THE ORE MINERALOGY OF THE OTISH MOUNTAINS URANIUM DEPOSIT, QUEBEC: SKIPPENITE, Bi$_2$Se$_2$Te$_2$, AND WATKINSONITE, Cu$_2$PbBi$_4$(Se,S)$_6$, 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 albilitation, 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, soudekite, clausthalite, aikinite, wittichenite, molybdenite, pyrite, chalcopyrite, galena, digenite, covellite, electrum, native bismuth, and several unidentified bismuth selenides-tellurides. Skippenite, Bi$_2$Se$_2$Te$_2$, is rhombohedral, R$_3$m, $a = 4.183(4)$ Å, $V = 441.3$ Å$^3$, $Z = 3$. The calculated density is 7.94 g/cm$^3$. Strongest lines in the powder pattern: 4.85(6)(00.6), 3.584(6)(10.1), 3.074(10)(01.5), 2.267(7)(01.0), 2.090(8)(11.0); $\lambda$(422)(40.5). 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). VHN$_{25} = 63$. Microprobe analyses yield the empirical formula (Bi$_{2.65}$Cu$_{0.26}$Pb$_{0.07}$)Se$_{2.09}$Te$_{0.76}$S$_{0.10}$. The mineral is named in honor of Prof. G. Skippen, Carleton University, Ottawa. Skippenite is associated with bismuth selenides whose composition is close to Bi$_2$(Se,Te,S)$_2$ and (Bi,Pb)$_2$(Se,Te)$_3$. Watkinsonite, Cu$_2$PbBi$_4$(Se,S)$_6$, is monoclinic, P2$_1$/m, Pm or P2, $a = 12.921(3)$, $b = 3.997(1)$, $c = 14.989(3)$ Å, $\beta = 109.22(2)^\circ$, $V = 731$ Å$^3$, $Z = 2$, calculated density 7.82 g/cm$^3$. 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. VHN$_{25} = 99$. Rhombohedral, R$_3$m, $a = 4.271(2)$, $c = 40.27(4)$ Å, $V = 635.8$ Å$^3$, $Z = 3$. 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 Pb$_{0.92}$Bi$_{1.08}$(Se$_{1.80}$Te$_{0.18}$S$_{0.34}$), suggesting Se and Te ordering within layers of semimetallic atoms; the ideal formula is PbBi$_2$Se$_2$Te$_2$. The composition of soudekite is Cu$_{1.03}$Pb$_{1.00}$Bi$_{0.04}$(S$_{1.66}$Se$_{1.35}$Te$_{0.05}$). Microprobe analyses of aikinite revealed Se-content of 4.5 wt.%; the ideal formula is Cu$_{1-x}$Pb$_{1-x}$Bi$_{1-x}$(S$_{2.65}$Se$_{0.35}$), with $x = 0.8$. 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, soudekite, aikinite, wittichenite, selenides, tellurides.

