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MINERALS OF THE SYSTEM Bi–Te–Se–S RELATED TO THE TETRADYMITE ARCHETYPE: REVIEW OF CLASSIFICATION AND COMPOSITIONAL VARIATION

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Abstract

Our compilation of ~900 published results of analyses for minerals of the tetradymite series (tellurobismuthite, tetradymite, guanajuatite, paraguanajuatite, kawazulite, skippenite, tsumoite, hedleyite, pilsenite, laitakarite, ikunolite, joséite-A, joséite-B) allows compositional fields among naturally occurring Bi–Te–Se–S compounds to be established. New compositional data for ingodite, laitakarite, pilsenite, kawazulite and tellurobismuthite extend previously known compositional limits. Recognized minerals can, for the most part, be satisfactorily and conveniently classified according to the ratio Bi(+ Pb)/(Te + Se + S), into the subsystems (isoseries) Bi_2Te_3–Bi_2Se_3–Bi_2S_3, Bi_4Te_3–Bi_4Se_3–Bi_4S_3 and BiTe–BiSe–BiS. Most minerals show limited compositional variation, but this is generally more extensive in the Se-bearing phases (*e.g.*, laitakarite) and in certain members of the system Bi–Te, such as hedleyite and tsumoite. Substitution of minor Pb for Bi is widespread throughout the group, especially in the Bi_4Te_3–Bi_4Se_3–Bi_4S_3 subgroup. Several possible additional minerals or compositional variants of existing minerals would appear to exist in nature, including Bi_4Te_2Se, $Bi_4Te(Se,S)_2$, Bi_3Te_2Se and $Bi_3(Te,S,Se)_4$. Within the above groups, Bi(+ Pb)/(Te + Se + S) stoichiometry is remarkably constant, in accordance with known and derived structures in which all phases (except those in which Pb is essential) can be envisaged in terms of various combinations of nonvalent five-atom Bi_2X_3 and two-atom Bi_2 layers. Deviation from Bi(+ Pb)/(Te + Se + S) stoichiometry within the isoseries may be linked to stacking disorder. Noting the appearance of many other phases and stoichiometries in experimental work in the system Bi–Te–Se–S and its subsystems, as

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well as the homologous character of this series, we predict that a significant number of additional mineral phases exist in nature and will be discovered in the future. Many of these, however, cannot be identified by chemical microanalysis alone.

Keywords: bismuth chalcogenides, tetradymite series, system Bi–Te–Se–S, systematics, electron-microprobe analysis.

SOMMAIRE

Notre compilation d'environ 900 résultats publiés d'analyses de minéraux de la série de la tétradymite (tellurobismuthite, tétradymite, guanajuatite, paraguanajuatite, kawazulite, skippenite, tsumoïte, hedleyite, pilsenite, laitakarite, ikunolite, joséite-A, joséite-B) nous permet de définir les champs compositionnels des composés naturels du système Bi–Te–Se–S. Nous fournissons des données nouvelles pour ingodite, laitakarite, pilsenite, kawazulite et tellurobismuthite qui étendent les limites compositionnelles établies. Dans la plupart des cas, les minéraux connus peuvent être convenablement classifiés selon le rapport Bi(+ Pb)/(Te + Se + S) en sous-systèmes (isoséries) Bi_2Te_3–Bi_2Se_3–Bi_2S_3, Bi_4Te_3–Bi_4Se_3–Bi_4S_3 et BiTe–BiSe–BiS. La plupart des minéraux font preuve de variations compositionnelles limitées, mais ces variations sont plus grandes dans les phases sélénifères, par exemple la laitakarite, et dans certains membres du système Bi–Te, par exemple hedleyite et tsumoïte. La substitution de faibles quantités de Pb au Bi est répandue, particulièrement dans le sous-groupe Bi_4Te_3–Bi_4Se_3–Bi_4S_3. Plusieurs phases minérales possibles et des variantes de minéraux connus semblent exister dans la nature, y inclus Bi_4Te_2Se, $Bi_4Te(Se,S)_2$, Bi_3Te_2Se et $Bi_3(Te,S,Se)_4$. Au sein des groupes, la stoechiométrie est remarquablement constante en termes de Bi(+ Pb)/(Te + Se + S), en accord avec les structures connues et dérivées dans lesquelles tous les composés (sauf ceux où le Pb est essentiel) seraient en fait des combinaisons de couches neutres de Bi_2X_3 à cinq atomes et des couches de Bi_2 à deux atomes. Les écarts à la stoechiométrie en termes de Bi(+ Pb)/(Te + Se + S) dans les isoséries pourraient résulter de défauts d'empilement. Suite à la présence de plusieurs autres phases et autres stoechiométries dans les travaux expérimentaux dans le système Bi–Te–Se–S et ses sous-systèmes, et de la possibilité de séries d'homologues, un nombre important de minéraux nouveaux pourrait exister dans la nature, l'objet de découvertes futures. Plusieurs de ceux-ci ne pourront toutefois pas être identifiés par microanalyse seule.

(Traduit par la Rédaction)

Most-clés: chalcogénures de bismuth, série de la tétradymite, système Bi–Te–Se–S, systématique, analyse par microsonde électronique.

INTRODUCTION

Mineral species of bismuth with tellurium, selenium and sulfur (bismuth chalcogenides) occur in a wide range of magmatic, hydrothermal or metamorphogenic gold, copper–gold and polymetallic ores (Afifi *et al.* 1988b, Simon *et al.* 1997). Despite the publication of several hundred papers over the past 100 years devoted to nomenclature, compositions and occurrences of these compounds, the so-called tetradymite group of Strunz & Nickel (2001), a number of systematic relationships remain obscure, even in the simple Bi–Te or Bi–Se systems. Uncertainties exist about the extent of solid solution within subsystems (*e.g.*, Bi_4Te_3–Bi_4Se_3–Bi_4S_3 and Bi_2Te_3–Bi_2Se_3–Bi_2S_3), the crystal chemistry and compositional fields of some less well-characterized members of the group, and the extent of element order or disorder that can be structurally accommodated into minerals such as tsumoite, ingodite or nevskite. The group of compounds in the four-component system Bi–Te–Se–S (and also the five-component system Bi–Pb–Te–Se–S) represents a particular challenge, not least because the number of natural occurrences of these phases that have been comprehensively documented remains limited.

The above difficulties are compounded by the rarity of some species, the varying quality of published microanalytical data, an apparent tendency toward non-stoichiometry among some minerals, the often ambiguous correlation between data from synthetic experiments and natural occurrences, and not least, by the typical very small size of mineral grains, often precluding full chemical or structural characterization. Many of these difficulties have been apparent in earlier treatments of the system or subsystems (*e.g.*, Godovikov *et al.* 1971b, Zav'yalov & Begizov 1983b, Bayliss 1991, Gu *et al.* 2001).

