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COMPOSITIONAL DATA FOR Bi–Pb TELLUROSULFIDES

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ABSTRACT

Compounds containing essential Bi, Pb, Te and S are rare in nature. Aleksite, $\text{PbBi}_2\text{Te}_2\text{S}_2$, is known from less than ten localities worldwide, and the single other recognized mineral, saddlebackite, $\text{Pb}_2\text{Bi}_2\text{Te}_2\text{S}_3$, is known only from the type locality, the Boddington Au deposit, Western Australia. Another phase, unnamed $\text{PbBi}_4\text{Te}_4\text{S}_3$, had earlier been recognized as homogeneous grains and lamellar intergrowths within an assemblage consisting of aleksite, tellurobismuthite and tetradymite from St. David's mine, Clogau, Wales, U.K. Re-investigation of this assemblage, including careful micro-analysis to avoid obvious intergrowths of phases, reveals an almost continuous range of compositions between tetradymite and aleksite. Investigations of complex sulfosalts–telluride assemblages from Iilijärvi, a satellite deposit within the Orijärvi orefield, southwest Finland, have revealed compositions approximating to the range $\text{Pb}_5\text{Bi}_4\text{Te}_4\text{S}_7$ – $\text{Pb}_7\text{Bi}_4\text{Te}_4\text{S}_9$. These occur as fine intergrowths, rarely as larger single lamellae, also with aleksite, within a matrix of giessenite, galena and cosalite. The samples contain abundant gold, seen also as symplectite intergrowths with rutile. Investigation of the microparagenesis of precious-metal-bearing galena – chalcopyrite – pyrite mineralization in quartz veins at Fragant ("Langenleiten"), Carinthia Province of Austria, revealed the presence of several compositionally different Bi–Pb tellurosulfides. Aleksite is the most abundant, followed by unnamed phases with compositions close to $\text{Pb}_3\text{Bi}_4\text{Te}_4\text{S}_5$, $\text{Pb}_5\text{Bi}_4\text{Te}_4\text{S}_7$ and $\text{Pb}_6\text{Bi}_4\text{Te}_4\text{S}_8$. They occur as inclusions in galena and are variably associated with sulfosalts such as lillianite, cosalite, felbertalite and aikinite. The compositional dataset from the above occurrences is difficult to interpret

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without accompanying structural data. The data, however, suggest the existence of an incremental chemical series with the general formula $Pb_NBi_4Te_4S_{N+2}$. Alternatively, these are not discrete, essentially immiscible phases within a chemically defined modular series, but are simply compositions across a continuous compositional series. If the existence of a series can be proven, tetradyomite, $Bi_4Te_4S_2$, would correspond to $N = 0$, unnamed $PbBi_4Te_4S_3$, to $N = 1$, aleksite, to $N = 2$, unnamed $Pb_3Bi_4Te_4S_5$, to $N = 3$, and saddlebackite, to $N = 4$, where the N values reflect chemical composition, rather than structurally defined homologous order. Indirect support for such a hypothesis comes from the recognition in the literature of four phases ($N = 1, 2, 3$ and 4) as synthetic products (phases D, E, F and J) obtained at 500°C . The unnamed phases from Iilijärvi and Fragant may correspond to unspecified higher members of the same series. The lamellar banding with galena and tetradyomite, and extended compositional fields observed in the Clogau and Iilijärvi specimens, are highly reminiscent of similar issues in Bi-sulfosalt series, allowing us to speculate that we may be looking at a typical accretional homologous series, with incremental growth in the thickness of layers. In such a scenario, random sequences of stacking of discrete members of the series at the lattice scale are considered to apply, causing chemical variation.

Keywords: tellurosulfides, aleksite, compositional data, unnamed phases, Clogau, Wales, Iilijärvi, Finland, Fragant, Austria.

SOMMAIRE

Les composés contenant la combinaison de Bi, Pb, Te et S sont rares dans la nature. L'aleksite, $PbBi_2Te_2S_2$, a été signalée à moins de dix localités dans le monde, et le seul autre minéral, la saddlebackite, $Pb_2Bi_2Te_2S_3$, n'a été trouvé qu'à sa localité-type, le gisement aurifère de Boddington, en Australie occidentale. Une autre phase, $PbBi_4Te_4S_3$, avait auparavant été signalée en grains homogènes et en intercroissances lamellaires dans un assemblage d'aleksite, de tellurobismuthite et de tetradyomite à la mine St. David, Clogau, Pays de Galles. Nous avons examiné ce matériau de nouveau en effectuant des micro-analyses soignées afin d'éviter les intercroissances de phases évidentes. Il en ressort un intervalle de compositions presque continu entre tetradyomite et aleksite. Nos études d'assemblages complexes de sulfosels et de tellurures provenant de Iilijärvi, un gisement satellite lié au champ minéralisé de Orijärvi, dans le sud-ouest de la Finlande, a révélé des compositions dans l'intervalle $Pb_5Bi_4Te_4S_7$ – $Pb_7Bi_4Te_4S_9$. Celles-ci se présentent en intercroissances fines, et rarement en lamelles isolées, avec l'aleksite dans une matrice de giessenite, galène et cosalite. Les échantillons sont enrichis en or, qui forme aussi une texture symplectitique avec le rutile. Une étude des microparagenèses impliquant la galène porteuse de métaux précieux, la chalcopyrite et la pyrite dans des veines de quartz à Fragant ("Langenleiten"), province de Carinthie, en Autriche, révèle la présence de plusieurs tellurosulfures de Bi–Pb différant en composition. L'aleksite est le minéral le plus abondant, et ensuite, les phases sans nom ayant des compositions voisines de $Pb_3Bi_4Te_4S_5$, $Pb_5Bi_4Te_4S_7$ et $Pb_6Bi_4Te_4S_8$. Elles se présentent en inclusions dans la galène et sont variablement associées aux sulfosels tels lillianite, cosalite, felbertalite et aikinite. L'ensemble des données de tous ces indices est difficile à interpréter sans information structurale. Nos données, toutefois, font penser à l'existence possible d'une série chimique en incréments ayant la formule générale $Pb_NBi_4Te_4S_{N+2}$. Comme alternative, il ne s'agit pas de phases distinctes, essentiellement immiscibles au sein d'une série modulaire définie chimiquement, mais plutôt tout simplement de compositions dans une série de solutions solides continue. Si on parvient à prouver l'existence d'une série par incréments, la tetradyomite, $Bi_4Te_4S_2$, correspondrait à $N = 0$, la phase $PbBi_4Te_4S_3$ sans nom, à $N = 1$, l'aleksite, à $N = 2$, la phase $Pb_3Bi_4Te_4S_5$ sans nom, à $N = 3$, et la saddlebackite, à $N = 4$; ici, les valeurs de N indiquent la composition chimique plutôt que le degré d'ordre parmi les homologues définis structurellement. L'existence dans la littérature de quatre phases ($N = 1, 2, 3$ et 4) comme produits de synthèse (phases D, E, F et J) obtenus à 500°C appuie indirectement l'hypothèse. Les phases sans nom provenant de Iilijärvi et Fragant correspondraient à des membres non spécifiés à valeurs de N plus élevées dans la même série. L'aspect de bandes lamellaires avec galène et tetradyomite, et les champs étendus de composition dans les échantillons provenant de Clogau et Iilijärvi, rappellent des questions semblables dans la série de sulfosels de bismuth, ce qui nous permet de croire que nous pourrions avoir ici une série d'homologues typique, montrant une accréation dans l'épaisseur des couches. Dans un tel schéma, un empilement aléatoire de membres distincts de la série à l'échelle de la maille pourrait bien expliquer les variations en composition.

(Traduit par la Rédaction)

Mots-clés: tellurosulfures, aleksite, données compositionnelles, phases sans nom, Clogau, Pays de Galles, Iilijärvi, Finlande, Fragant, Autriche.

INTRODUCTION

Mineral compounds containing essential Bi, Pb, Te and S are minor constituents in a number of gold-bearing ore deposits. The first Pb–Bi tellurosulfide to be given mineral status, aleksite ($PbBi_2Te_2S_2$), was described by Lipovetskiy *et al.* (1978) from the Alekseyev mine, Sutamskii region, Stanovoi Range, Siberia, Russia. Type-locality aleksite, first mentioned as mineral "D" by Lipovetskiy *et al.* (1976), occurs as platy grains

up to 1 mm in size within sulfide–quartz veins. Other occurrences of aleksite include the Kochkar deposit, Ural Mountains, Russia (Spiridonov *et al.* 1989), the Clogau mine, Dolgellau gold belt, Gwynedd, Wales, U.K. (Bevins & Stanley 1990), the Ardino polymetallic skarn, Rhodopes, Bulgaria (Bonev & Neykov 1990), the Corrego Criminoso mining district, Brazil (de Souza Lima *et al.* 1996) and the San-notake district, Japan (Ueno *et al.* 1996). Aleksite is also confirmed from the Săcărîmb gold–telluride deposit, Romania (Shimizu

et al. 1999, pers. commun., 2003). A further occurrence of aleksite is Fragant (“Langenleiten”), Carinthia Province of Austria (Paar 2000), a small silver–gold deposit (Rochata 1878), in which a number of unnamed Bi–Pb tellurosulfides are associated with aleksite.

The single other recognized Pb–Bi–Te–S mineral, saddlebackite, $\text{Pb}_2\text{Bi}_2\text{Te}_2\text{S}_3$, is known only from the type locality, the Boddington gold deposit, Western Australia (Clarke 1997) and from Kochkar, where it had been recognized as a possible new mineral two years earlier (Spiridonov 1995). In the description of saddlebackite as a new mineral, Clarke (1997) emphasized that the species was probably structurally related to aleksite and tetradymite.

In four of the aforementioned descriptions (Lipovetskiy *et al.* 1976, Bevins & Stanley 1990, Bonev & Neykov 1990, Clarke 1997), a further phase was reported, with the composition $\text{PbBi}_4\text{Te}_4\text{S}_3$. This was termed “Phase C” in the first of the above descriptions, a descriptor we shall also use in this paper, in which we present new paragenetic and micro-analytical data for the aleksite–“phase C” assemblage from the Clogau mine, North Wales. We also describe the occurrence, the composition and the paragenesis of other unnamed Bi–Pb–Te–S compounds from the Ilijärvi deposit, southwest Finland, and from Fragant, Austria. These latter group of phases have compositions in the range $\text{Pb}_5\text{Bi}_4\text{Te}_4\text{S}_7$ – $\text{Pb}_7\text{Bi}_4\text{Te}_4\text{S}_9$, *i.e.*, richer in both Pb and S than aleksite or saddlebackite.

THE OCCURRENCES WE STUDIED

The Clogau mine, Wales, U.K.

The Clogau mine lies in the southern part of the Dolgellau gold belt on the southeastern margin of the Harlech Dome in North Wales, U.K. (Shepherd & Bottrell 1993). The vein systems are identified as pre-tectonic with respect to the early Devonian deformation (Mason *et al.* 1999, Platten & Dominy 1999), although Shepherd & Bottrell (1993) reported an age of 405 ± 6 Ma for the mineralization at Clogau. Quartz – sulfide – gold veins have been worked periodically since the 1850s, and a substantial body of data exists on their composition and conditions of formation (*e.g.*, Bottrell & Spiro 1988, Bottrell *et al.* 1988, Shepherd *et al.* 1991). Bismuth- and tellurium-bearing minerals were described by Gilbey (1968) and later confirmed by Naden (1988), who stressed a correlation in timing between telluride and gold mineralization in the deposit. A first description of the aleksite-bearing assemblage from Clogau was given by Bevins & Stanley (1990). We have re-investigated specimen E.1309 (Natural History Museum, U.K.), in which aleksite and “phase C” occur together with galena and tellurobismuthite. One of us (C.J.S.), together with coworkers, began to investigate this sample in detail in the early 1990s, obtaining X-ray diffraction, electron-microprobe and optical reflectance

documentation, some of which is reported in the present contribution.