SOMMAIRE

Les gisements uranifères du bassin des monts Otish (Québec) sont liés à des dykes et sills de dolérites, fortement albitéisés. Deux épisodes minéralisants ont été reconnus. Le premier, contemporain de l’alбитisation, comporte la brannèrite 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 sélénures, tellurures et sulfures comprenant: skippenite, watkinsonite, poubaite, soudekite, clausthalite, aikinite, wittichenite, molybdenite, pyrite, chalcopyrite, galena, digenite, covellite, electrum, bismuth natif, et plusieurs sélénures et tellurures de Bi non identifiés. La skippenite, Bi$_2$Se$_2$Te$_2$, est rhomboédrique, R$_3$m, $a = 4.183(4)$, $c = 29.12(8)$ Å, $V = 441.3$ Å$^3$, $Z = 3$. 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)(01.0), 2.090(8)(11.0); $\lambda$(422)(40.5). Aggrets 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). VHN$_{25} = 63$. Les analyses à la microsonde électronique ont donné une for-
mule empirique (Bi$_2$O$_3$Cu$_{0.04}$Pb$_{0.01}$)Se$_2$O$_{0.00}$Te$_{0.07}$S$_{0.13}$). Nommé en l'honneur du Prof. G. Skippen, Université de Carleton, Ottawa. La skippennite est parfois associée à des selénures de Bi dont la composition est proche de Bi$_2$(Se,Te,S)$_2$ et de (Bi,Pb)$_2$(Se,Te)$_3$. La watkinsonite, Cu$_2$PbBi$_2$(Se,S)$_6$, est monoclinique, $P2_1/m$, $Pm$ ou $P2_1$, avec $a$ 12.921(3), $b$ 3.997(1), $c$ 14.989(3) Å, $\beta$ 109.22(2)$^\circ$, $V = 731$ Å$^3$, $Z = 2$, 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. VHN$_{2s}$ = 166. On n’a observé ni clivage, ni macules. Pouvoir réflecteur (air): 46.6–43.2(420), 48.6–45.4(540), 49.0–45.8(700 nm). La formule cristallo-chimique calculée à partir des analyses à la microsonde électronique est Cu$_2$PbBi$_2$Se$_2$Te$_2$. La formule idéale doit s’écrire Cu$_2$Pb$_{\, 0.7}$Bi$_{\, 2}$(Se,S,Te)$_{\, 9}$, avec $x \leq 0.30$. 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 poubaitie et de la soudekite. La poubaitie présente un clivage parfait suivant (0001); VHN$_{2s}$ = 99. Rhomboédrique, $R3m$, $a$ 4.271(2), $c$ 40.27(4) Å, $V = 635.8$ Å$^3$, $Z = 3$. Les raies les plus intenses du diagramme de poudre sont: 3.638(6)$^|(011.2)$, 3.105(10)$^|(01.20)$, 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 Pb$_{0.92}$Bi$_{1.08}$(Se$_{1.80}$Te$_{1.86}$S$_{0.34}$), faisant entrevoir une distribution ordonnée de Se et Te dans les couches d’atomes semi-métalliques et une formule idéale PbBi$_2$Se$_2$Te$_2$. La composition de la soudekite correspond à Cu$_{1.03}$Pb$_{1.00}$Bi$_{1.00}$(Si$_{1.60}$Se$_{1.55}$Tet$_{0.00}$). Les analyses de l’aïnikitte ont révélé une teneur en Se de 4.55%; sa formule idéale s’écrit Cu$_{1.00}$Pb$_{1.00}$Bi$_{1.00}$(S$_{2.65}$Se$_{0.35}$), avec $x = 0.08$. 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, skippennite, watkinsonite, nouveaux minéraux, poubaitie, aïnikitte, wittichenite, selénures, 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 considerably 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 selénides (Kuusamo, Finland: Vuorelainen et al. 1964) and molybdenum selénides (Kapijimpanga, Zambie: Čech et al. 1973) have been observed.

**Mineralization with bismuth selénides is less common.** Besides the classical occurrence of guanajuatite and paraguanajuatite at Guanajuato, Mexico (Ramdohr 1948), bismuth selénides and lead–bismuth seléniferous 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 seléniferous bismuth sulfofats in the Juno deposit, Tennant Creek, Northern Territory, Australia, where Mumme (1975, 1976) and Mumme & Watts (1976) identified three new copper–lead–bismuth seléniferous sulfofats (junoite, proudite and pekoite). This type of mineralization is characterized by an intimate association of sulfides and selénides, by replacement of S by Se giving rise to selénium-bearing sulfides, and by the presence of gold (Falun, Juno mine), which seems to be typical.

The association of Cu–, Pb–, Bi–sulfides, selénides and tellurides with uranium is rather exceptional. Until now, only three occurrences, Oldřichov, Czechoslovakia (Čech & Vavrin 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, skippennite and watkinsonite, approved by the Commission on New Minerals and Mineral Names, I.M.A. Type material of skippennite 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 include pebbly sandstones, siltstones, and mudstones. The deposit must be considered an exception because of the widespread replacement of Se by S in some sulfides (chalcopyrite–eskebornite series), as documented by Johan et al. (1982). Rarely, nickel selénides (Kuusamo, Finland: Vuorelainen et al. 1964) and molybdenum selénides (Kapijimpanga, Zambie: Čech et al. 1973) have been observed.