OBJECTIVES AND APPROACH

Unlike the Bi-dominant sulfosalts, for which enormous progress has been achieved in recent years in understanding the structural architecture of numerous homologous and homeotypic series (*e.g.*, Makovicky 1989, 1997a, b), tellurides and selenides have been difficult to investigate at the same scale, owing to their invariably smaller grain-size and intergrown character. Furthermore, the crystallochemical character of Bi tellurides and selenides, involving (theoretically) zerovalent Bi_2 layers, precludes application of a simple arithmetic charge-balance calculation to check the quality of microanalyses. Therefore, there exists an imbalance between the volume of microanalytical data available for these phases and the degree of crystal-structural characterization. Whereas it is desirable to put a name to a mineral only once corroborative single-crystal X-ray data are available, this has only exceptionally been the case among tellurides and selenides of Bi. Some species could thus be incorrectly identified or named in the literature.

In this review, we also highlight the fundamental discrepancy between the compositional identity of naturally occurring tellurides and selenides of Bi, and data from experiments. The formation of series of structurally related compounds, in close compositional proximity to one another, that can be potentially stacked in a disordered manner, has been incorporated in descriptions of natural specimens only to a limited degree. "Disorder", in terms of exchange of the Bi and Te positions (*e.g.,* Bayliss 1991) among Bi telluride and selenide minerals, has been accepted to explain nonstoichiometry, rather than any combinatorial intergrowth of series members (homologues) at the lattice or supra-lattice scales. We emphasize the necessity of structural characterization of natural Bi tellurides and selenides at an appropriate scale, *e.g.,* by high-resolution transmission electron microscopy. The results will help resolve issues that have implications not only for classification, nomenclature and naming of new species in the future, but also for the understanding of the fundamental crystal-chemistry of this mineral group. The occurrence of Bi tellurides and selenides as accessories in gold–silver ores of various types, as much as the material science interest in these compounds by virtue of their thermoelectric properties, are both valid reasons to consider the present review as an interim status report that may stimulate further research.

The motivation for this annotated compilation and presentation of new data comes from the lack of a single appropriate reference that can provide the essential facts and contemporary interpretation of these minerals; most standard texts on ore mineralogy are now outdated in this regard. Although thankfully the exception rather than the rule, use of incorrect formulae and inappropriate or discredited nomenclature remains profligate in the literature. Further justification for this work stems from the huge interest given to Bi_2Te_3, $Bi_2Te_{3-x}Se_x$ and related compounds in recent years by material scientists, who are in many cases apparently unaware of their natural analogues.

As we draw on the compiled published data and present new compositional data from several natural occurrences, our paper represents an attempt to clarify the current state of knowledge on the systematics and chemistry of minerals in the system Bi–Te–Se–S. A future companion paper will address aspects of paragenesis, conditions of formation and stability among the minerals, with an emphasis on the potential offered by these minerals as tracers of ore genesis, with direct application to the study of gold deposits. In this review of data published over the past four decades, we emphasize the unusual rather than the commonplace. We deliberately place weight on compositional data that deviate from the ideal, that extend compositional boundaries and define fields of solid solution. By doing so, we accept that the reader may receive an artificially skewed perception of compositional variation among Bi tellurides and selenides. In reality, most published analytical data provide close-to-ideal compositions, and accordingly plot on top of one another on the accompanying figures.

A potential problem with this type of compilation is that we needed to take much of the published analytical data at face value. Identifications and interpretations can be amended on the basis of additional information since the time of publication, and some published data may also be dismissed as pertaining to mixtures in the light of new data, but the quality of analyses, standardization procedures, accuracy and precision, as well as calculation and reporting, have been the responsibility of the original authors.

Our review deals first with general aspects and problems common to all minerals of the tetradymite group. This is followed by a treatment of the known subsystems and, subsequently, a section that introduces unnamed phases that may belong to other subsystems.

Crystal Structure, Classification and Nomenclature

In this contribution, we will demonstrate certain flaws in the traditional way of classifying this mineral group (*e.g.,* Bayliss 1991, Gaines *et al.* 1997, Strunz & Nickel 2001). We will cite an underlying conflict between the definition of tight compositional limits according to stoichiometry and (a) the tendency of atoms to substitute at different scales within and between subseries, and (b) the layered and potentially homologous character of the compounds.

Crystal structure

Unit-cell and space-group data on all minerals in this group are summarized in Table 1, together with their classification in the Strunz system (Strunz & Nickel 2001). Ideal compositions are shown schematically in the ternary space Bi–Te–(S + Se) (Fig. 1). Bismuthinite and guanajuatite (isotypic with stibnite) are not in the tetradymite group, in which all minerals have $R\overline{3}m$, or $P\overline{3}m1$ symmetry. Idealized structures for Bi_2Te_3 (tellurobismuthite), Bi_2Te_2S (tetradymite), BiTe (tsumoite) and Bi_4Te_3 (pilsenite) are shown in Figure 2.

The layered atomic structure of all Bi–Se–Te–S compounds contrasts with the structural arrangements of the Bi sulfosalts. The latter are recombination structures, but are based on rods, blocks or layers of simple archetypal units (Makovicky 1997a), without anion–anion or cation–cation bonding. Structural features of the Bi–Se–Te–S compounds are linked to their trigonal layer structures, in which Bi is coordinated by S, Se, Te in the form of a trigonal antiprism (Kupčík 1972). All compounds can be derived from just two structural

