very small grain-size. The compound Bi_2Se_2 was synthesized by Gobrecht *et al.* (1962); it has a rhombohedral unit-cell with a 4.15, c 22.84 Å. The natural equivalent of this compound is nevskite described by Netchelioustov *et al.* (1984).

$(\text{Bi},\text{Pb})_2(\text{Se},\text{Te},\text{S})_3$

In addition to skippenite, poubaite and $\text{Bi}_2(\text{Se},\text{Te},\text{S})_2$, a bismuth selenide whose composition corresponds to $(\text{Bi},\text{Pb})_2(\text{Se},\text{Te},\text{S})_3$ is commonly associated with skippenite, watkinsonite and, rarely, poubaite.

Results of microprobe analyses (Table 7) calculated on the basis of $3(\text{Se} + \text{Te} + \text{S})$ show a composition close to the stoichiometry $(\text{Bi},\text{Pb})_2(\text{Se},\text{Te},\text{S})_3$. However, two compositional ranges may be distinguished: 1. Pb-bearing lamellae (compositions 4 and 5, Table 7) form the core zone of some crystals of skippenite. Their $(\text{Bi} + \text{Pb} + \text{Cu})/\text{Me}$ ratio is 2.025/3, corresponding to the general formula ${}^{VI}\text{Me}_2(\text{Se},\text{Te},\text{S})_3$. The introduction of copper into the structure may reflect the scheme of substitution $\text{Cu}^+ + \text{Bi}^{3+} \rightleftharpoons 2\text{Pb}^{2+}$, well known in bismuth–lead sulfosalts (Makovicky 1981). Microprobe analyses suggest that Pb and Bi atoms are statistically distributed in octahedral sites between layers consisting of rhombohedral dense-packing of $(\text{Se},\text{Te},\text{S})$ atoms (Agaev & Semiletov 1968, Zhukova & Zaslavskii 1972). However, as pointed out by Miller (1981), there is no space for the extra atoms in the paraguanaujatite-like structure, unless voids appear in the $(\text{Se},\text{Te},\text{S})$ layers. 2. Domains of Pb-poor $\text{Bi}_2(\text{Se},\text{Te},\text{S})_3$ (compositions 1, 2 and 3, Table 7) contain 17–22 mol. % Bi_2Te_3 . The sulfur content is very consistent, generally lower than 5 mol. % Bi_2S_3 . Our results indicate the existence of a limited solid-solution between Bi_2Se_3 and $\text{Bi}_2\text{Se}_2(\text{Te},\text{S})$ (skippenite).

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The natural equivalent of synthetic Bi_2Se_2 is nevskite, described by Netchelioustov, G.N., Chistjakova, N.I. & Zavjalov, E.N. (1984): Nevskite, $\text{Bi}(\text{Se},\text{S})$, a bismuth selenide. *Zap. Vses. Mineral. Obshchest.* **113**, 351-355. (In Russ.).