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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. Souèckite (so) and watkinsonite (w) replace skippenite (s) with perfect {0001} cleavage, along grain boundaries. Watkinsonite is replaced by souèckite. Reflected plane-polarized light, oil immersion. Scale bar represents 100 μm. B. Watkinsonite (w) is replaced by polysynthetically twinned souèckite (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 Bi₂(Se,Te,S)₂(a). Bi₂(Se,S)₂(b) associated with clauschalite and chalcophyrite penetrates along watkinsonite (w) grain boundaries. D. SEM photograph of skippenite (s) rimmed by a symplectitic intergrowth of Cu-bearing clauschalite 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. Bi₂(Sₑ,Te,S₂)₂ → skippenite → watkinsonite → clausthalite → chalcopyrite → electrum, 2. poubaite → watkinsonite → soucekite, 3. soucekite → wittichenite, and 4. aikinite → clausthalite–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 Bi₂(Se,Te,S₂)₂ → Bi₂(Sₑ,Te,S₂)₃ → Bi₂Se₂(Se,Te,S₂)(skippenite) → (Bi,Pb)₁(Sₑ,Te,S₃) → PbBi₃Se₂Te₂(poubaite) → Cu₂PbBi₄(Se₂,S₂,Te₈)(watkinsonite) → CuPbBi(S,Sₑ)₂(soucekite) → Cu₁Bi₂(wittichenite), and for the second period of mineralization: CuPbBi(S⁺Sₑ)₂(aikinite) → Pb(Se,S₂) → PbSe → Bi₂(Se,S₂)₃ → CuFeS₂ → (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 clausthalite-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 soucekite 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 Bi/(Se + Te + S) and Pb/(Pb + 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 Se/(Se + Te + S) ratio varies only slightly (0.78–0.70) from Bi₂(Se₂,Te,S₈)₂ to lead-bearing paraguanaganaitite, but decreases suddenly to 0.45 with the crystallization of poubaite. 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 Pb/(Pb + Bi) and decreasing Se/(Se + Te + S), but unlike the preceding case, the variation of Se/(Se + Te + 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 clausthalite–galena solid solution, evolving progressively toward the PbSe end-member and, finally, by Bi₂(Se,S₂)₃. All these phases are almost tellurium-free. An interesting relationship was observed between clausthalite on one hand and watkinsonite and skippenite on the other. Clausthalite penetrates along a watkinsonite–skippenite contact or along interstices between grains of watkinsonite, and replaces both older phases, giving rise to a submicroscopic symplectitic intergrowth (Fig. 1d). Microprobe analyses show that clausthalite 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 clausthalite associated with chalcopyrite is sulfur-free. The average empirical formula of clausthalite may be written (Pb₀.₇₇Cu₀.₁₂Fe₀.₀₈Bi₀.₀₆)(Se₀.₈₄S₀.₁₆). 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. Clausthalite–galena solid solution and clausthalite are, together with a mineral whose composition is close to Bi₂(Se,S₂)₂, the latest selenides of the Otish Mountains suite. Similarly, in the Chaméane uranium deposit, a late generation of clausthalite 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-
fide association is characterized by a predominance of Se-free chalcopyrite. An SEM study revealed the presence of a clausithalite-chalcopyrite symplectitic intergrowth where these minerals are in contact. The final hydrothermal stages led to the extensive transformation of some selenides (mainly sou6ekite), 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$_2$Se$_2$Te

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 tetradymitne or telluro-bismuthite. 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...
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 R₀ of poubaite (Fig. 3), paraguanajuatite, tetradyrmite, joseite or tellurobismuthite (Picot & Johan 1982). The reflectance measurements performed on randomly oriented grains indicate that R₀-values cannot be attributed to Ru. This suggests that skippenite is optically negative.

Vickers microhardness VHN (10 indentations, 25-g load) is 63.0 (range 52.2-74.2). Deformed garnet crystals reveal a rather constant chemical composition (Table 2), possessing a unit-cell that contains 15 layers (Strunz 1963). By analogy with these compounds, we attribute space group R₃m to skippenite. According to Semiletov (in Strunz 1963), the layers in Bi₂Se₃ are formed in the following order: AcBAc - BaCBa - CaACa, where A, B, C = Se and a, b, c = Bi. By analogy with tetradyrmite, the most probable sequence of stacking for the skippenite structure might be: A’aB’C’ = Te₆S₆; A,B,C = Se and a,b,c = Bi. Skippenite is isostructural with kawazulite Bi₂Se₆Te₂ (Kato 1970). The calculated density is 7.80 g/cm³ for Bi₂Se₂(Se₀.₇₅S₀.₁₃) and 7.94 g/cm³ for Bi₂Se₃Te₂.