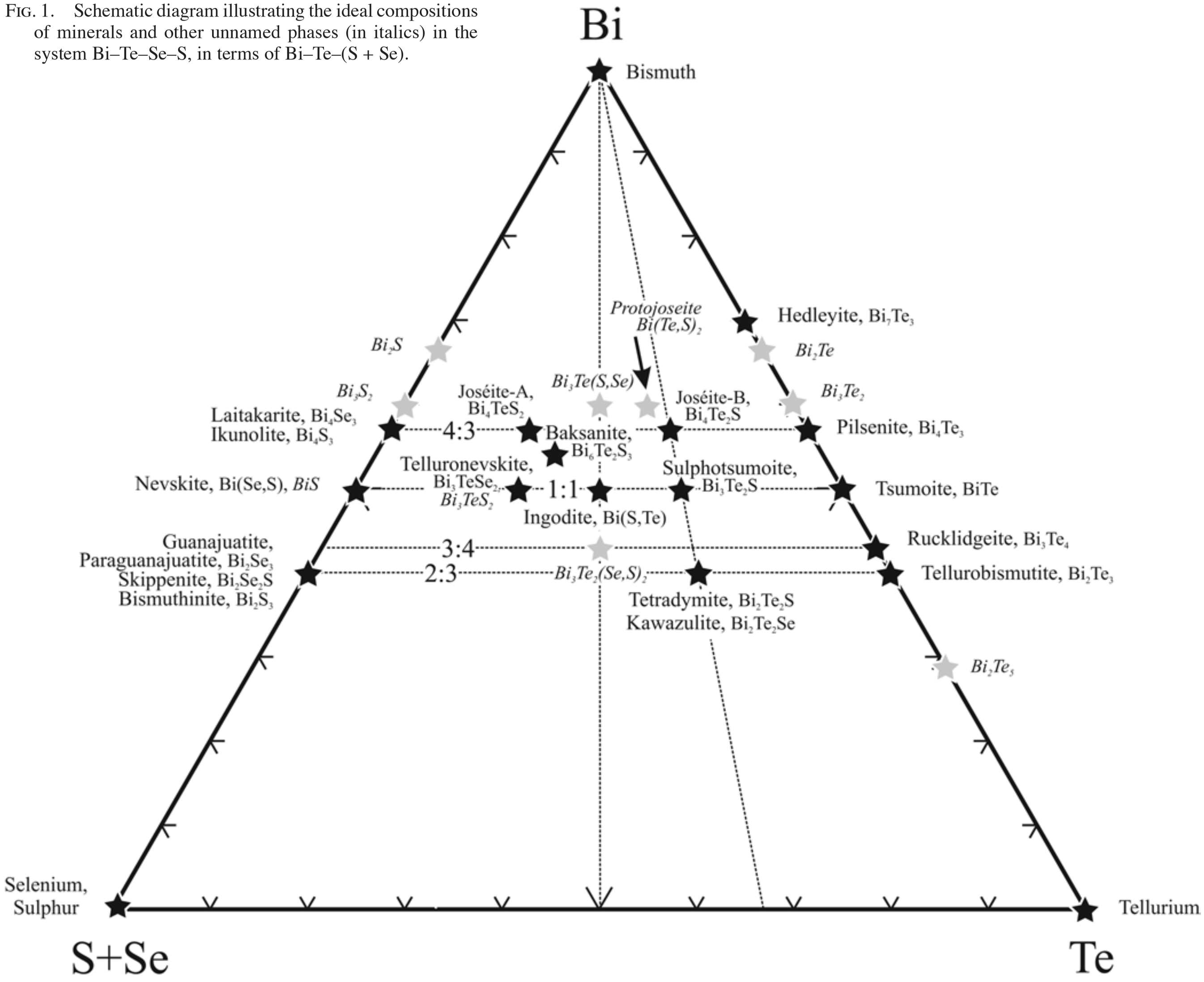

FIG. 1. Schematic diagram illustrating the ideal compositions of minerals and other unnamed phases (in italics) in the system Bi–Te–Se–S, in terms of Bi–Te–(S + Se).

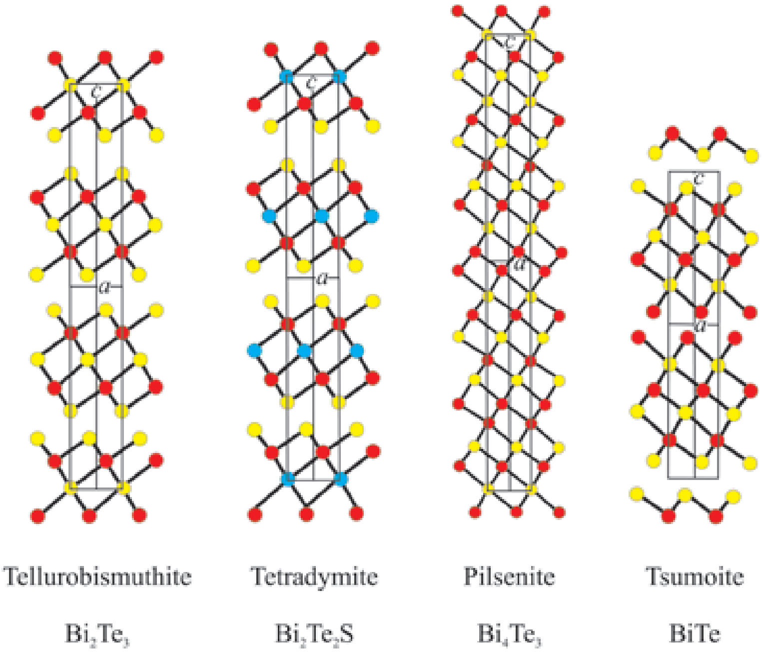

FIG. 2. Schematic depiction of the structures of tellurobismuthite (Bi_2Te_3; Feutelais *et al.* 1993), tetradymite (Bi_2Te_2S; Harker 1934), pilsenite (Bi_4Te_3; Yamana *et al.* 1979) and tsumoite (BiTe; Yamana *et al.* 1979). Bismuth atoms are shown in red, tellurium in yellow, and sulfur in blue.

units: the zerovalent Bi_2 and charge-balanced Bi_2X_3 modules, where X represents Te, Se or S. However, the difficulty in establishing a universally accepted boundary between sulfides (selenides, tellurides) and sulfosalts, that satisfies both chemical composition and hierarchical crystal-chemistry, has led to those sulfotellurides (-sulfides, -selenides) that contain Pb (rucklidgeite, kochkarite, aleksite, *etc.*) being included among sulfosalts (Moëlo & Makovicky 2006).

In the system Bi–Se, numerous compounds with variable Bi:Se ratio have been synthesized, each with defined structures (Abrikosov & Stasova 1985, Sher *et al.* 1986, Okamoto 1994, and references therein). These include Bi_7Se_3, Bi_2Se, Bi_5Se_3, Bi_3Se_2, Bi_4Se_3, Bi_6Se_5, Bi_8Se_7, BiSe, Bi_8Se_9, Bi_6Se_7, Bi_4Se_5, Bi_3Se_4 and Bi_2Se_3. A similar scenario, involving stacked layers of Bi_2 and Bi_2Te_3, can be envisaged for the system Bi–Te (Abrikosov & Bankina 1958, Stasova 1967, Stasova & Karpinskii 1967, Abrikosov & Stasova 1985, Okamoto & Tanner 1990, Feutelais *et al.* 1993). Alongside Bi_7Te_3 (hedleyite), Bi_4Te_3 (pilsenite), BiTe (tsumoite) and Bi_2Te_3 (tellurobismuthite), stacking variants observed in products of syntheses include Bi_2Te, Bi_4Te_5 and Bi_6Te_7. Shelimova *et al.* (2000) referred to the series as a homologous series of layered compounds $n Bi_2 \bullet m Bi_2Te_3$. Phase compositions listed by these authors span the field from hedleyite to tellurobismuthite, and include some compositions not listed by previous authors: Bi_7Te_3, Bi_2Te, Bi_4Te_3, Bi_6Te_5, Bi_8Te_7, $Bi_{22}Te_{21}$, BiTe, $Bi_{32}Te_{33}$, $Bi_{14}Te_{15}$, $Bi_{26}Te_{29}$, Bi_8Te_9 (synthesized also by Feutelais *et al.* 1993), $Bi_{26}Te_{30}$, Bi_6Te_7, $Bi_{32}Te_{39}$, Bi_4Te_5, $Bi_{38}Te_{48}$, Bi_2Te_3.