Ilijärvi, Finland

Selenides and tellurides of bismuth are conspicuous trace components of base-metal – gold ores in the Orijärvi area, southwestern Finland. Our reinvestigation of specimens from Orijärvi (Ciobanu *et al.* 2002), including type-material laitakarite (Laitakari 1934, Vormä 1960), has also included material from the satellite deposit at Ilijärvi, 1.3 km northwest of Orijärvi (Mäkelä 1989). The ores are dominated by pyrite, chalcopyrite, sphalerite and galena, within a matrix of quartz, biotite, cordierite and gahnite, and are hosted by 1.9-Ga-old supracrustal rocks, deformed and metamorphosed during the Svecokarelian orogeny. The Orijärvi region is widely known for the pioneering research in metamorphic petrology by Eskola (1914, 1915, 1950) and for the occurrence of complex triple- and double-chain pyriboles (Schumacher & Czank 1987).

Selenium-bearing sulfosalts of bismuth were previously reported from Ilijärvi (Borgström 1915, Vaasjoki & Kaitaro 1951). Our studies have focused largely on material collected by Aarne Laitakari in the 1930s and deposited in the collection of Turku University; this material has been supplemented by specimens collected from outcrops at the mine site in 2002. In addition to the Se-bearing sulfosalt assemblage (giesenite–cosalite), our re-investigations have revealed abundant symplectitic intergrowths of gold with rutile and a number of selenium- and tellurium-bearing phases hosted within the sulfosalt assemblage (Ciobanu *et al.* 2002). We have interpreted these assemblages, and the preserved textures among component minerals, in terms of synmetamorphic remobilization from the “main” Orijärvi ore, coupled with extensive desulfidation and subsequent limited sulfidation contemporaneous with retrograde recrystallization.

Fragant, Austria

Tellurides of bismuth (tetradymite, joséite-type phases and pilsenite) are common constituents in structurally controlled and late-Alpine gold-bearing mineralization (“Tauerngoldgang-type”) in various districts of Salzburg and Carinthia provinces, Austria. The ores are dominated by pyrite, arsenopyrite, chalcopyrite, galena and sphalerite, and are associated with a very complex spectrum of Ag(Cu)–Pb–Bi–(Sb) sulfosalts (Putz *et al.* 2003). The host rocks are either metagranitic rocks of Variscan age (Central Gneiss) or (pre)-Permian to Mesozoic rocks of the cover sequences. Fragant (“Langenleiten”) is a small silver–gold deposit located in the southernmost part of the Sonnblick mountain range (Carinthia Province, Austria), close to the boundary with polymetamorphic complexes south of the Tauern Window. The structurally controlled mineraliza-

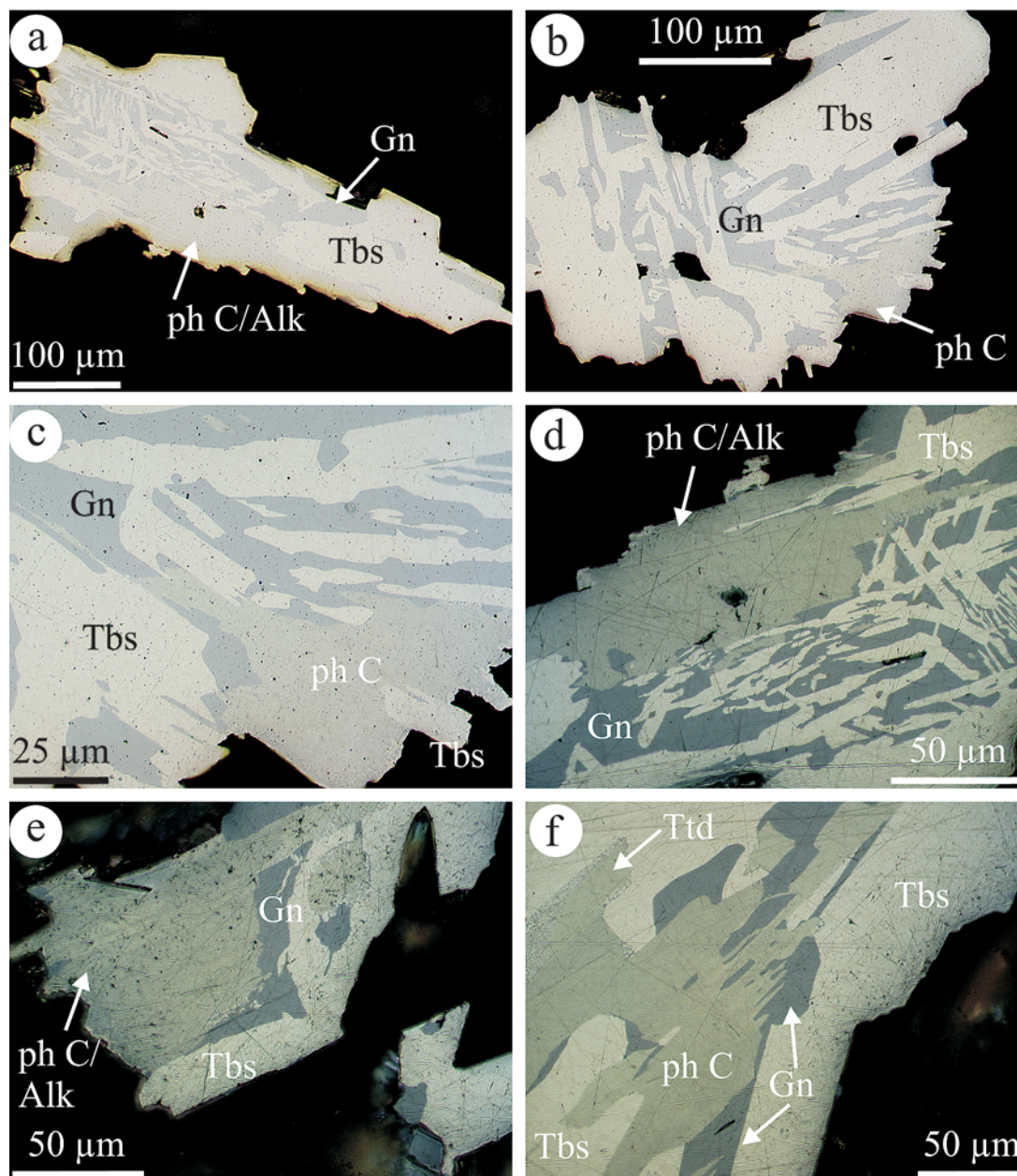


FIG. 1. Photomicrographs of telluride assemblages in specimen from Clogau [section E1309, The Natural History Museum, London, U.K.] in reflected light, taken in air (a–c) and oil immersion under slightly crossed polars (d–f) to accentuate differences among phases. Abbreviations: Gn: galena, Tbs: tellurobismuthite, ph C: “phase C”, $\text{PbBi}_4\text{Te}_4\text{S}_3$, Alk: aleksite, Ttd: Pb-bearing tetradytmite. Note, in particular, the abundant symplectitic intergrowths of galena and tellurobismuthite, contrasting with the larger patches of “phase C” or aleksite (or both). Tetradytmite typically occurs at the margins of larger bodies of “phase C”.

tion occurs in a major shear-zone on top of the Central Gneiss, where extremely deformed segments of the same gneiss and calcareous mica-schists host the ore. The ore assemblage is dominated by galena, pyrite and chalcopyrite, forming irregular (patchy) inclusions in a quartz vein, which reaches up to 1 m in thickness. The Bi–Pb tellurosulfides are present as small inclusions in galena and are variably associated with sulfosalts such as cosalite (dominant), lillianite, felbortalite (Topa *et al.* 2001) and aikinite. Native gold occurs as rare grains in galena. Hand specimens yielded up to 1 ppm Au and 678 ppm Ag. The deposit is of metamorphic origin and was formed during the retrograde stage of the Alpine regional metamorphism.

DESCRIPTION OF THE SAMPLES

Clogau

Specimen E.1309 contains pyrrhotite, chalcopyrite and galena as major sulfides, with a telluride assemblage consisting of tellurobismuthite, hessite and two Bi–Pb tellurosulfides (aleksite and “phase C”), as well as minor gold. In the Clogau specimen, lath-like grains composed of aleksite, “phase C”, tellurobismuthite, minor tetradymite and galena, 100–1000 μm in size, occur throughout the chlorite – calcite – quartz matrix. Under oil immersion, all these minerals are generally seen to be intergrown with one another, in some cases as fine-grained symplectites (Figs. 1, 2). Although some patches of aleksite and “phase C” appear homogeneous, others display an intimate intergrowth as lamellar banding, and may also include galena, which may be a decomposition or exsolution product. Optically, “phase C” and aleksite are rather similar in appearance. Both are green-grey in color, especially against tellurobismuthite and galena, which appear pinkish white and grey, respectively, and display moderate birefractance. Under oil immersion, the slightly higher reflectance of “phase C” is evident. A single grain of saddlebackite, not previously recognized in the Clogau assemblage, was identified, intergrown with aleksite.

Ilijärvi

Specimens from Ilijärvi are dominated either by galena, pyrrhotite and sphalerite, with considerable variations in sulfide assemblage on the hand-specimen scale. Samples display a distinct Sb- and Te-rich signature, rather than a Se-dominant character as at Orijärvi. Minor sulfides include chalcopyrite, pyrite, marcasite, molybdenite, arsenopyrite and cobaltite. The Bi-sulfosalts giessenite, $\text{Cu}_2\text{Pb}_{26}(\text{Bi},\text{Sb})_{20}\text{S}_{57}$, and cosalite, $\text{Pb}_2\text{Bi}_2(\text{S},\text{Se})_5$, occur within galena. Both sulfosalts display substitution of Bi by Sb; ~10 mol.% in the case of cosalite and in the range 15–30 mol.% for giessenite. The Bi–Te–Se–S phases are abundant minor minerals within the galena–sulfosalt assemblages. Hedleyite,

Bi_7Te_3 , joséite-B, $\text{Bi}_4\text{Te}_2\text{S}$, joséite-A, Bi_4TeS_2 and ikonolite, $\text{Bi}_4(\text{S},\text{Se})_3$, with intergrowths among pairs of these phases, are abundant.

Aleksite and the unnamed phases that we focus on in this paper ($\text{Pb}_5\text{Bi}_4\text{Te}_4\text{S}_7$ – $\text{Pb}_7\text{Bi}_4\text{Te}_4\text{S}_9$ range) occur as individual and composite lamellae within galena and the Bi-sulfosalts (Figs. 3, 4). The phases in the Ilijärvi specimens are grey with a slightly darker tint against joséite-A, joséite-B or hedleyite.

Fragant, Austria

The specimens investigated are dominated by galena embedded in a quartz matrix and accompanied by subordinate amounts of pyrite and chalcopyrite. Galena contains numerous inclusions of various sulfosalts, such as cosalite, Ag-poor members of the lillianite–gustavite homologous series, felbortalite and aikinite (Fig. 5a). All of them attain sizes up to several 100 μm . The Bi–Pb tellurosulfides, of which aleksite, $\text{PbBi}_2\text{Te}_2\text{S}_2$, is the most abundant (Fig. 5a), are commonly intergrown with either cosalite or lillianite, rarely with felbortalite, but never with aikinite. They form lamellae up to 200 μm in length but only rarely exceed 20 μm in width.