Microprobe analyses performed on various grains reveal a rather constant chemical composition (Table 3). The average empirical formula calculated on the basis of (Se+Te+S) is (Bi₂₀₅Cu₀₀₅Pb₀₁₁Se₀₂₀₀ (Te₀₇₅S₀₁₃), which is very close to the ideal composition Bi₂Se₆Te₂. 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 watkinsonite. For this reason, we have incorporated these elements into the empirical formula of skippenite, but we are unable to propose a suitable
mechanism of substitution. Miller (1981) reported an unidentified bismuth mineral (mineral B), whose composition is close to Bi₅Se₅Te₂, from the Mazenod Lake deposit, Northwest Territories.

Watkinsonite: Cu₂PbBi₃(Se,S,Te)₆

Aggregates of watkinsonite 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. VHN₉₅ (average of 10 indentations) is 166 (range 185–155).

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 souéckite (Čech & Vavrin 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 Cu₂₂Pb₁₂Bi₃₇₀(Se₆.₂₁S₁.₇₉Tₑ₀.₃). Silver was detected in some grains, but its concentration does not exceed 0.06 atoms per formula unit. The Se/(S + Se) 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 Cu₂PbBi₃(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

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<th>TABLE 3. CHEMICAL COMPOSITION OF SKIPPENITE AND POUBAITE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SKIPPENITE</strong></td>
</tr>
<tr>
<td>Cu wt.%</td>
</tr>
<tr>
<td>Pb</td>
</tr>
<tr>
<td>Bi</td>
</tr>
<tr>
<td>Se</td>
</tr>
<tr>
<td>Te</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

| **POUBAITE**                                           |
| Cu wt.%        | 1   | 2   | 3   | 4   | 5   | 6   |
| Pb             | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| Bi             | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| Se             | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| Te             | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| Total          | 100.00| 100.00| 100.00| 100.00| 100.00| 100.00|

<table>
<thead>
<tr>
<th>TABLE 4. SELECTED PROBE DATA FOR WATKINSONITE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cu wt.%</strong></td>
</tr>
<tr>
<td>Pb</td>
</tr>
<tr>
<td>Bi</td>
</tr>
<tr>
<td>Se</td>
</tr>
<tr>
<td>Te</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

CAMECA electron microprobe (BGRM-CNRS microprobe laboratory, Orléans); standards: Fe₅S₈, PbS, Cu, Bi, Te, Se metals; atomic proportions calculated for 8(Se+S+Te).
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: 

$$\text{Cu}_2\text{Pb}_1\text{Bi}_4\text{Se}_{2.5}\text{S}_{0.74}\text{Te}_{0.06}$$

with \(x = 0.30\).

A fragment of watkinsonite scraped off a polished section was studied by the Weissben method (Ni-filtered Cu radiation). The photographs show evidence of monoclinic symmetry, \(P2/m, P2_1, \) or \(P m\).

Unit-cell parameters refined by least-squares from anisotropic sections (approximately parallel to \([0001]\), and reflections approximately perpendicular to \([0001]\) yielded \(V = 635.8 \text{ Å}^3\). The density calculated for the composition \(\text{Cu}_2\text{Pb}_1\text{Bi}_4\text{Se}_{2.5}\text{S}_{0.74}\text{Te}_{0.06}\) 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 \(\text{Cu}_2\text{Se} - \text{PbSe} - \text{BiSe}_3\), falls on the tie-line \(\text{PbBi}_2\text{Se}_2 - \text{CuBiSe}_3\). The compound \(\text{PbBi}_2\text{Se}_2\) possesses a layered, \(\text{Bi}_2\text{Se}_3\)-like structure ([Agaev & Semiletov 1968]; the natural analogue, poubaite, was described by Čech & Vaviln (1978) (see below). The \(\text{S}\)-analogues of galenobismuthite and cuprobismuthite are not known. \(\text{AgBiSe}_3\) (bohdanoviczite) has a hexagonal structure close to that of matildite.