Each of the phases can be considered as stacking variants within part of a single homologous series, the name "bismuth–tetradymite homologous series" being used for the entire family of minerals and synthetic compounds that may be derived from the tetradymite structure (Moëlo & Makovicky 2006). Imanov & Semiletov (1971) have shown that the structure of each phase can be expressed in terms of Bi_2X_3 ("five-atom unit" = tetradymite archetype) and Bi_2 ("two-atom unit") layers (X = Te, Se, S), with various combinations over the compositional field in the central part of the system Bi–Se. Thus, Bi_2X_3 (Bi_2Te_3, *etc.*) has the regular "555" structure, each unit cell consisting of three Bi_2X_3 units. In the case of BiX, a Bi_2 unit is inserted between every second Bi_2X_3 unit ("552" structure). Bi_4X_3 has the "52" structure, each Bi_2Se_3 unit separated by a Bi_2 unit. More complex structures can be derived using the same principles, including subseries in which no named minerals presently exist, *e.g.*, Bi_3X_2, which would have a (252525252) structure. In Figure 3, we have illustrated

TABLE 1. MINERALS OF THE SYSTEM Bi–Te–Se–S: CLASSIFICATION, UNIT-CELL DIMENSIONS, REFERENCES AND TYPE LOCALITIES

Formula	Mineral	Strunz class	Space group	*a* Å	*b* Å	*c* Å	Z	Reference and Type locality
			The system Bi–Te					
Bi_7Te_3	hedleyite	II/D.13-10	$R\bar{3}m$, 3 2/*m*	4.47		119	6	Warren & Peacock (1945) Good Hope, Hedley, B.C., Canada
Bi_4Te_3	pilsenite	II/D.11-50	$R\bar{3}m$, 3 2/*m*	4.446		41.94	3	Ozawa & Shimazaki (1982) Nagybörzsöny, Hungary
BiTe	tsumoite	II/D.10-50	$P\bar{3}m1$, 3 2/*m*	4.422		24.05	6	Shimazaki & Ozawa (1978) Tsumo mine, Hiroshima, Shimane, Japan
Bi_2Te_3	tellurobismuthite	II/D.09-20	$R\bar{3}m$, 3 2/*m*	4.384		30.45	3	Zav'yalov & Begizov (1977) Field's vein, Dahlonega, Georgia, USA
			The Bi_2Te_3-Bi_2Se_3-Bi_2S_3 subsystem ("tellurobismuthite" isoseries)					
	Stibnite–bismuthinite series (Strunz class II/D.08)							
Bi_2S_3	bismuthinite	II/D.08-40	*Pbnm*, 2/*m*2/*m*2/*m*	11.13	11.27	3.97	4	Kupčík & Veselá-Nováková (1970) Llallagua, Huanuni, Tazna, Chorolque, Potosi, Bolivia
Bi_2Se_3	guanajuatite	II/D.08-50	*Pbnm*, 2/*m*2/*m*2/*m*	11.32	11.48	4.17	4	Earley (1950) Santa Catarina and La Industrial mines, Guanajuato, Mexico
	Tetradymite group, tellurantimony–kawazulite series (Strunz class II/D.09)							
Bi_2Te_3	tellurobismuthite	II/D.09-20	$R\bar{3}m$, 3 2/*m*	4.380		30.51	3	Little Madrid mine, Hidalgo Co., New Mexico, USA
Bi_2Se_3	paraguanajuatite	II/D.09-30	$R\bar{3}m$, 3 2/*m*	4.125		28.56	3	Santa Catarina, Guanajuato, Mexico
Bi_2Se_2Te	skippenite	II/D.09-50	$R\bar{3}m$, 3 2/*m*	4.183		29.12	3	Johan *et al.* (1987) Otish Mountains, Quebec, Canada
Bi_2Te_2S	tetradymite	II/D.09-60	$R\bar{3}m$, 3 2/*m*	4.25		29.6	3	Glatz (1967), Pauling (1975) Narverud, Telemark, Norway
Bi_2Te_2Se	kawazulite	II/D.09-70	$R\bar{3}m$, 3 2/*m*	4.24		29.66	3	Kato (1970) Kawazu mine, Shizuoka, Honshu, Japan
			The BiTe–BiSe–BiS subsystem (the "tsumoite" isoseries)					
	Tetradymite group, nevskite–tsumoite series (Strunz class II/D.10)							
Bi(Se,S)	nevskite	II/D.10-10	$P\bar{3}m1$, 3 2/*m*	4.197		22.80	6	Nechelyustov *et al.* (1984) Nevskii, northeastern Russia
Bi(S,Te)	ingodite	II/D.10-30	$P\bar{3}m1$, 3 2/*m*	4.248		23.22	6	Zav'yalov & Begisov (1981) Ingoda, Transbaikal, Russia
Bi_3TeS_2	*sztrokayite*	II/D.10-35	-					Nagy (1983) Nagybörzsöny, Hungary
Bi_3Te_2S	sulphotsumoite	II/D.10-40	$P\bar{3}m1$, 3 2/*m*	4.316		23.43	2	Zav'yalov & Begisov (1982) Magadan, Egerlyakh, Yakutia, Russia
BiTe	tsumoite	II/D.10-50	$P\bar{3}m1$, 3 2/*m*	4.422		24.05	6	
Bi_3TeSe_2	telluronevskite	II/D.10-55	$P3m1$, 3 2/*m*	4.264		23.25	2	Řídkošil *et al.* (2001) Bihorlat Mountains, Slovak Republic
Bi_3TeS	*protojoséite*	II/D.10-65	$R\bar{3}m$, 3 2/*m*(?)	4.335		57.92	6	Zav'yalov & Begisov (1983) Băiţa Bihor, Romania (Rezbanya)
$Bi_6Te_2S_3$	baksanite	II/D.10-70	$P\bar{3}m1$, 3 2/*m*	4.249		62.82	3	Pekov *et al.* (1996) Tyny'auz deposit, Caucasus, Russia

The Bi_4Te_3-Bi_4Se_3-Bi_4S_3 subsystem (the “joséite” isoseries)

	Tetradymite group, ikunolite – joséite-B series (Strunz class II/D.11)						
Bi_4S_3	ikunolite	II/D.11-10	$R\bar{3}m$, 3 2/*m*	4.150	39.19	3	Kato (1959) Ikuno mine, Hyogo, Japan
Bi_4Se_3	laitakarite	II/D.11-20	$R\bar{3}m$, 3 2/*m*	4.225	39.93	3	Vorma (1960) Orijärvi, Finland
Bi_4TeS_2	joséite-A	II/D.11-30	$R\bar{3}m$, 3 2/*m*	4.25	39.77	3	Thompson (1949) San José, Minas Gerais, Brasil
Bi_4Te_2S	joséite-B	II/D.11-40	$R\bar{3}m$, 3 2/*m*	4.34	40.83	3	Thompson (1949) Hudson Bay mine, B.C., Canada
Bi_4Te_3	pilsenite	II/D.11-50	$R\bar{3}m$, 3 2/*m*	4.446	41.94	3	Nagybörzsöny, Hungary