Aleksite may be closely associated with three other, unnamed Bi–Pb tellurosulfides, compositionally $\text{Pb}_5\text{Bi}_4\text{Te}_4\text{S}_7$ (LA 12/B) (Fig. 5b), $\text{Pb}_6\text{Bi}_4\text{Te}_4\text{S}_8$ (LA 12/C) and $\text{Pb}_3\text{Bi}_4\text{Te}_3\text{S}_5$ (99/89 b); the latter is present as rare and individual tabular grains in galena. A compound very close in composition to “phase C”, chemically $\text{PbBi}_4\text{Te}_4\text{S}_3$, has been observed once and is intimately intergrown with aleksite (99/89 b).

MICRO-ANALYTICAL DATA

Electron-probe micro-analysis of the Pb–Bi–Te–S phases has been carried out in three different laboratories, using different instruments, operating conditions and with some variation in analytical standards. The majority of the data reported in the tables was obtained using the JEOL JXL–8600 instrument at the Natural History Museum, London. Conditions and standards for micro-analysis used in this laboratory are reported in the footnote to Table 1. Details for other laboratories (Institute of Mineralogy, University of Salzburg, Austria; Adelaide Microscopy, University of Adelaide, Australia) are given in the footnotes to Tables 1 and 3, respectively.

As the phases are intergrown in all sets of specimens, we have taken care to discard all analytical datasets in which the presence of microscopic or submicroscopic intergrowths was observed or suggested by back-scattered-electron imaging. In the Clogau specimens, this applies especially to intergrowths of “phase C” with aleksite and with tellurobismuthite. Two additional problems we encountered, which have implications for the quality of the analytical data, were the fine size of some grains (especially in the Ilijärvi material, where

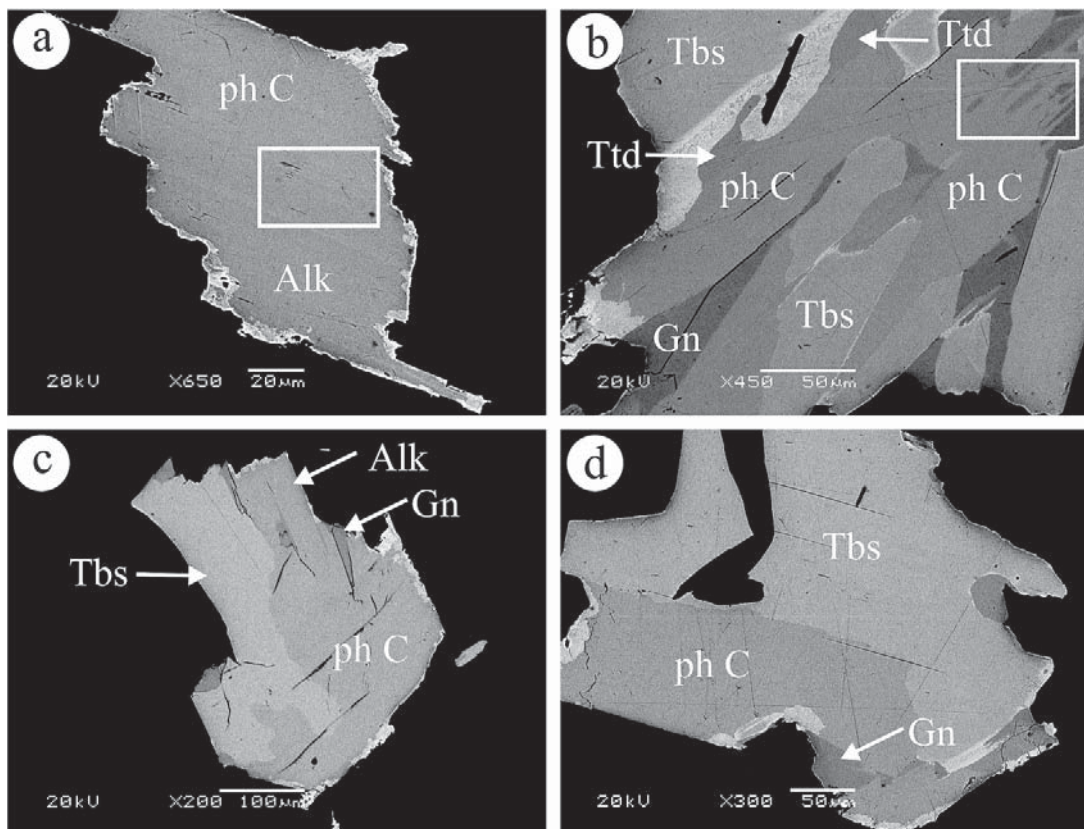


FIG. 2. Back-scattered electron images of assemblages in the Clogau specimens. (a) Larger lath-like, composite grain of "phase C", $\text{PbBi}_4\text{Te}_4\text{S}_3$ (ph C) and aleksite (Alk). Boundary between domains of the two minerals (white box) features fine ($1\text{--}2\ \mu\text{m}$) lamellar intergrowths. (b) Sub-symplectitic intergrowth of "phase C", tellurobismuthite (Tbs), galena (Gn) and Pb-bearing tetradymite (Ttd). Note lamellar exsolution of galena within "phase C" (white box). The white areas are submicroscopic intergrowths (decomposition products?) containing bismuth and various tellurides. (c, d) Larger, homogeneous bodies of "phase C" showing sharp boundaries against tellurobismuthite and galena. The grain in (c) contains a single homogeneous lath of aleksite.

some lamellae are no more than $1\text{--}3\ \mu\text{m}$ in diameter or in depth) and the particularly poor polish taken by all these phases. Repeated repolishing exposed both these problems, leading us to refrain from repeated efforts to improve the surface polish, at the risk of losing details that had been carefully mapped by SEM.

Aleksite and "Phase C"

Compositional data for species in the range of aleksite and "phase C" from Clogau, Ilijärvi and Fragant are given in Tables 1 and 2. Plotted compositions (Fig. 6) show a relatively narrow, but nevertheless significant spread of $\text{Pb}/(\text{Pb} + \text{Bi})$ and $\text{Te}/(\text{Te} + \text{S})$ values across and beyond the ideal compositions of the two phases, with little evidence of an extensive compositional gap

between the two. We note that a number of analytical datasets falling within this compositional gap were removed since they likely pertain to mixtures. The spread of the $\text{Pb}/(\text{Pb} + \text{Bi})$ and $\text{Te}/(\text{Te} + \text{S})$ values for aleksite from Fragant appears less extensive, although it will be noted that the dataset is smaller. Published data for "phase C" (Lipovetskiy *et al.* 1976, Bonev & Neykov 1990, Clarke 1997) are included in Table 2 for purposes of comparison.

Saddlebackite

Only a single grain was identified in the Clogau specimen, with a composition close to $\text{Pb}_2\text{Bi}_2\text{Te}_2\text{S}_3$ (Table 1).

Pb-bearing tetradymite

We have analyzed tetradymite in the Clogau material and established contents of Pb that range from <1 wt.% up to as much as 8 wt.%, *i.e.*, close to that of “phase C”. We advise caution in the interpretation of these data, since we cannot be certain if this is Pb-bearing tetradymite or a submicroscopic mixture of tetradymite with Pb–Bi–Te–S phases.

Unnamed phases from Ilijärvi and Fragant

The two largest lamellae in the Ilijärvi samples were both analyzed with different electron microprobes. The largest lamella (grain 3; Fig. 3a), apparently homogeneous in back-scattered electron images, gives composi-

tions in the range $\text{Pb}_6\text{Bi}_4\text{Te}_4\text{S}_8 - \text{Pb}_7\text{Bi}_4\text{Te}_4\text{S}_9$ (Table 3, Fig. 6), indicating inhomogeneity. The second lamella (grain 6, with a rim of hessite; Fig. 4b) has a somewhat different composition. Data points show variation in $\text{Pb}/(\text{Pb} + \text{Bi})$ and $\text{Te}/(\text{Te} + \text{S})$, but are clustered closer to $\text{Pb}_5\text{Bi}_4\text{Te}_4\text{S}_7$, with some individual compositions extending toward $\text{Pb}_6\text{Bi}_4\text{Te}_4\text{S}_8$. Analyses of the smaller lamellae and blebs in the specimens also gave a variety of compositions in the same general range. The total dataset, in which analyses yielding poor totals or charge balance and any points in which intergrowths were seen or suspected have been excluded, shows a range of $(\text{Pb} + \text{Bi})/(\text{Te} + \text{S})$ values spread across a relatively broad compositional range between $\text{Pb}_5\text{Bi}_4\text{Te}_4\text{S}_7$ and $\text{Pb}_7\text{Bi}_4\text{Te}_4\text{S}_9$ (Fig. 6). For this reason, we choose not to distinguish distinct stoichiometries.