In the plane \(\text{Cu}_2\text{S} - \text{PbSe} - \text{Bi}_2\text{S}_3\), the composition of a sulfur analogue of watkinsonite falls within the limit of the \(\text{CuBi}_2\text{S}_3\) solid-solution field at 500°C and on the tie-line limiting the \(\text{Cu}-\text{rich}\) side of the field aikinite–bismuthinite solid solution – \(\text{CuBi}_2\text{S}_3\) at 400°C (Chang & Hoda 1977). It seems, then, that the stability field of \(\text{Se}\)-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 & Nowaeki (1973) for synthetic \(\text{CuBi}_5\text{S}_8\), but the space group differs from the C-centered cell reported by previous authors. However, the composition \(\text{CuBi}_5\text{S}_8\) results from structure determinations, which disagree with the attribution of the formula \(\text{CuBi}_2\text{S}_3\) to this compound. This indicates that the stability field of \(\text{CuBi}_2\text{S}_3\) solid solution may be enlarged toward \(\text{Bi}_2\text{S}_3\) relative to that reported by Chang & Hoda (1977). Assuming the substitution \(\text{Cu}^+ + \text{Pb}^{2+} = \text{Bi}^{3+} + 2^+\), \(\text{CuBi}_2\text{PbSe}_2\) may be a homologue of \(\text{CuBi}_2\text{Se}_3\) or \(\text{Cu}_6\text{Pb}_5\text{Se}_{12}\) even though these compounds remain unknown in the \(\text{Cu} - \text{Pb} - \text{Bi}\) system.

**Poubaite: \(\text{PbBi}_2\text{Se}_2\text{Te}_2\)**

Lath-shaped crystals with perfect \(\{001\}\) cleavage, similar in composition to poubaite (Čech & Vavřín 1978) occur associated with součekite and witichenite. 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. VHN\(_{25}\) = 99 (average of 10 indentations, range 74.2–121.9). A weak hardness anisotropy was observed; for sections approximately perpendicular to \{001\} yielded VHN\(_{25}\) = 91(15) was measured, whereas strongly anisotropic sections (approximately parallel to \{001\}) yielded VHN\(_{25}\) = 107(11).

Microprobe analyses (Table 3) are compatible with the formula \(\text{PbBi}_2\text{Te}_2\text{Se}_4\), and reveal an average (\(\text{Te/Se}\))\(_{\text{at}}\) 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 \(\text{PbBi}_2\text{Te}_2\text{Se}_4\) by Agaev & Semiletov (1968), the powder diagram was indexed on a hexagonal unit-cell belonging to space group \(R\overline{3}m\), with \(a = 4.271(2), c = 40.27(4) \text{ Å}, V = 635.8 \text{ Å}^3\). The values of these parameters are close to those obtained by Čech & Vavřín (1978) (\(a = 4.25, c = 39.77 \text{ Å}\) for poubaite from Oldřichov, Czechoslovakia.

Taking into account the fact that for poubaite from Otish Mountains, the (\(\text{Te/Se}\))\(_{\text{at}}\) value is close to 1, sulfur atoms might be equally distributed among Te and Se structural sites, and the empirical formula may be written \(\text{PbBi}_2\text{Se}(\text{Te,S})\text{Se}_{2}\). It is noteworthy that the composition of poubaite given by Čech & Vavřín (1978) corresponds to the formula \(\text{PbBi}_2\text{Se}_2\text{(Te,S)}\text{Se}_{0.8}\), 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 \(\text{PbBi}_2\text{Se}(\text{Te,S})\text{Se}_{0.8}\) to poubaite, with Se>T=Te and Se>S. Consequently, they considered the material to be a sulfurian–tellurian poubaite. Thus the ideal
formula for a Te- and S-free pounbaite end-member must be PbBi$_2$Se$_4$, corresponding to the synthetic compound whose structure was determined by Agaev & Semiletov (1968). Our results indicate, however, that the ideal composition of pounbaite corresponds to the formula PbBi$_2$Se$_2$Te$_2$ and that pounbaite may be a selenium equivalent of aleksite, PbBi$_2$S$_2$Te$_2$ (Ilovetski et al. 1978).

This generates a nomenclature problem within the ternary system PbBi$_2$S$_4$ - PbBi$_2$Se$_4$ - PbBi$_2$Te$_4$. The compounds PbBi$_2$Se$_4$ and PbBi$_2$Te$_4$ were prepared by synthesis and extensively studied. They are isos-structural, which suggests large miscibility (Agaev & Semiletov 1968, Zhukova & Zaslavskii 1972). The mineral rucklidgeite, described as (Bi,Pb)$_3$Te$_4$ (Zavjalov & Begizov 1977), has a composition corresponding to PbBi$_2$Te$_4$ and is identical to synthetic PbBi$_2$Te$_4$. On the other hand, the rhombohedral form of PbBi$_2$S$_4$ with a tetradymitite-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 definition, all compositions of pounbaite from the Otish Mountains deposit fall near the limit, but inside the PbBi$_2$Te$_4$ solid-solution field (field B, Fig. 4), whereas the composition of pounbaite from Oldřichov falls in the PbBi$_2$Se$_4$ solid-solution field (field A, Fig. 4). However, if the ordering of Se, Te and S is taken into consideration, the composition of pounbaite from Oldřichov falls on the join PbBi$_2$Se$_2$S$_2$ - PbBi$_2$Se$_2$Te$_2$ (Fig. 4).