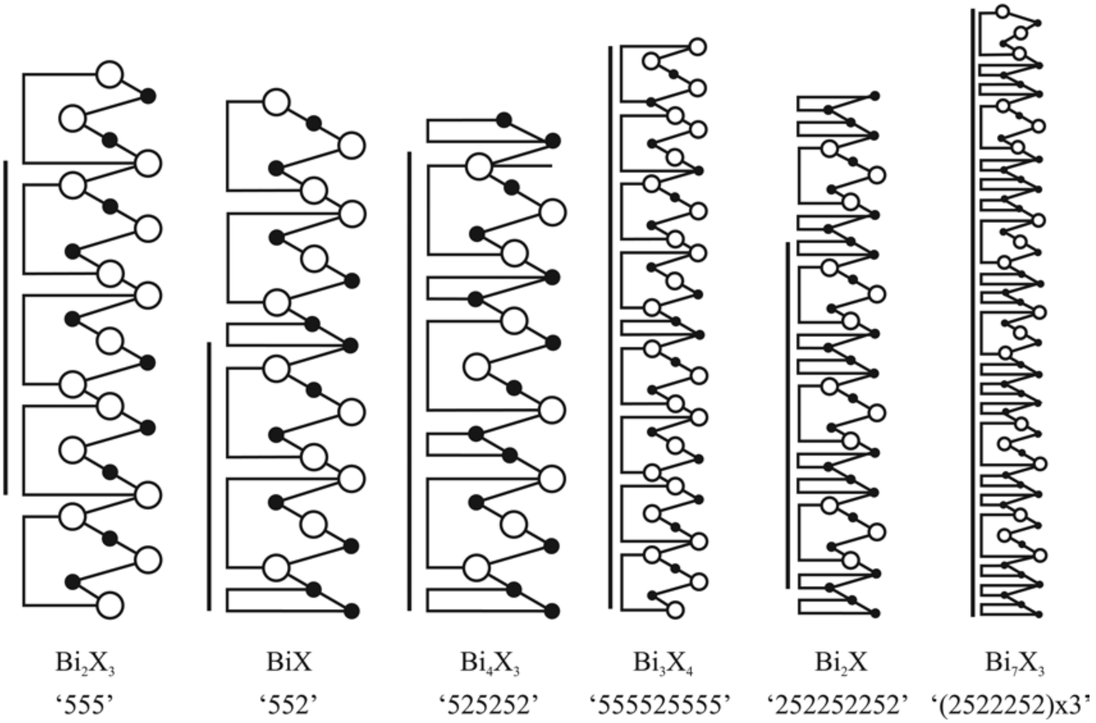

FIG. 3. Schematic depiction of the atomic arrangement of atoms in Bi_2X_3 (“555”), Bi*X* (“552”) and Bi_4X_3 (“525252”) structures, using the schematic style of Gaudin *et al.* (1995), following Imanov & Semiletov (1971). At right, hypothetical structural solutions are depicted for Bi_3X_4 (“555525555”), Bi_2X (“252252252”) and Bi_7X_3 (“2522253”) × 3, one possible solution for the hedleyite structure).

these structures using the schematic style of Gaudin *et al.* (1995), and also Bi_3X_4 (“555525555”), Bi_2X (“252252252”) and Bi_7X_3 (“2522252” × 3), the latter being one possible solution for the hedleyite structure. The difficulty in inserting regular, successive Bi_2 units, exemplified by Bi_7Te_3, and the potential this offers for order–disorder and stacking faults, go some way toward explaining the variation in Bi:Te ratio in hedleyite, which we will describe in a subsequent section. Imanov & Semiletov (1971) gave structural solutions for Bi_7X_9, Bi_4X_5, Bi_8X_9 and Bi_8X_7 using the same approach, and demonstrated how the space group and unit-cell dimensions can be calculated for any given composition.

The idea of a homologous series derived from tetradymite is not new. The concepts behind a layered structure grew from the crystal-structure description of tetradymite (Harker 1934; see also Wyckoff 1964, and the later discussion by Pauling 1975). Indeed, in their report on telluride phase-relations, Afifi *et al.* (1988a) stated "Telluribismuth (*sic*) is the tellurium-rich end of a homologous series of bismuth tellurides which include hedleyite…, unnamed Bi_2Te…, and tsumoite". Strunz (1963) considered a series of "more or less homeotypic layered structures" extending from native bismuth, synthetic Bi_2Se_2, synthetic Bi_2Se_3 with tetradymite and tellurobismuthite, synthetic Bi_3Se_4 with ikunolite, laitakarite and joséite-A, paraguanajuatite [$Bi_4(Se,S)_5$; Strunz used the formula of Ramdohr (1948)] to hedleyite ($Bi_{14}Te_6$; Warren & Peacock 1945). Strunz (1963) also included the now discredited "platynite" ($Pb_4Bi_7Se_7S_4$; Flink 1910). Despite errors in formulae, the principle of an expanding series of layers (3 × 2, 3 × 4, 3 × 5, 3 × 7, 3 × 9, 3 × 20) is still essentially true and is upheld by more recent studies (*e.g.,* Okamoto 1994).

The tetradymite series fulfills the requirements of a homologous series with the general formula $n(Bi,Pb)_2•mBi_2(Te,Se,S)_3$ and shared tetradymite-type architecture, in which all compounds with the same n and m are related to the same homologous type. We argue, however, that variation in the stacking sequence as a function of (small) changes in chemical composition underpins any structural model for the series. We highlight the work of Lind & Lidin (2003), who considered compounds of the system Bi–Se (and, implicitly, other constituent subsystems of the tetradymite series) as displaying a continuous and composition-dependent variation in stacking sequence, with all compounds, commensurate or incommensurate, describable in terms of structural modulation over an average structure. The same authors employ superspace formalism "onto (the) series (Bi–Se) of polytype compounds…. showing the effectiveness of a single structural model on a series of related compounds with long periods and different stacking sequences".

The above use of the term "polytype" warrants comment. The individual phases are not polytypes, and the tetradymite series is not a polytypic series, in any defined sense (*e.g.*, Guinier *et al.* 1984; see also Makovicky & Hyde 1992). Like Imamov & Semiletov (1971), however, we consider that the $n(Bi,Pb)_2•mBi_2(Te,Se,S)_3$ compounds are "characteristic polytypical forms", albeit with variable composition because of the stacking of the two distinct but internally unchanging structural units. A polytypoid-type approach may be valid for the group [Lind & Lidin (2003) also considered this option], not least because of the considerable potential for development of order–disorder, short- or long-range polysomes and polytypes.

Returning to charge balance among phases in the group, Gaudin *et al.* (1995) have shown that a balance in oxidation state for the layered structures can be proposed for all Bi_xX_y compounds. Importantly, the Bi_2 layers are theoretically zerovalent, and Bi_4Te_3 can thus be written $(Bi^0)_2(Bi^{3+})_2(Te^{2-})_3$. In practice, however, Gaudin *et al.* (1995) demonstrated that 26% of the Bi atoms in the Bi_2 layer are replaced by Se atoms, implying a complexity beyond the simple model.