TABLE 1. REPRESENTATIVE COMPOSITIONS, WITH STATISTICAL DATA, OF ALEKSITE AND SADDLEBACKITE

	Ag	Cu	Pb	Fe	Cd	Bi	Sb	Te	Se	S	Total	Formula*
Aleksite												
Clogau mine												
7-128	-	-	19.64	-	-	45.31	0.46	27.78	0.20	6.34	99.73	$\text{Pb}_{1.82}(\text{Bi}_{4.14}\text{Sb}_{0.08})_{\Sigma 4.22}\text{Te}_{4.16}(\text{S}_{3.78}\text{Se}_{0.04})_{\Sigma 3.82}$
7-135	0.10	-	20.30	-	-	45.03	0.47	27.63	0.22	6.51	100.25	$\text{Pb}_{1.86}(\text{Bi}_{4.08}\text{Sb}_{0.08})_{\Sigma 4.16}\text{Te}_{4.10}(\text{S}_{3.84}\text{Se}_{0.06})_{\Sigma 3.90}$
4-43	-	-	20.80	-	0.14	44.46	0.51	27.14	0.21	6.50	99.80	$\text{Pb}_{1.90}(\text{Bi}_{4.04}\text{Sb}_{0.08})_{\Sigma 4.12}\text{Te}_{4.04}(\text{S}_{3.84}\text{Se}_{0.06})_{\Sigma 3.90}$
2-30	0	0	21.34	-	0.08	44.64	0.51	26.72	0.14	6.55	99.99	$\text{Pb}_{1.96}(\text{Bi}_{4.06}\text{Sb}_{0.08})_{\Sigma 4.14}\text{Te}_{3.98}(\text{S}_{3.83}\text{Se}_{0.04})_{\Sigma 3.92}$
2-35	0.14	-	22.25	-	-	44.09	0.45	26.44	0.16	6.64	100.17	$\text{Pb}_{2.04}(\text{Bi}_{4.00}\text{Sb}_{0.08})_{\Sigma 2.08}\text{Te}_{3.92}(\text{S}_{3.92}\text{Se}_{0.04})_{\Sigma 3.96}$
2-31	0.12	0.09	22.33	-	-	43.72	0.42	26.23	0.21	6.69	99.82	$\text{Pb}_{2.04}(\text{Bi}_{3.96}\text{Sb}_{0.08})_{\Sigma 4.02}\text{Te}_{3.90}(\text{S}_{3.94}\text{Se}_{0.06})_{\Sigma 4.00}$
Mean (n=15)	0.05	0.05	20.60	0.02	0.03	44.50	0.46	27.08	0.18	6.49	99.44	$\text{Pb}_{1.90}(\text{Bi}_{4.06}\text{Sb}_{0.08})_{\Sigma 4.14}\text{Te}_{4.04}(\text{S}_{3.86}\text{Se}_{0.04})_{\Sigma 3.90}$
Std. Dev.	0.06	0.05	1.06	0.02	0.04	0.66	0.05	0.53	0.03	0.13		
Ilijärvi												
21-7	0.08	-	18.74	-	-	46.62	0.33	25.06	0.81	6.65	98.29	$\text{Pb}_{1.74}(\text{Bi}_{4.28}\text{Sb}_{0.06})_{\Sigma 4.34}\text{Te}_{3.76}\text{Se}_{0.20}\text{S}_{3.98}$
21-6	-	-	20.0	-	-	46.12	0.19	25.09	1.33	6.61	99.38	$\text{Pb}_{1.84}(\text{Bi}_{4.18}\text{Sb}_{0.04})_{\Sigma 4.22}\text{Te}_{3.72}\text{Se}_{0.32}\text{S}_{3.90}$
21-5	-	-	22.35	-	-	48.05	0.27	24.54	-	6.58	101.80	$\text{Pb}_{2.04}(\text{Bi}_{4.36}\text{Sb}_{0.04})_{\Sigma 4.40}\text{Te}_{3.66}\text{S}_{3.90}$
10-1	-	-	22.93	-	-	42.94	0.14	24.82	0.71	6.66	98.20	$\text{Pb}_{2.12}(\text{Bi}_{3.96}\text{Sb}_{0.02})_{\Sigma 3.98}\text{Te}_{3.74}\text{Se}_{0.18}\text{S}_{4.00}$
*c1	-	-	24.3	-	-	44.4	0.22	25.2	0.74	6.39	101.25	$\text{Pb}_{2.22}(\text{Bi}_{4.04}\text{Sb}_{0.04})_{\Sigma 4.08}\text{Te}_{3.76}\text{Se}_{0.18}\text{S}_{3.78}$
*c2	-	-	23.5	-	-	44.9	0.24	25.0	0.82	6.62	101.08	$\text{Pb}_{1.14}(\text{Bi}_{4.04}\text{Sb}_{0.04})_{\Sigma 4.08}\text{Te}_{3.70}\text{Se}_{0.20}\text{S}_{3.90}$
Fragant ⁽¹⁾												
99/89b mean (n = 7)												
	0.02	-	21.31	-	-	44.69	-	28.42	-	6.94	101.36	$\text{Pb}_{1.90}\text{Bi}_{3.96}\text{Te}_{2.12}\text{S}_{4.00}$
Std. dev.	0.03	-	0.91	-	-	0.06	-	0.36	-	0.12		
99/95 mean (n = 17)												
	-	-	20.97	-	-	44.97	-	28.82	-	6.84	101.60	$\text{Pb}_{1.88}\text{Bi}_{3.98}\text{Te}_{4.18}\text{S}_{3.94}$
Std. dev.	-	-	1.75	-	-	1.22	-	0.95	-	0.19		
Saddlebackite												
Clogau mine												
*9-1	-	-	37.1	-	-	34.0	0.4	21.1	0.13	8.45	101.18	$\text{Pb}_{4.16}(\text{Bi}_{3.78}\text{Sb}_{0.08})_{\Sigma 3.86}(\text{Te}_{3.84}\text{Se}_{0.04})_{\Sigma 3.88}\text{S}_{6.12}$
*9-2	-	-	37.1	-	-	33.8	0.4	20.8	-	8.43	100.53	$\text{Pb}_{4.18}(\text{Bi}_{3.78}\text{Sb}_{0.08})_{\Sigma 3.86}\text{Te}_{3.92}\text{S}_{6.14}$

* The formula is calculated on the basis of 14 or 18 atoms per formula unit; minor amounts of Ag, Cu, Cd and Fe are ignored. -: less than the minimum limit of detection. Analytical conditions: NHM (London): JEOL JXL-8600; 15 kV, 20 nA, *SKa* (ZnS), *AgLa* (Ag), *SbLa* (Sb_2S_3), *CdLb* (CdS), *TeLa* (Bi_2Te_3), *SeKa* (PbSe), *BiLa* (Bi_2Te_3), *PbLa* (PbS), *CuKa* (CuFeS_2). (1) Salzburg: JEOL JXL-8600; 25 kV, 35 nA, *SKa* (Bi_2S_3), *AgLa* (Ag), *SbLa* (Sb_2S_3), *CdLa* (CdTe), *TeLa* (CdTe), *SeKa* (Bi_2Se_3), *BiLa* (Bi_2S_3), *PbLa* (PbS), *CuKa* (CuFeS_2).

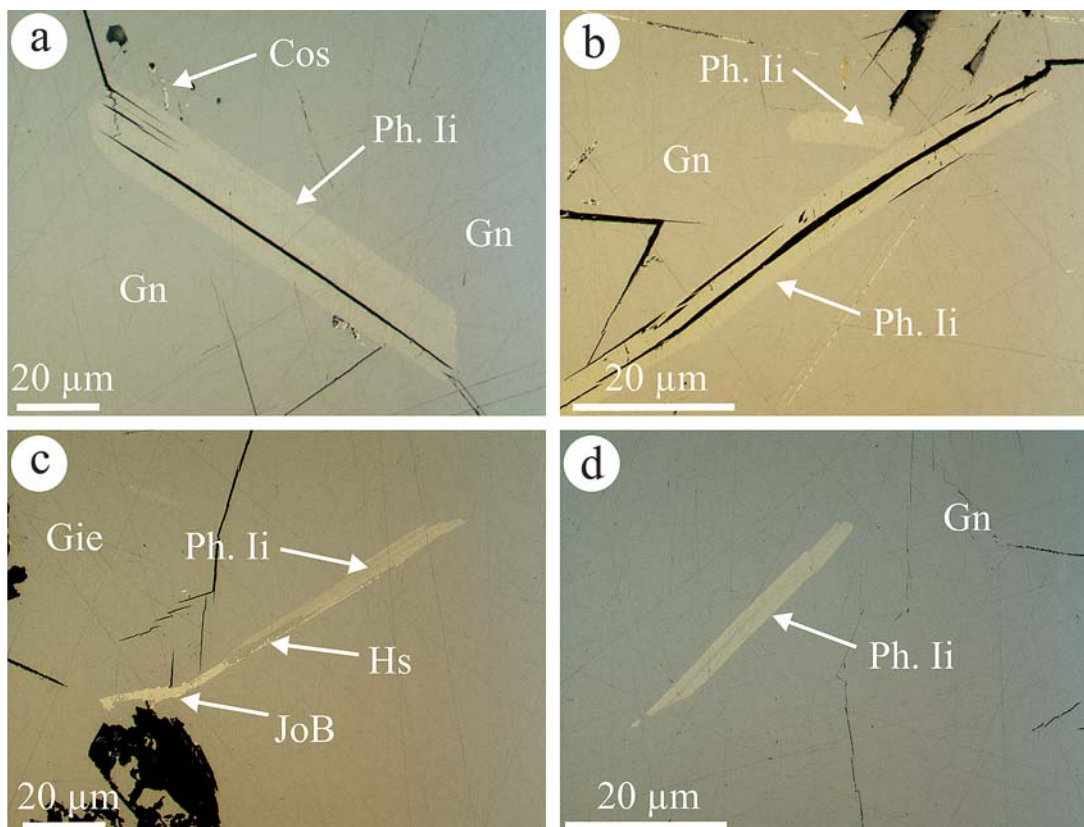


FIG. 3. Photomicrographs of telluride assemblages in the Ilijärvi specimens in reflected light, taken in oil immersion under slightly crossed polars to accentuate differences among phases. (a) "Grain 3": large single lamella of $\sim\text{Pb}_7\text{Bi}_4\text{Te}_4\text{S}_9$ (some results closer to $\text{Pb}_6\text{Bi}_4\text{Te}_4\text{S}_8$) within galena (Gn) and associated with minor cosalite (Cos). (b) Narrow, deformed and fractured lamella of $\sim\text{Pb}_6\text{Bi}_4\text{Te}_4\text{S}_8$ within galena (Gn). Note that during deformation, cleavage domains in the extremely soft tellurides have been opened. c, d) Two smaller lamellae of telluride within giessenite (Gie) and galena (Gn). Hs: hessite; JoB: joséite-B.

In the Fragrant specimens, we have analyzed several lamellae either intergrown with aleksite or individually embedded in galena. All lamellae proved to be homogeneous. The chemical compositions obtained are close to $\text{Pb}_3\text{Bi}_4\text{Te}_4\text{S}_5$ (one analysis only), $\text{Pb}_5\text{Bi}_4\text{Te}_4\text{S}_7$ and $\text{Pb}_6\text{Bi}_4\text{Te}_4\text{S}_8$ (Table 4, Fig. 6).

REFLECTANCE DATA

Reflectance data for the most homogeneous grains of "phase C" and aleksite from Clogau, and from the large lamella (grain 2, $\sim\text{Pb}_6\text{Bi}_4\text{Te}_4\text{S}_8$) in the Ilijärvi specimens, are given in Table 5 and plotted (air only, for clarity) in Figure 7. Data were generated using the same apparatus, methodology, conditions and standards (WTiC) as in the Quantitative Data File for Ore Minerals (Criddle & Stanley 1986). For comparison, reflectance

FIG. 5. Back-scattered-electron images of assemblages in the Fragrant specimens. (a) Aleksite (ALK) is associated with anglesite (black) and cosalite (Cos); the matrix is galena_{ss} (Gn_{ss}). (b) A lamellae of unnamed $\text{Pb}_5\text{Bi}_4\text{Te}_4\text{S}_7$ (Un) is intergrown with lillianite (${}^4\text{L}_{35}$); the associated phases are felbertalite (Fel) and cosalite (Cos), and the matrix is galena_{ss}.