**Součekite:** CuPbBi(S,Se,Te)$_3$

Součekite was described as a new mineral by Čech & Vavřin (1979), from quartz–carbonate veins at Oldřichov, Czechoslovakia, where it occurs with pounbaite (Čech & Vavřin 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 watkinsonite and pounbaite (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 CuPbBi$_3$ dimorphs.

---

**Fig. 4.** Composition of pounbaite projected onto the plane PbBi$_2$Se$_4$ - PbBi$_2$Te$_4$ - PbBi$_2$S$_4$; 1 Oldřichov (Čech & Vavřin 1978), 2 Otish Mountains. See text for other explanations.
Microprobe analyses (Table 6) led to the empirical formula $\text{Cu}_{1-x}\text{Pb}_{1-x}\text{Bi}_{1-x}^{1-2x}(\text{S}_{1-x}\text{Se}_{1-x}\text{Te}_{1-x})$. Compared to data published by Čech & Vavřín (1979), soudekite from the Otish Mountains is slightly richer in Se and Te. Actually, its composition approaches the formula $\text{Cu}_{1-x}\text{Pb}_{1-x}\text{Bi}_{1-x}^{1-2x}(\text{S}_{1-x}\text{Se}_{1-x}\text{Te}_{1-x})$, 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 $\text{Pb}^{2+} + \text{Cu}^{+} = \text{Bi}^{3+} + \square$ reported for aikinite does not seem to exist in soudekite.

As mentioned above, the $S/(S + \text{Se} + \text{Te})$ 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 soudekite 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 $3(\text{Se} + \text{Te} + \text{S})$ 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 soudekite structure, and suggests a formula unit $\text{Cu}_4\text{Pb}_4\text{Bi}_4\text{S}_{12}(\text{Se},\text{S},\text{Te})$. 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: $a = 8.176(3), b = 8.520(3), c = 8.105(3)$ Å, leading to a slightly larger unit-cell volume ($565.2 \text{ Å}^3$), compatible with higher atomic proportions of Se and Te in soudekite from the Otish Mountains deposit.

**Alkinite: $\text{Cu}_{1-x}\text{Pb}_{1-x}\text{Bi}_{1-x}^{1-2x}(\text{S},\text{Se})$**

Only the association alkinite + clausenthalite–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 alkinite, despite its coexistence with a selenium-rich phase, contrasts with a relatively high Se-concentration in soudekite, indicating the strong preference of this element for the bournonite-like structure. The Te-content is lower than that in soudekite but significantly higher than that of witichenite (Table 6).

If calculated on the basis of $3(\text{Se} + \text{Te} + \text{S})$, 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 alkinite may be expressed by the general formula $\text{Cu}_{1-x}\text{Pb}_{1-x}\text{Bi}_{1-x}^{1-2x}$, 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 alkinite–bismuthinite series revealed that at a higher temperature ($> 300^\circ C$), 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 information of solid investigations on the alkinite–bismuthinite series and proposed the general formula $\text{Cu}_{1-x}\text{Pb}_{1-x}\text{Bi}_{1-x}^{1-2x}$ ($x_{\text{max}} = 4$), which is to be compared with $\text{Cu}_{1-x}\text{Pb}_{1-x}\text{Bi}_{1-x}^{1-2x}$ ($x_{\text{max}} = 6$) deduced by Mumme & Watts (1976).