Excellent conductivity within the layers, but not across them, in these and closely related compounds, has attracted much interest from materials science for application in thermoelectric devices (*e.g.*, Kuznetsova *et al.* 2000, Touzelbaev *et al.* 2001, Venkatasubramanian *et al.* 2001). As summarized by Shelimova *et al.* (2001), the quest for the most effective thermoelectric materials has led to the creation of various new ternary and quaternary compounds with complex structures, narrow band-gaps and electronic structures near the Fermi energy (*e.g.*, Chung *et al.* 1997).

The proposed structure for Bi_3X_4 deserves comment, in that although the "555525555" solution is realistic for $Bi_3(Te,Se,S)_4$ compounds, a comparable, yet distinct seven-atom unit is proposed for rucklidgeite ($Pb_xBi_{3-x}Te_4$) and other Pb-bearing compounds. A seven-atom layer "X–Bi–X–Bi–X–Bi–X" does obey charge-balance requirements (Gaudin *et al.* 1995), but substitution of one Pb atom for Bi allows for $PbBi_2Te_4$ (rucklidgeite) to be optimally viewed as a "777" structure (Petrov & Imamov 1970, Imamov *et al.* 1970, Zhukova & Zaslavskii 1976, Frangis *et al.* 1989, 1990). It is therefore plausible that hierarchical series of Pb–Bi sulfotellurides are built around the same "tetradymite" five-atom unit as described above, but with involvement of seven- and even nine-atom layers, with the possibility of combinations between adjacent types of layers (see below).

Stability and solid solution

To many investigators, the binary systems Bi–Te and Bi–Se have represented an effectively unlimited solid-solution series extending from 30 to 60% atomic Se (Bi_7S_3 to Bi_2Se_3; *cf.* Brown & Lewis 1962). Solid solution plays an important role, especially at higher temperatures, as we will subsequently show, but in the Bi–Te and Bi–Se series, a large number of compounds and phases have been synthesized, many of which have no natural analogues. Imanov & Semiletov (1971) made the point that the entire Bi–Te or Bi–Se series can be thought of as a solid solution, in the sense of an effectively continuous transition from the Bi_2Te_3-type structure to the Bi structure *via* intermediate compounds. The most likely compounds formed are those with low-integer ratios of Bi_2Te_3 to Bi_2. Each synthetic phase has been prepared at a set of specific conditions, but their fields of stability are uncertain, and it is not clear if they can persist during prolonged annealing over geologically realistic time-scales. In the system Bi–Se, Bi_2Se_3, consisting of a continuous array of Bi_2Se_3 layers only, is the single stable phase at high contents of Se. However, Bi_4Se_3, with alternating Bi_2 and Bi_2Se_3 layers, is stable in Bi-rich bulk compositions. Because Bi_4Se_3 commonly coexists with Bi, we may realistically conclude that other structures richer in Bi, *e.g.,* Bi_5Se_3, Bi_2Se and Bi_7Se_3, are only exceptionally preserved in nature, if ever.

Given the likely narrow stability-intervals of many phases, temperature controls play a significant role in defining natural compositions and assemblages. Moreover, a temperature-constrained solid solution also exists for some phases in the system. Shelimova *et al.* (2000) reported a solid solution (β) from 33.3 to 36.6 atom % Te (~Bi_2Te), and a second, wider solid-solution (γ) from 44.7 to 58.1 atom % Te, centered on tsumoite, which may help account for the extensive non-stoichiometry in these parts of the Bi–Te join. These data confirm those of Yusa *et al.* (1979), who demonstrated solid solution across the compositional range $Bi_{57}Te_{43}$–$Bi_{43}Te_{57}$ at 400°C. Since BiTe melts at temperatures as high as 554°C, a solid solution exists at temperatures typical of many magmatic or metasomatic ore deposits. The roles played by rates of cooling, or chemical fluctuation during cooling, are poorly constrained.

Extensive solid-solution has been invoked by Bayliss (1991) and termed "disorder". Focusing on tsumoite in particular, Bayliss argued for interchangeable occupancy of Bi and Te sites, causing extensive (isostructural) variation in Bi:Te ratio. The compositional range of tsumoite was said to encompass other binary tellurides such as hedleyite and pilsenite. Such "disorder" has been since used to account for a wide variety of values of the Bi:Te ratio observed in natural tellurides of Bi. Dobbe (1993) considered that his suite of compositional data from Tunaberg, Sweden, supported the idea of a single solid-solution, a tsumoite-type phase (bismuthian tsumoite) extending between values of the Bi:Te ratio of 1.35 to 2.61, *i.e.,* including the compositional range of both hedleyite and pilsenite. Taken to its logical conclusion, this would mean that it is impossible to name more or less any phase in the system Bi–Te without single-crystal X-ray data. The Bi $\rightleftharpoons$ Te solid solution may be real and significant in some cases, perhaps very significant under conditions of a rapid quench. Nevertheless, our own data, and those that we have compiled, coupled with the more modest solid-solution ranges identified above (*e.g.,* Yusa *et al.* 1979), suggest that most natural specimens are not "disordered" (*sensu* Bayliss) to such an extent that they cannot be identified on the basis of compositional data.

A further explanation of compositional variation in natural specimens is the suggestion (*e.g.*, Gaudin *et al.* 1995) that Bi_2 planes may be randomly incorporated (order–disorder) into BiX, and presumably other structures, such as Bi_7X_3. The layered structure of bismuth chalcogenides offers considerable potential for the development of order–disorder, short- or long-range polysomes, yet this has, to our knowledge, not been investigated in any detail. Okamoto (1994) has raised the possibility of short-range fluctuations in composition developing within a single "phase" during prolonged annealing, if the starting composition is midway between two already close compositions, *e.g.*, Bi_6Se_5 and Bi_8Se_7. We shall return to this in the discussion, since the question of what constitutes a "phase" in the chemical sense has direct relevance to the identification and naming of mineral species. As yet unpublished results of HRTEM invesigations of natural specimens by two of us (CLC and NJC) confirm the validity of the two-layer approach, and as well bear out the idea that stacking disorder between different arrangements of the two types of layer is an important operator causing variation in apparent chemical composition.

The ternary system Bi–Te–S was investigated by Yusa *et al.* (1979). Synthetic tetradymite ($Bi_2Te_{1.9}S_{1.1}$) and two compounds, $Bi_{48}Te_{21}S_{31}$ and $Bi_5Te_3S_2$, were generated at 400°C. The latter were described as joséite-A and joséite-B, but the cell dimensions given suggest ingodite and sulphotsumoite. Nevertheless, a degree of non-stoichiometry in these compounds does suggest that solid solution exists also in ternary compounds at geological reasonable temperatures. More recently, Ghoumari Bouanani *et al.* (1996) noted the importance of solid-state unmixing in the system Bi_2Se_3–Bi_2Te_3, the coexisting phases having wide ranges of solid solution. Additional crystal-structure determinations on natural ternary and quaternary phases will, however, be essential to evaluate the role of "disorder" in geological specimens.