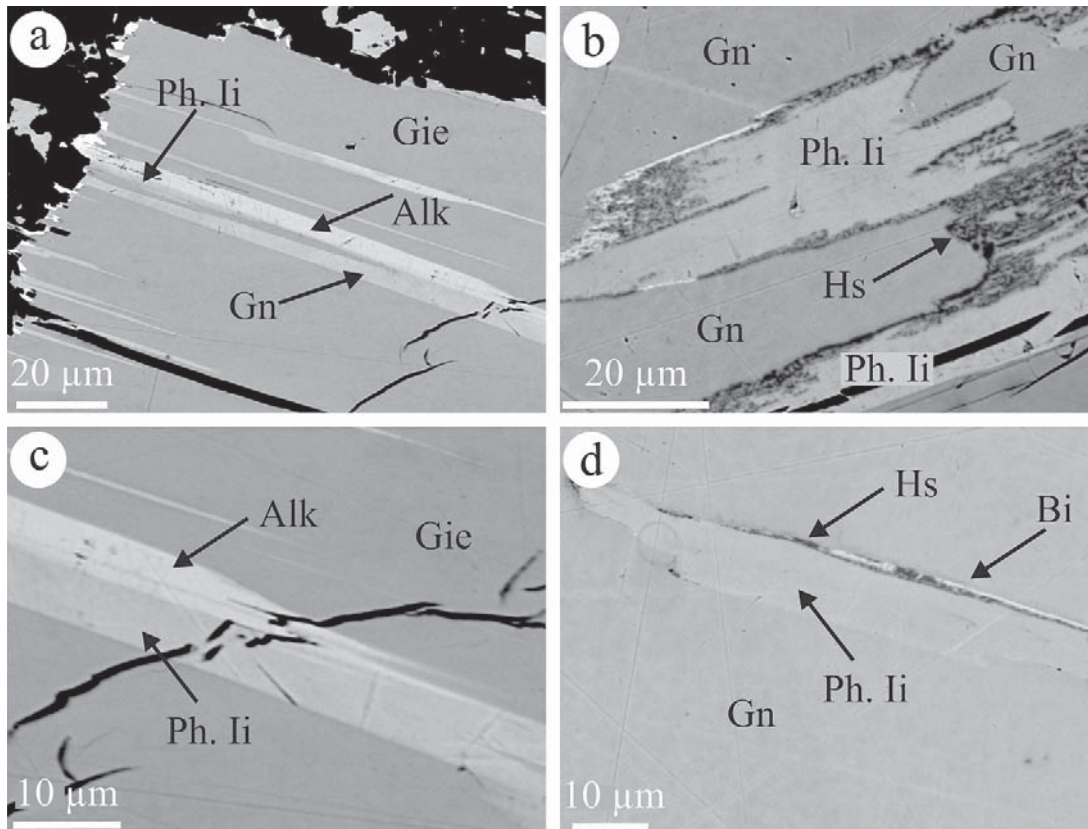
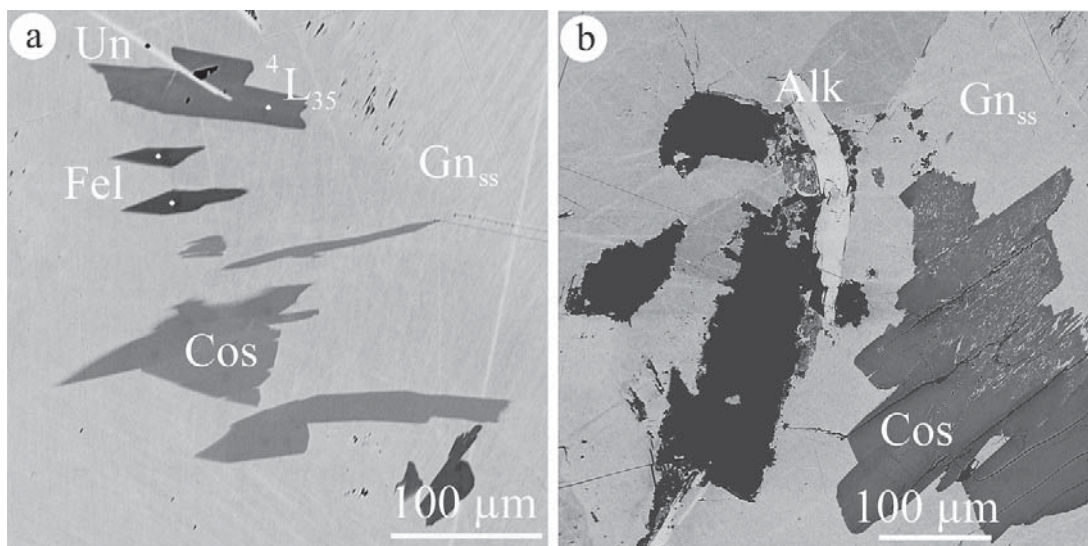


FIG. 4. Back-scattered-electron images of assemblages in the Ilijärvi specimens. (a) Lamellae of aleksite (Alk), galena (Gn) and $\sim\text{Pb}_6\text{Bi}_4\text{Te}_4\text{S}_8$ within giessenite (Gie). (b) "Grain 6": body of homogeneous $\sim\text{Pb}_6\text{Bi}_4\text{Te}_4\text{S}_8$ within galena (Gn), featuring a patchy rim of hessite (Hs). (c) "Grain 21": Coexisting lamellae of $\sim\text{Pb}_6\text{Bi}_4\text{Te}_4\text{S}_8$ and aleksite (Alk) within galena. (d) Homogeneous $\sim\text{Pb}_6\text{Bi}_4\text{Te}_4\text{S}_8$ within galena (Gn). Rim consists of hessite (Hs) and native bismuth (Bi).



data for tetradymite are reproduced from that reference work. We note similarities in the reflectance spectra of tetradymite (and also ingodite and joséite- B), through “phase C” to aleksite, but with quantifiable differences among the minerals and also a distinct trend observable in the dataset. Reflectance values, both in air and oil immersion, are progressively lower, and the spectra, flatter in appearance, with a corresponding decrease in the difference between R_o and R_e . The spectra for “phase C” and aleksite are similar, differing by no more than 2–3% across the wavelength spectrum. The spectra for aleksite are broadly similar, but not fully consistent with the spectrum given by Lipovetskiy *et al.* (1978).

Reflectance curves for the unnamed phase from Lili-järvi are also rather flat, but unlike the other minerals, they have a characteristic negative slope. Differences between R_o and R_e are minimal (<1%) in air, but slightly more pronounced in oil immersion.

X-RAY-DIFFRACTION DATA

The small size, intergrown character and soft, platy, commonly bent character of the phases in both sets of specimens made extraction difficult in the study of the Clogau material and impossible for the Lilijärvi and Fragant phases. Nevertheless, the acquisition of powder-diffraction data for “phase C” and aleksite was undertaken for the Clogau samples (W.G. Mumme, pers. commun. to C.J.S., 1998). The patterns are similar, but apparently distinct, with peaks that have slightly different positions and intensities (an effective doubling of some peaks). The patterns and tentative indexing allowed calculation of unit cells: aleksite a 4.24, c 79.64 Å, $Z = 3$; “phase C”: a 4.25, c 69.71 Å, $Z = 3$.

Liu & Chang (1994) conducted a series of synthesis studies on the system Pb–Bi–Te–S in which the synthetic equivalents of aleksite and saddlebackite, as

TABLE 2. REPRESENTATIVE COMPOSITIONS, WITH STATISTICAL DATA, OF “PHASE C” (PbBi₄Te₄S₃) AND Pb-BEARING TETRADYMITITE

	Ag	Cu	Pb	Fe	Cd	Bi	Sb	Te	Se	S	Total	Formula*
“Phase C”												
Clogau mine (this study)												
3-94	-	-	11.58	-	0.07	50.74	0.49	30.72	0.20	5.45	99.24	Pb _{0.94} (Bi _{4.06} Sb _{0.07}) _{Σ4.13} Te _{4.03} (S _{2.85} Se _{0.04}) _{Σ2.89}
3-83	0.16	-	11.61	-	-	50.89	0.52	31.08	0.20	5.68	100.13	Pb _{0.92} (Bi _{4.01} Sb _{0.07}) _{Σ4.08} Te _{4.01} (S _{2.92} Se _{0.04}) _{Σ2.96}
2-32	0.07	-	12.02	-	-	50.12	0.53	30.74	0.18	5.52	99.18	Pb _{0.97} (Bi _{4.00} Sb _{0.07}) _{Σ4.07} Te _{4.02} (S _{2.88} Se _{0.04}) _{Σ2.92}
4-54	-	0.13	12.79	-	-	49.56	0.60	30.41	0.21	5.69	99.38	Pb _{1.02} (Bi _{3.93} Sb _{0.08}) _{Σ4.01} Te _{3.95} (S _{2.94} Se _{0.04}) _{Σ2.98}
3-113	-	-	12.84	-	-	49.92	0.52	30.71	0.20	5.69	99.88	Pb _{1.02} (Bi _{3.95} Sb _{0.07}) _{Σ4.02} Te _{3.98} (S _{2.92} Se _{0.04}) _{Σ2.97}
2-37	-	0.14	13.11	-	-	49.85	0.53	30.30	0.23	5.76	99.92	Pb _{1.04} (Bi _{3.93} Sb _{0.07}) _{Σ4.00} Te _{3.91} (S _{2.96} Se _{0.05}) _{Σ3.01}
5-64	-	0.06	13.31	-	-	49.40	0.54	29.97	0.19	5.78	99.25	Pb _{1.07} (Bi _{3.92} Sb _{0.07}) _{Σ3.99} Te _{3.90} (S _{2.99} Se _{0.04}) _{Σ3.03}
Mean (n=41)	0.03	0.03	12.55	0.02	0.04	49.81	0.49	30.47	0.18	5.64	99.28	Pb _{1.00} (Bi _{3.97} Sb _{0.07}) _{Σ4.04} Te _{3.98} (S _{2.92} Se _{0.04}) _{Σ2.96}
Std. dev.	0.04	0.04	1.48	0.03	0.04	0.92	0.06	0.63	0.03	0.16		
Fragant (this study) ⁽¹⁾												
99/89b		0.01	14.4			49.1		31.1		6.25	100.86	Pb _{1.12} Bi _{3.76} Te _{3.93} S _{3.15}
Aleksiev (Lipovetskiy <i>et al.</i> 1976)												
			10.7			52.2		30.9		5.5	99.3	Pb _{0.87} Bi _{4.16} Te _{4.06} S _{2.88}
Andrino (Bonev & Neykov 1990), average of three												
	0.17	0.82	11.72	0.44		51.15		29.74	0.61	5.54	100.04	Pb _{0.93} Bi _{4.03} Te _{3.83} (S _{2.84} Se _{0.13}) _{Σ2.97}
Boddington (Clarke 1997), average of three												
			12.52			49.27		33.84		5.63	101.26	Pb _{0.98} Bi _{3.84} Te _{4.32} S _{2.86}
Pb-bearing tetradymite												
Clogau mine (this study), average of three												
	0.06	0.02	6.58	0.03	0.05	53.92	0.44	32.70	0.18	5.08	99.07	(Pb _{0.23} Bi _{1.83}) _{Σ2.06} Te _{1.80} Se _{0.02} S _{1.12}

* The formula is calculated on the basis of 12 atoms per formula unit; minor amounts of Ag, Ag, Cd and Fe are ignored. -: less than the minimum limit of detection. Analytical conditions: as given in Table 1. ⁽¹⁾ See Table 1.