### Table 6. Microprobe Data for Soudekite, Aikinite and Witichenite

<table>
<thead>
<tr>
<th></th>
<th>Soudekite</th>
<th>Aikinite</th>
<th>Witichenite</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cu wt. %</strong></td>
<td>$9.91$</td>
<td>$10.13$</td>
<td>$10.20$</td>
</tr>
<tr>
<td><strong>Pb</strong></td>
<td>$31.87$</td>
<td>$31.64$</td>
<td>$31.86$</td>
</tr>
<tr>
<td><strong>Se</strong></td>
<td>$15.05$</td>
<td>$16.07$</td>
<td>$15.94$</td>
</tr>
<tr>
<td><strong>Te</strong></td>
<td>$7.26$</td>
<td>$7.17$</td>
<td>$7.59$</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>$98.90$</td>
<td>$100.01$</td>
<td>$99.69$</td>
</tr>
</tbody>
</table>

### Table 7. Microprobe Data for $\text{Bi}_2(\text{Se},\text{Te}),_2$ and $\text{Bi}_2(\text{Pb},\text{Se},\text{Te}),_3$

<table>
<thead>
<tr>
<th></th>
<th>$\text{Bi}_2(\text{Se},\text{Te}),_2$</th>
<th>$\text{Bi}_2(\text{Pb},\text{Se},\text{Te}),_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cu wt. %</strong></td>
<td>$0.36$</td>
<td>$0.36$</td>
</tr>
<tr>
<td><strong>Pb</strong></td>
<td>$0.27$</td>
<td>$0.27$</td>
</tr>
<tr>
<td><strong>Se</strong></td>
<td>$1.67$</td>
<td>$1.67$</td>
</tr>
<tr>
<td><strong>Te</strong></td>
<td>$0.83$</td>
<td>$0.83$</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>$98.79$</td>
<td>$98.79$</td>
</tr>
</tbody>
</table>

**atomic proportions calculated on the basis of $2(\text{Se} + \text{Te})$ for $\text{Bi}_2(\text{Se},\text{Te}),_2$; and of $3(\text{Se} + \text{Te})$ for $\text{Bi}_2(\text{Pb},\text{Se},\text{Te}),_3$; 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 \( \text{Cu}_{1-x}\text{Pb}_{1-x}\text{Bi}_{1-x}(\text{Se}_{0.65}\text{Te}_{0.35})_x \), with \( x \approx 0.08 \) (Table 6).

Our single-crystal study (Weissenberg photographs, Ni-filtered Cu radiation) confirms the data of Moore (1967), Ohmara & Nowacki (1970), Kohatsu & Wunsch (1971) and Mumm & Watts (1976). The orthorhombic unit-cell belongs to the space group \( \text{Pbmn} \) 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; \( V = 534.5 \) Å\(^3\). 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: \( \text{Cu}_3\text{Bi}_2\text{S}_3 \)**

Wittichenite forms a rim, partly transformed into covellite, around aggregates of soucekite. 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 (soucekite).

However, in the Längban 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: \( \text{Pb(Se,Te,S)} \)**

Associated with soucekite 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 soucekite was reported by Čech & Vavrin (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 different 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 \( \text{Bi}_2(\text{Se},\text{Te})_2 \). Only two analyses have been performed on this mineral, which is intimately associated with clausthalite and chalcocyprite. Unfortunately, an X-ray study of these phases could not be carried out owing to the very small grain-size. The compound \( \text{Bi}_2\text{Se}_2 \) 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 nesvskite described by Netchelious et al. (1984).

\( \text{(Bi,Pb)}_2/2(\text{Se,Te,S})_3 \)

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

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 \( \text{(Bi,Pb)}_2(\text{Se},\text{Te},\text{S})_3 \). 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 \( ^{\text{VI}}\text{Me}_2(\text{Se},\text{Te},\text{S})_3 \). The introduction of copper into the structure may reflect the scheme of substitution \( \text{Cu}^+ + \text{Bi}^{3+} + 2\text{Pb}^{2+} \), 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 \( \text{(Se},\text{Te},\text{S})_3 \) atoms (Agaev & Semiletov 1968, Zhukova & Zaslavskii 1972). However, as pointed out by Miller (1981), there is no space for the extra atoms in the paraguanaujaitie-like structure, unless voids appear in the \( \text{(Se},\text{Te},\text{S})_3 \) 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.% \( \text{Bi}_2\text{Te}_3 \). The sulfur content is very consistent, generally lower than 5 mol.% \( \text{Bi}_2\text{S}_3 \). Our results indicate the existence of a limited solid-solution between \( \text{Bi}_2\text{Se}_3 \) and \( \text{Bi}_2\text{Se}_3(\text{Te},\text{S}) \) (skippenite).

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