Extensive solid-solution between S- and Se-bearing end-members can be documented in many series (*e.g.*, tetradymite – kawazulite, joséite-B – Bi_4Te_2Se). There is less evidence for direct interchangeability between Te and (S,Se). Other common substitutions involve replacement of Bi by Pb (which is generally minor, but can be significant, especially in the Bi_4Te_3 – Bi_4Se_3 – Bi_4S_3 isostructural series), and modest replacement of Bi by Sb. Substitution is limited by the need to conserve group symmetry. Several other elements (*e.g.,* Ag, Cu, Fe, Co, Ni, Zn, Cd, As) are reported in analytical data from the literature. In many situations, these elements appear attributable to interference from the immediate matrix.

Classification and nomenclature

Each structural variant represents a homologue type. All compounds related to a specific homologue type are isotypic (or homeotypic) and represent an isoseries. Each isoseries may represent, in turn, a number of (complete or partial) solid-solution series; *e.g.*, $Bi_2(Te,Se,S)_3$, $Bi_3(Te,Se,S)_4$, Bi(Te,Se,S), $Bi_4(Te,Se,S)_3$, *etc*. For convenience, the minerals can be subdivided into subgroups according to stoichiometry (isoseries), *i.e.*, the ratio between Bi (+ Pb) and the non-metals S, Se and Te, and, to some extent also in terms of crystal structure (Table 1). Thus, we treat the minerals in terms of the following subgroups: (i) the system Bi–Te (with Bi–Se and Bi–S), (ii) the subsystem Bi_2S_3–Bi_2Se_3–

Bi_2Te_3, (iii) the subsystem Bi_4S_3–Bi_4Se_3–Bi_4Te_3, (iv) phases with Bi:(Te,Se,S) ≈ 1. "Other stoichiometries", including the subsystem Bi_3S_4–Bi_3Se_4–Bi_3Te_4, and Pb-bearing Bi–Te–Se–S phases, are discussed in subsequent sections.

THE SYSTEM BI–TE

Four distinct binary mineral species have been defined: hedleyite, pilsenite, tsumoite and tellurobismuthite, with the ideal compositions Bi_7Te_3, Bi_4Te_3, BiTe and Bi_2Te_3, respectively (Table 1). A fifth mineral, Pb-free rucklidgeite, Bi_3Te_4, is discussed below. Two unnamed phases with compositions close to Bi_2Te and Bi_3Te_2 are discussed in the section "other stoichiometries". In this superficially simple series, all phases except hedleyite, and to some extent, tsumoite, are well defined, with generally limited compositional ranges.

Hedleyite

Hedleyite is attributed the formula Bi_7Te_3, although some authors have given the formula as Bi_8Te_3 or $Bi_{2+x}Te_{1-x}$, stressing the range of natural compositions (Fig. 4). The literature data for hedleyite (*e.g.*, Warren & Peacock 1945, Nechelyustov *et al.* 1974, Eshimov & Khamrabayeva 1974, Ishmurzin *et al.* 1975, Lindahl 1975, Dobbe 1993, Meisser & Della Valle 1993, Losos

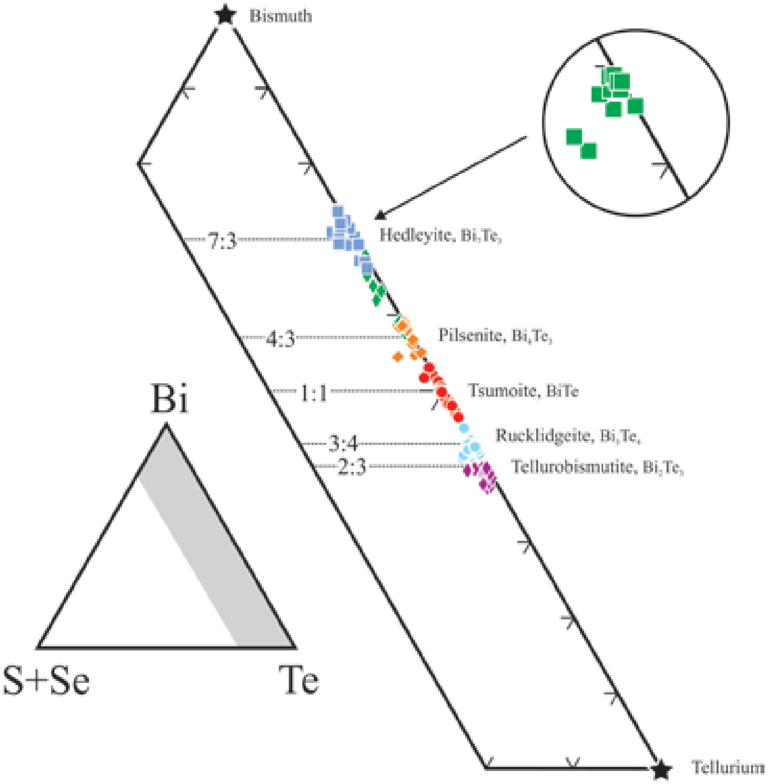

FIG. 4. Composition of minerals in the system Bi–Te in terms of Bi–Te–(S + Se). Data for tsumoite and hedleyite are from Warren & Peacock (1945), Eshimov & Khamrabayeva (1974, 1987), Nechelyustov *et al.* (1974), Ishmurzin *et al.* (1975), Lindahl (1975), Shimazaki & Ozawa (1978), Zav'yalov *et al.* (1978), Zav'yalov & Begizov (1983a), Lithoshko *et al.* (1984), Nysten & Annersten (1984), Criddle & Stanley (1986, 1993), Nysten (1990), Dobbe (1993), Banás *et al.* (1993), Spiridonov (1995, 1996), Clarke (1997), Wang (1997), Huang (1998), Losos *et al.* (1998), Vavřín & Frýda (1998), Fuertes-Fuente *et al.* (2000), and Krupenik *et al.* (2000). Data sources for tellurobismuthite, pilsenite and rucklidgeite are given in the captions of Figures 5, 8 and 14, respectively. Green diamonds: "bismuthian tsumoite" of Dobbe (1993). Compositions of hedleyite from the Maiskoe deposit, Ukraine (this study) are shown as green squares in the magnified circle (top right of figure).

et al. 1998, Fuertes-Fuente *et al.* 2000, Krupenik *et al.* 2000; Fig. 4) indicate that natural compositions may extend beyond Bi_7Te_3 (30 atom % Te) to Bi_8Te_3 (27.2 atom % Te) and may approach Bi_3Te (25 atom % Te) and even Bi_7Te_2 in some cases (Strakhovenko 1996). The inappropriate term "bismuthian hedleyite" has been used to describe compositions richer in Bi than Bi_7Te_3. Other compositions with lower values of the Bi:Te ratio have also been ascribed to hedleyite [*e.g.*, $Bi_{6.68–6.79}Te_{3.21–3.32}$ of Meisser & Della Valle (1993); $Bi_7Te_{3.3}$ of Huang (1998)].