TABLE 3. REPRESENTATIVE COMPOSITIONS, WITH STATISTICAL DATA, OF THE Pb–Bi–Te–S PHASES IN SPECIMENS FROM IILIJÄRVI

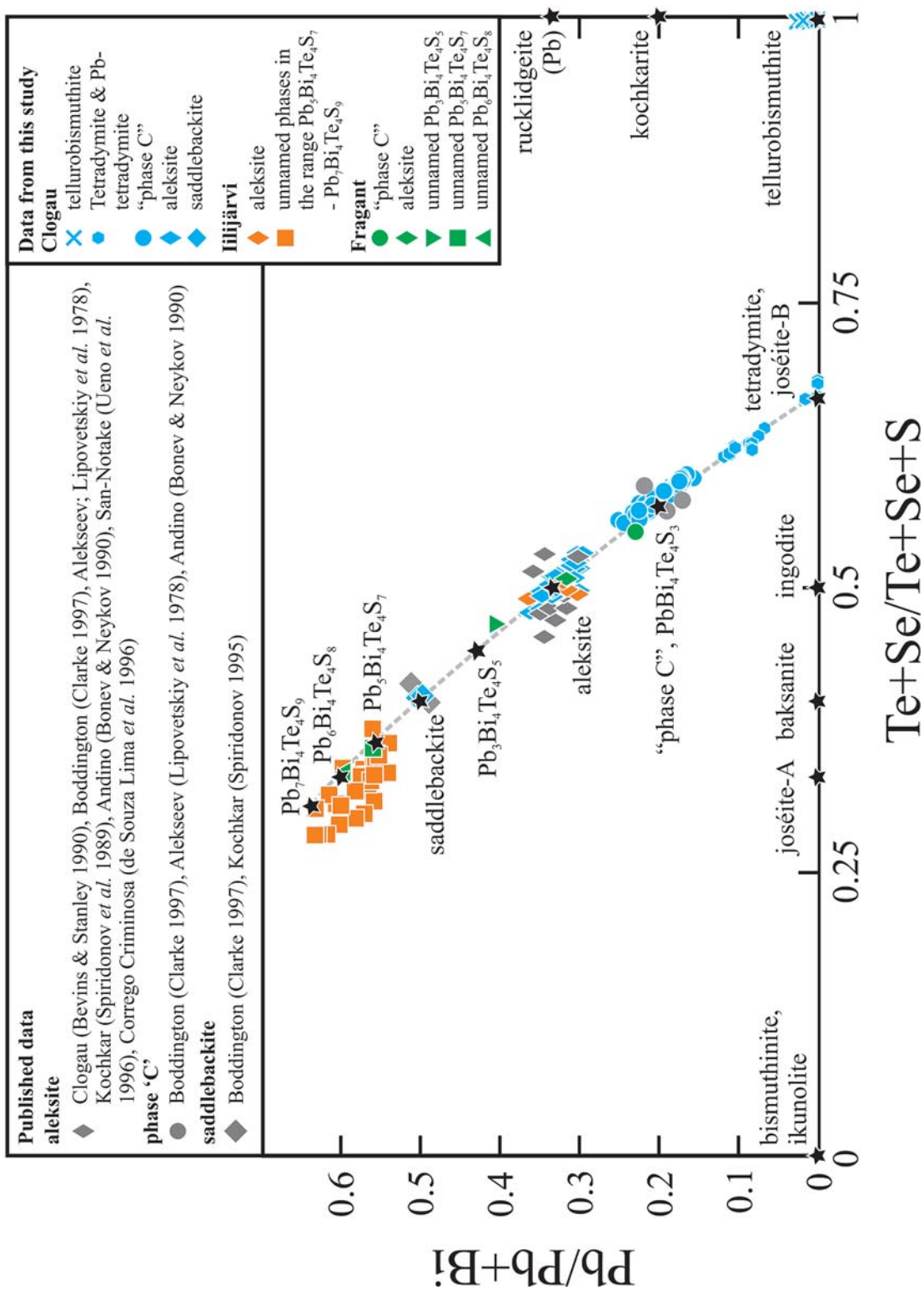
	Ag	Pb	Bi	Sb	Te	Se	S	Total	Formula [§]
Grain "3" (large lamella)									
3-75	0.20	46.21	29.09	0.12	13.59	0.90	9.55	99.66	Pb _{6.28} (Bi _{3.92} Sb _{0.03}) _{Σ3.95} (Te _{3.00} Se _{0.32}) _{Σ3.32} S _{8.39}
3-76	0.14	47.04	28.05	0.10	13.69	0.90	9.67	99.58	Pb _{6.37} (Bi _{3.77} Sb _{0.02}) _{Σ3.79} (Te _{3.01} Se _{0.32}) _{Σ3.33} S _{8.47}
3-79	0.08	42.78	31.53	0.09	15.36	0.99	9.02	99.85	Pb _{5.88} (Bi _{4.29} Sb _{0.02}) _{Σ4.31} (Te _{3.43} Se _{0.36}) _{Σ3.79} S _{8.01}
3-82	0.28	44.49	30.04	-	14.99	0.96	9.31	100.07	Pb _{6.05} Bi _{4.05} (Te _{3.31} Se _{0.34}) _{Σ3.65} S _{8.18}
*3.2	-	45.4	30.1	0.14	15.0	0.78	8.78	100.20	Pb _{6.30} (Bi _{4.14} Sb _{0.02}) _{Σ4.17} (Te _{3.38} Se _{0.28}) _{Σ3.66} S _{7.87}
*3.3	0.09	46.1	29.5	0.09	14.8	0.82	8.99	100.39	Pb _{6.34} (Bi _{4.02} Sb _{0.02}) _{Σ4.04} (Te _{3.31} Se _{0.30}) _{Σ3.61} S _{7.99}
*3.4	0.08	45.5	28.5	0.14	14.5	0.72	8.66	98.10	Pb _{6.44} (Bi _{4.00} Sb _{0.03}) _{Σ4.03} (Te _{3.33} Se _{0.27}) _{Σ3.60} S _{7.92}
*3.5	0.00	46.2	29.7	0.14	14.6	0.80	8.82	100.26	Pb _{6.41} (Bi _{4.08} Sb _{0.03}) _{Σ4.11} (Te _{3.29} Se _{0.29}) _{Σ3.58} S _{7.90}
*3.6	0.12	45.9	29.2	0.14	15.0	0.86	8.89	100.11	Pb _{6.34} (Bi _{4.09} Sb _{0.03}) _{Σ4.03} (Te _{3.36} Se _{0.31}) _{Σ3.67} S _{7.93}
*3.7	0.15	46.7	28.8	0.10	14.6	0.88	8.99	100.22	Pb _{6.43} (Bi _{3.93} Sb _{0.02}) _{Σ3.95} (Te _{3.26} Se _{0.32}) _{Σ3.58} S _{8.00}
*3.8	0.11	47.3	28.8	0.10	14.4	0.82	9.26	100.79	Pb _{6.44} (Bi _{3.89} Sb _{0.02}) _{Σ3.91} (Te _{3.18} Se _{0.29}) _{Σ3.47} S _{8.15}
*Mean									
(n=7)	0.08	46.16	29.23	0.12	14.70	0.81	8.91	100.01	Pb _{6.38} (Bi _{4.01} Sb _{0.03}) _{Σ4.04} (Te _{3.30} Se _{0.29}) _{Σ3.59} S _{7.97}
*S.D.	0.06	0.67	0.57	0.02	0.24	0.05	0.19	0.87	
**3-4	0.29	45.42	30.10	0.22	14.66	1.13	9.18	101.00	Pb _{6.16} (Bi _{4.05} Sb _{0.05}) _{Σ4.10} (Te _{3.23} Se _{0.40}) _{Σ3.63} S _{8.04}
**3-12	0.17	43.28	27.61	0.09	15.74	0.80	9.15	96.85	Pb _{6.03} (Bi _{3.81} Sb _{0.02}) _{Σ3.83} (Te _{3.56} Se _{0.29}) _{Σ3.85} S _{8.23}
**Mean									
(n=6)	0.17	44.11	30.21	0.16	15.23	0.98	9.10	99.98	Pb _{6.04} (Bi _{4.09} Sb _{0.04}) _{Σ4.13} (Te _{3.38} Se _{0.35}) _{Σ3.73} S _{8.05}
Grain "6" (lamella with rim of hessite)									
132	0.29	41.92	31.75	-	16.32	0.96	8.71	99.93	Pb _{5.79} Bi _{4.35} (Te _{3.66} Se _{0.35}) _{Σ4.01} S _{7.77}
133	0.12	42.22	32.26	-	16.28	0.93	8.99	100.80	Pb _{5.75} Bi _{4.36} (Te _{3.60} Se _{0.33}) _{Σ3.93} S _{7.92}
134	0.15	42.06	32.88	0.07	16.15	0.95	8.83	101.10	Pb _{5.75} (Bi _{4.46} Sb _{0.02}) _{Σ4.48} (Te _{3.59} Se _{0.34}) _{Σ3.93} S _{7.80}
135	0.12	40.89	32.58	0.10	16.84	0.95	8.60	100.07	Pb _{5.66} (Bi _{4.47} Sb _{0.02}) _{Σ4.49} (Te _{3.78} Se _{0.34}) _{Σ4.12} S _{7.69}
137	0.47	42.31	28.76	-	16.76	0.85	8.80	97.96	Pb _{5.89} Bi _{3.97} (Te _{3.79} Se _{0.31}) _{Σ4.10} S _{7.92}
138	0.19	42.34	31.62	-	15.81	1.00	8.79	99.81	Pb _{5.85} Bi _{4.33} (Te _{3.55} Se _{0.36}) _{Σ3.91} S _{7.84}
139	0.17	41.99	32.21	-	15.98	1.03	8.80	100.18	Pb _{5.78} Bi _{4.40} (Te _{3.57} Se _{0.37}) _{Σ3.94} S _{7.83}
140	0.26	40.71	33.46	-	16.72	1.07	8.77	100.98	Pb _{5.56} Bi _{4.53} (Te _{3.71} Se _{0.38}) _{Σ4.09} S _{7.75}
142	0.09	41.02	33.01	0.13	16.71	0.94	8.70	100.60	Pb _{5.64} (Bi _{4.50} Sb _{0.03}) _{Σ4.53} (Te _{3.73} Se _{0.34}) _{Σ4.07} S _{7.73}
Mean									
(n=9)	0.21	41.72	32.06	0.03	16.40	0.96	8.78	100.16	Pb _{5.74} (Bi _{4.37} Sb _{0.01}) _{Σ4.38} (Te _{3.66} Se _{0.35}) _{Σ4.01} S _{7.81}
S.D.	0.12	0.65	1.37	0	0.37	0.06	0.11	0.95	
**6-4	-	41.82	33.49	0.07	16.90	1.06	8.56	101.90	Pb _{5.73} (Bi _{4.55} Sb _{0.02}) _{Σ4.57} (Te _{3.76} Se _{0.38}) _{Σ4.14} S _{7.57}
Other small lamellae									
201	0.10	40.14	34.28	-	16.29	0.96	8.82	100.58	Pb _{5.51} Bi _{4.67} (Te _{3.63} Se _{0.34}) _{Σ3.97} S _{7.82}
**21-1	0.09	42.20	31.6	0.10	17.40	0.98	8.07	100.44	Pb _{5.92} (Bi _{4.39} Sb _{0.02}) _{Σ4.41} (Te _{3.96} Se _{0.36}) _{Σ4.42} S _{7.31}
**4-2	0.00	39.67	33.54	0.21	18.34	-	8.19	99.95	Pb _{5.59} (Bi _{4.69} Sb _{0.05}) _{Σ4.74} Te _{4.20} S _{7.47}

The formula was calculated on the basis of 22 atoms. Copper, Cd and Fe were not detected in any of the analyses. -: less than the minimum limit of detection. [§] Minor amount of Ag ignored. Analytical conditions: without asterix: NHM (London), conditions as in Table 1. * Electron-microprobe analyses done at Salzburg (see Table 1). ** Electron-microprobe analyses done in Adelaide: CAMECA SX-51, 15 kV, 20 nA, *SKα* (PbS), *AgLα* (Ag), *SbLα*, *TeLα* (synthetic Bi₂Te₃), *SeKα* (synthetic Bi₄Se₃), *BiLa* (synthetic Bi₂Te₃), *PbLa* (PbS), *CuKα* (CuFeS₂).

well as "phase C", were obtained. Cell dimensions for these synthetic phases are compared with the data given above and other published unit-cell data for natural Bi–Pb tellurosulfides in Table 6. In the case of "phase C", agreement between unit-cell dimensions for the natural and synthetic phase seems excellent.

DISCUSSION

Given that we have studied the unnamed phases in the Ilijärvi specimens with three electron microprobes, using different operating conditions and analytical standards, and see no significant differences in the



populations, we discount errors in micro-analysis as an explanation for the considerable variation in the dataset. Given the spread in the data, we acknowledge that the compositions from Flagant and Iilijärvi are not sufficiently consistent to assign a formula or formulae to the unnamed phases, other than to say they fall in the range $\text{Pb}_5\text{Bi}_4\text{Te}_4\text{S}_7 - \text{Pb}_7\text{Bi}_4\text{Te}_4\text{S}_9$. They are, nevertheless, distinct from aleksite.

An accretional homologous series?

A chemical dataset for Bi–Pb tellurosulfides should show either of the following aspects: (a) narrow ranges of chemical composition clustering around individual members of the series, surrounded by large compositional gaps. Such a scenario would sustain the idea of a series populated with discrete, stoichiometric phases; (b) continuous or semicontinuous variation in chemical composition across the series. The latter case can be explained either by more-or-less random submicroscopic intergrowths between stoichiometric members, submicroscopic mixtures between members of the series with galena or other minerals, or alternatively, complete solid-solution between two end-members.

The compositional data we have compiled do not comply with either explanation and therefore do not provide an answer as to whether there exists a definable series populated by discrete phases, or rather a continuous compositional range. We acknowledge that clustering around stoichiometric members is weaker than might be expected if the phases belong to an accretional homologous series with the general formula $\text{Pb}_N\text{Bi}_4\text{Te}_4\text{S}_{N+2}$. In such a hypothesis, in which N values are purely chemical and do not necessarily reflect homologous order, tetradytmite, $\text{Bi}_4\text{Te}_4\text{S}_2$, has $N = 0$, “phase C” has $N = 1$, aleksite, $N = 2$ and saddlebackite, $N = 4$, respectively. In this manner, the unnamed phases from Iilijärvi and Fragant would have N values between 5 and 7, and 5 and 6 (plus $N = 3$), respectively. The hypothetical extension of a series to such Pb-rich phases is, of course, highly speculative at this point, with no supporting structural data available at present.

The question of whether the discrete phases we have analyzed are real, and thus belong to a modular series, or whether there is continuous variation across

the series, cannot be resolved without further work. Our data show a near-complete compositional range among Pb- and S-rich tellurosulfides ($\text{Pb}_5\text{Bi}_4\text{Te}_4\text{S}_7 - \text{Pb}_7\text{Bi}_4\text{Te}_4\text{S}_9$), as well as evidence of compositional continuity in the compositional range between tetradytmite and aleksite. The latter may, however, be the result of fine intergrowths of individual minerals in the system $\text{Pb}_N\text{Bi}_4\text{Te}_4\text{S}_{N+2}$. Since structural data are lacking for most members of the series, we prefer not to formally define a series at this juncture, but will nevertheless examine evidence favoring its existence and possible explanation of the extensive compositional fields in terms of fine intergrowths.

In their studies of the system Pb–Bi–Te–S, Liu & Chang (1994) found three synthetic phases (D, E and J) of the seven phases they recognized, that correspond to “phase C”, aleksite and saddlebackite, respectively. A fourth synthetic phase (F) corresponds to $\text{Pb}_3\text{Bi}_4\text{Te}_4\text{S}_5$, the ideal $N = 3$ member of the series, which had not previously been found in nature, and may be present in the Fragant specimens if the single analysis we report is representative (it may just be coincidental). X-ray powder diffraction was carried out on the four run products (Liu & Chang 1994), allowing calculation of unit-cell data (Table 6). These authors did not synthesize phases with higher Pb or S contents at 500°C, which would correspond to compositions similar to those identified from Iilijärvi or Fragant. In this respect, it is important to note that estimates of metamorphic conditions for amphibolite-facies cordierite–anthophyllite rocks at Orijärvi are 560–620°C at 3–5 kbar (Schreurs & Westra 1985). Our paragenetic observations on the material reveal a sequence of crystallization among Bi-minerals from the metamorphic peak to below the

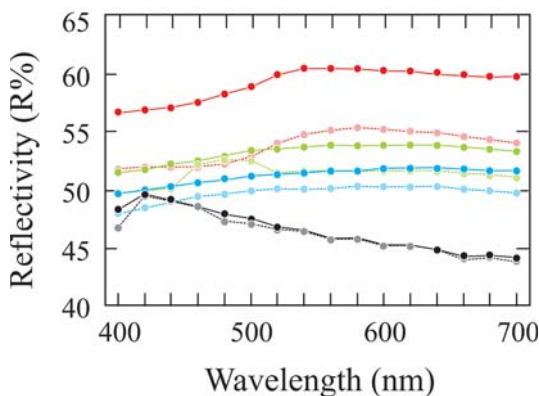


FIG. 7. Reflectivity spectra in air for tetradytmite (red and pink; from Criddle & Stanley 1986), “phase C”, $\text{PbBi}_4\text{Te}_4\text{S}_3$ (dark and light green) and aleksite (dark and light blue) from Clogau and $\sim\text{Pb}_6\text{Bi}_4\text{Te}_4\text{S}_8$ (“Grain 3”) from Iilijärvi (black and grey). For each mineral or phase, the pair of spectra corresponds to R_o and R_e .

FIG. 6. Compositional plot in terms of $\text{Pb}/(\text{Pb} + \text{Bi})$ versus $\text{Te}/(\text{Te} + \text{Se} + \text{S})$ for Pb–Bi–Te–S phases in the Clogau, Iilijärvi and Fragant specimens and, for comparison, compositions of pertinent published data for “phase C”, aleksite and saddlebackite. Ideal compositions for each mineral and unnamed phase in the Pb–Bi–Te–S system are represented in the diagram by black stars.

melting point of native bismuth (271°C), raising the possibility that these phases may well be stable at conditions that were not duplicated in the synthetic experiments of Liu & Chang (1994).

Crystal structures

The structures of minerals in the system Bi–Te–Se–S (excepting bismuthinite and guanajuatite) have conventionally been understood in terms of modular combina-

TABLE 4. REPRESENTATIVE COMPOSITIONS, WITH STATISTICAL DATA, OF THE Pb–Bi–Te–S PHASES IN THE FRAGRANT SPECIMENS

	Ag	Pb	Bi	Sb	Te	Se	S	Total	Formula
unnamed Pb ₃ Bi ₄ Te ₄ S ₃ 99/89b (single analysis)	0.10	27.1	40.5	0.20	23.8	-	7.3	99.0	Pb _{2.82} Bi _{4.18} Te _{4.03} S _{4.91}
unnamed Pb ₃ Bi ₄ Te ₄ S ₇ LA 12/B mean (n = 3) Std. dev.	0.10	40.3 1.19	32.0 1.04	-	18.9 0.6	-	8.50 0.11	99.8	Pb _{5.10} Bi _{4.02} Te _{3.88} S _{6.98}
unnamed Pb ₆ Bi ₄ Te ₄ S ₈ LA 12/C mean (n = 3) Std. dev.	-	43.8 0.9	29.4 0.6	-	17.8 0.5	-	8.80 0.15	99.8	Pb _{6.07} Bi _{4.05} Te _{4.03} S _{7.85}

The formula was calculated on the basis of 16 atoms (Pb₃Bi₄Te₄S₃), 20 atoms (Pb₃Bi₄Te₄S₇) and 22 atoms (Pb₆Bi₄Te₄S₈). Copper, Cd and Fe were not detected in any of the analyses. -: less than the minimum limit of detection. All electron-microprobe analyses were done at Salzburg (see Table 1).

TABLE 5. REFLECTANCE DATA FOR ALEKSITE, "PHASE C" (CLOGAU) AND ~Pb₆Bi₄Te₄S₈ FROM IILIJÄRVI

λ nm	Tetradymite*				Aleksite (Clogau)				"Phase C" (Clogau)				~Pb ₆ Bi ₄ Te ₄ S ₈ (Iilijärvi)			
	R _o	R _e	^{im} R _o	^{im} R _e	R _o	R _e	^{im} R _o	^{im} R _e	R _o	R _e	^{im} R _o	^{im} R _e	R _o	R _e	^{im} R _o	^{im} R _e
400	56.8	51.9	44.2	38.1	49.6	48.0	36.5	34.7	51.5	49.8	38.0	35.9	48.3	46.7	34.1	32.55
420	56.9	51.95	44.2	38.0	49.9	48.5	36.7	35.0	51.8	50.0	38.2	36.2	49.6	49.5	34.6	33.4
440	57.0	52.0	44.4	38.0	50.3	49.0	36.95	35.3	52.1	50.2	38.4	36.5	49.0	49.2	34.3	33.3
460	57.5	52.1	45.0	38.1	50.7	49.4	37.2	35.6	52.5	52.1	38.7	36.7	48.5	48.7	33.8	32.9
470	57.8	52.2	45.2	38.0	50.8	49.5	37.3	35.6	52.7	52.5	38.8	36.8	48.4	48.2	33.4	32.6
480	58.2	52.4	45.6	38.1	51.0	49.7	37.35	35.7	52.9	52.7	38.9	36.9	47.9	47.2	32.9	32.1
500	59.0	53.0	46.4	38.75	51.2	49.9	37.5	35.8	53.3	51.2	39.0	37.1	47.6	47.1	32.8	31.9
520	59.9	53.9	47.25	39.7	51.4	50.1	37.6	35.9	53.6	51.45	39.2	37.2	46.8	46.6	32.1	31.3
540	60.4	54.7	47.7	40.5	51.5	50.2	37.65	35.9	53.7	51.6	39.35	37.3	46.4	46.6	31.8	31.0
546	60.5	54.8	47.7	40.65	51.6	50.2	37.65	35.9	53.7	51.6	39.4	37.3	46.1	46.3	31.8	30.9
560	60.5	55.1	47.7	40.9	51.6	50.2	37.65	35.8	53.8	51.65	39.4	37.3	45.7	45.8	31.5	30.5
580	60.5	55.3	47.5	40.9	51.7	50.25	37.7	35.8	53.8	51.7	39.4	37.4	45.8	45.9	31.3	30.3
589	60.4	55.3	47.5	40.9	51.7	50.3	37.7	35.8	53.8	51.7	39.4	37.4	45.5	45.35	31.4	30.4
600	60.3	55.2	47.3	40.8	51.8	50.3	37.7	35.8	53.8	51.7	39.4	37.4	45.3	45.3	31.3	30.2
620	60.2	55.0	47.3	40.65	51.8	50.3	37.7	35.8	53.8	51.65	39.35	37.4	45.2	45.2	31.4	30.3
640	60.1	54.8	47.0	40.4	51.8	50.25	37.7	35.7	53.8	51.6	39.25	37.3	45.0	44.7	31.2	29.8
650	60.1	54.7	46.8	40.2	51.8	50.15	37.7	35.6	53.75	51.6	39.2	37.2	44.7	44.5	31.0	29.7
660	60.0	54.6	46.75	40.0	51.8	50.1	37.6	35.6	53.7	51.5	39.2	37.1	44.4	44.1	30.9	29.5
680	59.85	54.2	46.4	39.6	51.7	49.9	37.5	35.4	53.6	51.4	39.0	36.9	44.4	44.2	30.8	29.4
700	59.7	54.0	46.3	39.3	51.6	49.8	37.4	35.2	53.4	51.2	38.8	36.6	44.2	43.9	30.7	29.3

* from Criddle & Stanley (1986); specimen from Stianvica, Slovakia.

TABLE 6. UNIT-CELL DIMENSIONS AND LAYER SEQUENCES FOR Pb–Bi–Te–S MINERALS AND UNNAMED PHASES

N	Formula	Mineral	Studied material	Reference	a_{exp}	c_{exp}	Z	a_{calc}	c_{calc}	layers	Possible sequence
Possible chemical series $\text{Pb}_x\text{Bi}_4\text{Te}_4\text{S}_{N+2}$ (see also text for discussion)											
0	$\text{Bi}_2\text{Te}_2\text{S}$	tetradymite	$\text{Bi}_{14}\text{Te}_{13}\text{S}_8$	Pauling (1975)	4.25	29.6	3			5	TeBiS ₂ BiTe
1	$\text{PbBi}_4\text{Te}_4\text{S}_3$	"phase C"	synthetic phase D	Liu & Chang (1994)	4.24	23.12	1	4.21	23.14	7+5	TeBiSPbS ₂ BiTe/ TeBiS ₂ BiTe
			Clogau	This study	4.25	69.71	3			3*(7+5)	
2	$\text{PbBi}_2\text{Te}_2\text{S}_2$	aleksite	synthetic phase E	Liu & Chang (1994)	4.23	39.83	3	4.21	39.85	3*(7)	TeBiSPbS ₂ BiTe
			Clogau	This study	4.24	79.64	3			6*(7)	
			Alekseev	Lipovetskiy <i>et al.</i> (1978)	4.238	79.76	6			6*(7)	
3	$\text{Pb}_3\text{Bi}_4\text{Te}_4\text{S}_5$		synthetic phase F	Liu & Chang (1994)	4.23	60	2	4.21	59.99	2*(7+9)	TeBiSPbSPbS ₂ BiTe/ TeBiSPbS ₂ BiTe
4	$\text{Pb}_2\text{Bi}_2\text{Te}_2\text{S}_3$	saddlebackite	synthetic phase J	Liu & Chang (1994)	4.23	16.71	1	4.21	16.71	9	TeBiSPbSPbS ₂ BiTe
			Kochkar	Spiridonov (1995)	4.247	97.97	6			6*(9)	
			Boddington	Clarke (1997)	4.23	33.43	2			2*(9)	
Hypothetical extension of series to compositions richer in Pb											
5	$\text{Pb}_5\text{Bi}_4\text{Te}_4\text{S}_7$									9+11	TeBiSPbSPbSPbS ₂ BiTe/ TeBiSPbSPbS ₂ BiTe
6	$\text{Pb}_3\text{Bi}_2\text{Te}_2\text{S}_4$									11	TeBiSPbSPbSPbS ₂ BiTe
7	$\text{Pb}_7\text{Bi}_4\text{Te}_4\text{S}_9$									11+13	
Other species											
	Bi_2Te_3	tellurobismuthite		Wyckoff (1964)	4.3835	30.487	3			5	TeBiTeBiTe
			Zod	Berry & Thompson (1962)	4.384	30.45	3				
				Zav'yalov & Begizov (1977)	4.380	30.51	3				
	PbBi_4Te_7	kochkarite	synthetic PbBi_4Te_7	Zhukova & Zaslavskii (1970)	4.418	72.07	3				
			synthetic phase M	Liu & Chang (1994)	4.42	24.10	1	4.47	24.06	7+5	TeBiTePbTeBiTe/ TeBiTeBiTe
			Kochkar	Spiridonov <i>et al.</i> (1989)	4.416	72.09	3				
	PbBi_2Te_4	rucklidgeite	synthetic $\text{Bi}_{2.12}\text{Pb}_{0.95}\text{Te}_4$	Zav'yalov & Begizov (1977)	4.436	41.64	3			3*(7)	
			synthetic phase A	Liu & Chang (1994)	4.441	41.702	3	4.47	41.67	3*(7)	TeBiTePbTeBiTe
			Kochkar	Zav'yalov & Begizov (1977)	4.422	41.49	3				
			Zod	Zav'yalov & Begizov (1977)	4.414	41.34	3				
	$(\text{Bi,Pb})_3(\text{Se,Te})_4$	poubaite	Oldřichov	Čech & Vavřín (1978)	4.253	40.10	3			3*(7)	
	$\text{Pb}_2\text{Bi}_2(\text{Te,S})_5$		synthetic phase K	Liu & Chang (1994)	4.441	17.54	1	4.47	17.61	9	TeBiTePbTePbTeBiTe

tions of five-atom “tetradymite” units (Bi_2X_3 , where $\text{X} = \text{Te, Se, S}$) and two-atom Bi_2 units (Cook *et al.*, in press, and references therein). A distinct seven-atom unit has been proposed for rucklidgeite, $\text{Pb}_x\text{Bi}_{3-x}\text{Te}_4$ ($0 \leq x \leq 1$), in which the unit cell is composed of three seven-atom layer units “ X-Bi-X-Bi-X-Bi-X ” (Petrov & Imamov 1970, Imamov *et al.* 1970, Zhukova & Zaslavskii 1971, 1976, Frangis *et al.* 1989, 1990). Poubaitte, $\text{PbBi}_2(\text{Se,Te,S})_4$, is considered isotypic with rucklidgeite (Moëlo & Makovicky 2006). A hierarchical series of Pb–Bi tellurosulfides could, therefore, be postulated by combination of the five-atom “tetradymite” unit, and the seven-atom “rucklidgeite-like” unit, with the possibility of extension to nine- and even eleven-atom units in the case of more complex members of the series (Petrov & Imamov 1970). In addition, there exists a possibility of a combinatorial series, in which combinations of layer types can be invoked for structures with odd N values (*e.g.*, “phase C”, as a combination of five- and seven-atom layers). Liu & Chang (1994), among others, have found such a structural model compatible with observations. The fact is, however, that few structures are known with any certainty. In structural determinations of kochkarite, PbBi_4Te_7 , for example, Talybov & Vainstein (1961) were unable to fully resolve atom sites and occupancies. The extrapolation of poorly understood structures to other minerals and phases (*e.g.*, the possibility that kochkarite and $\text{PbBi}_4\text{Te}_4\text{S}_3$, or aleksite and rucklidgeite, might be isostructural pairs) is ill-advised until structural solutions for natural specimens of “phase C”, aleksite and saddlebackite are available. In their current review of sulfosalts, Moëlo & Makovicky (2006) placed six Pb-rich species (babkinitite, saddlebackite, poubaitte, rucklidgeite, aleksite and kochkarite) within the bismuth–tetradymite homologous series, broadly endorsing the stacking periodicity presented here.

Potential for modularity and intergrowths

The lamellar banding of “phase C” and the phase(s) in the Ilijärvi samples, their coexistence, their intergrowth with galena and tetradymite, and the extended compositional fields documented by electron-microprobe analysis are reminiscent of similar variation and intergrowths among some Bi-sulfosalt series (*e.g.*, Pring & Hyde 1987, Pring *et al.* 1999, Pring 2001, Pring & Etschmann 2002, Ciobanu *et al.* 2004). Disordered intergrowths of Bi-sulfosalts tend to give characteristic extended compositional fields, not dissimilar to those identified among the Pb–Bi tellurosulfides investigated in the present study. Direct comparison between the Bi–Pb tellurosulfides and sulfosalts is, however, hampered by the lack of structural data for most of the Bi–Pb tellurosulfides. Despite this uncertainty, which may yet be resolved by appropriate HRTEM investigations in the future, degrees of stacking disorder at the lattice scale could viably explain the large spread of compo-

sitions within mineral grains that otherwise appear homogeneous. For example, irregular intergrowths of individual members of a modular series (tetradymite, aleksite, “phase C”, *etc.*) in the Clogau samples would give compositional fields like those we report. Presumably, disorder also applies to the phase(s) in the Ilijärvi samples. Indeed, degrees of stacking disorder may even be amplified in Pb- and S-rich varieties, given their possibly much-reduced fields of stability.

A strong affinity among Bi–Pb tellurosulfides, galena and Bi–(Sb) sulfosalts is noted at Ilijärvi. The lamellar bands of aleksite and galena in host giessenite appear to represent an equilibrium assemblage. Similar types of polysomatic disorder are well known in biopyriboles and humite groups (*e.g.*, Veblen & Buseck 1979). The Orijärvi–Ilijärvi area is noted for the occurrence of complex, modular triple- and double-chain biopyriboles (Schumacher & Czank 1987).

Relationship with other related compounds

There are two recognized sulfur-free Pb–Bi–Te compounds (Table 6). Kochkarite is reported from its type locality and from Zod (Spirodonov *et al.* 1989). Rucklidgeite, PbBi_2Te_4 , was originally defined as $(\text{Bi,Pb})_3\text{Te}_4$ (Zavyalov & Begizov 1977), and it has since been suggested that the Pb content can vary (*e.g.*, Kase *et al.* 1993) within the limits PbBi_2Te_4 – Bi_3Te_4 (Bayliss 1991). Liu & Chang (1994) were able to synthesise kochkarite and rucklidgeite as phases M and A, respectively; a further phase of theirs, ‘K’, $\text{Pb}_2\text{Bi}_2(\text{Te,S})_5$, may be related. An unnamed phase, $\text{Pb}_5\text{Bi}_5\text{Te}_3\text{S}_7$, reported to be associated with kochkarite in the Kochkar deposit (Spirodonov *et al.* 1989), is difficult to reconcile with either series.

“*Jolotcaite*”, a Pb–Bi tellurosulfide with the composition $\text{PbBi}_3\text{Te}_4\text{S}_3$, was described by Damian *et al.* (1988) from Mesozoic gold-bearing veins from the Jolotca Valley, Ditrau, Romania. X-ray maps of the apparently homogeneous phase were presented, showing the distribution of component elements. The formula, as given, did not match any known mineral or unnamed phase. Damian *et al.* (2004) showed, however, that this phase is compositionally identical to “phase C”, *i.e.*, $\text{PbBi}_4\text{Te}_4\text{S}_3$. Although more homogeneous areas are identified, the phase appears to be intimately intergrown with aleksite, as in the Clogau specimens. This unusual assemblage also contains lillianite and heyrovskýite within a matrix dominantly consisting of pyrite with abundant allanite and monazite. A manuscript is presently in preparation in which the association and chemical composition of the tellurosulfides and sulfosalts will be reported in detail.

Pb-bearing tetradymite

Published electron-microprobe data for tetradymite commonly show the presence of several wt.% Pb (*e.g.*,

Plimer 1974, Spiridonov *et al.* 1978). The presence of lead may be caused by the presence of sub- μm inclusions of galena or other lead minerals, but could, alternatively, be real. In the Clogau specimens, we note that tetradymite can contain various amounts of Pb ranging, continuously from zero up to the composition of “phase C” (Fig. 6). Such a range in composition was observed earlier by Naden (1988), causing Bevins & Stanley (1990) to remark that “plumbian tetradymite is probably not tetradymite at all”. Future study of the Clogau specimens by the HRTEM technique may reveal whether the observed compositions can be attributed to submicroscopic intergrowths of tetradymite units with Pb–Bi tellurosulfides.

Genetic considerations

We note that most, if not all, occurrences of aleksite, saddlebackite and “phase C” (Clogau, Iilijärvi, Fragant, Boddington, Kochkar, Alekseev) are restricted to deposits that are linked in one way or another to formation or overprinting of a low-temperature assemblage by high-temperature hydrothermal or magmatic fluids. Archean mesothermal gold deposits such as Boddington (Allibone *et al.* 1998), Paleozoic lode-gold systems such as Kochkar (Kisters *et al.* 2000), regionally metamorphosed deposits like Clogau, Iilijärvi and Fragant, and skarn systems (Ardino) all fall in this category.

CONCLUSIONS

The electron-microprobe analysis of aleksite and “phase C” from Clogau reveals a range of compositions spanning the range $\text{Bi}_2\text{Te}_2\text{S} - \text{PbBi}_2\text{Te}_2\text{S}_2$, with some degree of clustering around the two stoichiometric compositions. Unnamed phase(s) in the Iilijärvi and Fragant specimens give compositions in the range $\text{Pb}_5\text{Bi}_4\text{Te}_4\text{S}_7 - \text{Pb}_7\text{Bi}_4\text{Te}_4\text{S}_9$. The lack of structural data leaves the question open whether these compositions in fact represent discrete phases within an incremental chemical series (accretional homologous series) with the general formula $\text{Pb}_N\text{Bi}_4\text{Te}_4\text{S}_{N+2}$, or a continuous field of compositional variation. In such a hypothetical series, in which N simply represents chemical composition and not homologous order, “phase C”, aleksite and saddlebackite have integer values of N. The tendency to extensive compositional fields could be explained by disordered unit-cell-scale intergrowths among members of the series. Intergrowths of Bi–Pb tellurosulfides are characteristic of several Au-bearing deposits and may be closely associated, paragenetically, with gold. All documented localities are from metamorphic terranes.

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