Our own experience is that hedleyite compositions are generally consistent over a certain range of Bi:Te within a given deposit, but tend to vary among deposits. An example, from the Maiskoe Au deposit, Ukrainian Shield, is given in Table 2 and plotted in Figure 4. In this deposit, ΣMe/(Te + Se + S) in hedleyite ranges from 1.93 to 2.24, less than the ideal 2.33. Selenium substitution in hedleyite appears to be low and, in fact, contents slightly above the 1 wt.% level in the data from Maiskoe (Table 2) appear to be the highest reported. The extent of Pb substitution for Bi in hedleyite seldom exceeds 1 wt. %.

We believe that there is a need to obtain crystallogaphic data on specimens of natural hedleyite, in an effort to understand the reasons for variation in the Bi:Te ratio. Two of us (CLC and NJC) have begun to use HRTEM methods to investigate the stacking periodicity in natural specimens with hedleyite-like compositions.

Tsumoite

Although perfectly stoichiometric in many individual occurrences, tsumoite has generally been considered to display a degree of non-stoichiometry (variation in Bi:Te). This is considered a common and characteristic feature of other compounds in which Bi/(Te + Se + S) is approximately equal to 1 (*e.g.*, ingodite and nevskite; see below).

As mentioned above, Bi-for-Te substitution has been invoked by Bayliss (1991) and Dobbe (1993), among others, to explain the broad compositional ranges that cover large parts of the system Bi–Te, overlapping with the compositions of hedleyite and pilsenite. Bayliss has cited corroborative experimental data (*e.g.*, Godovikov *et al.* 1966) to account for the wide range of Bi:Te values observed in natural tellurides of Bi over the years. Examples include the phase Bi_2Te, reported by several authors (*e.g.*, Gamyanin *et al.* 1980, 1982, Goncharov *et al.* 1984, Huang *et al.* 1991, Gu *et al.* 2001), which will be discussed further below, as well as the unnamed mineral of Aksenov *et al.* (1968c) with the formula $(Bi_{0.58}Te_{0.42})Te$, and also the synthetic phase of Godovikov *et al.* (1966), for which the crystal-structure model gives $Bi(Te_{0.75}Bi_{0.25})$. Bayliss (1991) concluded that there exists a single solid-solution phase (bismuth-rich tsumoite) extending between Bi:Te values of 1.35 to 2.61. Dobbe (1993) recommended crystallographic characterization as essential for identification of phases within this compositional range.

Published compositions of tsumoite (*e.g.*, Zav'yalov *et al.* 1978, Zav'yalov & Begizov 1983a, Lithoshko *et al.* 1984, Banás *et al.* 1993, Spiridonov 1995, Wang *et al.* 1997; Fig. 4) support a limited degree of Bi-for-Te substitution, but the available body of data suggests more limited solid-solution than implied by Dobbe (1993). In fact, we are aware of only two studies showing extensive variation of Bi:Te within a single deposit or group of deposits: Dobbe's (1993) documentation of Bi_xTe_y compounds in Tunaberg, Sweden, and the earlier work of Cabri & Laflamme (1976) demonstrating variance of Bi:Te in "wehrlite" (*sic*) from Cu–Ni deposits of the Sudbury area, Ontario, Canada. Without X-ray data, it is impossible to unequivocally deny the existence of a broad tsumoite solid-solution at Tunaberg; yet we would believe it plausible that other Bi_xTe_y phases, close but not identical to BiTe, are recorded in Dobbe's data. In fact, we speculate whether

TABLE 2. ELECTRON-MICROPROBE DATA ON HEDLEYITE FROM THE MAISKOE GOLD DEPOSIT, UKRAINIAN SHIELD

	Cu	Fe	Pb	Sb	Bi	S	Se	Te	Total	Formula	Σ*Me*/(Te+Se)
m11.147	-	-	-	-	79.28	-	0.12	22.18	101.58	$Bi_{6.84}(Te_{3.13}Se_{0.03})_{\Sigma3.16}$	2.16
m11.148	-	-	-	-	79.45	-	0.14	21.46	101.06	$Bi_{6.91}(Te_{3.06}Se_{0.03})_{\Sigma3.09}$	2.24
m11.149	-	-	-	-	79.06	-	0.29	21.23	100.57	$Bi_{6.89}(Te_{3.04}Se_{0.07})_{\Sigma3.11}$	2.22
m11.150	-	-	-	-	77.76	-	0.20	22.38	100.34	$Bi_{6.76}(Te_{3.19}Se_{0.05})_{\Sigma3.24}$	2.09
m4 a4.1	0.11	0.16	0.12	0.14	77.1			21.83	99.46	$(Bi_{6.81}Pb_{0.01}Sb_{0.02})_{\Sigma6.84}Te_{3.16}$	2.16
m4 a4.2	-	-	0.24	0.14	75.9	-	-	23.82	99.29	$(Bi_{6.55}Pb_{0.02}Sb_{0.02})_{\Sigma6.59}Te_{3.41}$	1.93
m4 a4.7	-	0.08	0.09	0.10	78.23	-	1.15	21.61	101.26	$(Bi_{6.69}Pb_{0.01}Sb_{0.02})_{\Sigma6.72}(Te_{3.02}Se_{0.26})_{\Sigma3.28}$	2.05

The formula of samples of hedleyite is calculated on basis of ten atoms.

much of the non-stoichiometric "tsumoite" described in the literature might actually be discrete phases such as Bi_8Te_7, $Bi_{22}Te_{21}$, $Bi_{32}Te_{33}$, $Bi_{14}Te_{15}$, $Bi_{26}Te_{29}$ or Bi_8Te_9 (all known from synthesis experiment), which are virtually impossible to distinguish from BiTe by electron-microprobe analysis alone.

Our compilation shows that concentrations of S and Se in tsumoite rarely exceed 1–2% (Fig. 4). Significant amounts of Pb substitution (as much as 4–5 wt.%) are noted in some cases (Fig. 4, inset).

"Wehrlite" (= "börzsönyite") (Hout 1841) is discredited as a mixture (Ozawa & Shimazaki 1982). Although the majority of the original Hungarian "wehrlite" type-material was found to be a mixture, Nagy (1983) did nevertheless identify a phase with the composition BiTe in a sample of "wehrlite" and gave lattice constants. Considerable confusion appears to persist in some textbooks as to the identities of "wehrlite" (given variously as BiTe, Bi_2Te, Bi_3Te_2, $Bi_{4-x}Te_{3+x}$ and $Bi_{2+x}Te_{3-x}$), as well as tsumoite and pilsenite (see Nagy 1983 for historical background). Wehrlite is a recognized name of a rock; tsumoite and pilsenite are accepted minerals with the formulae BiTe and Bi_4Te_3, respectively. There is currently no named mineral with the composition Bi_2Te or Bi_3Te_2.

Pilsenite

Pilsenite is the oldest recognized name for species in the group [first described by Kenngott (1853) from Deutschpilsen (= Nagybörzsöny, Hungary)]. Although various formulae have been given historically, pilsenite is stoichiometric Bi_4Te_3. Like other members of the Bi_4X_3 isoseries, pilsenite shows little variation in Bi/(Te + S + Se), and the common presence of minor Pb. Some S and Se may be present, although generally, limits of substitution appear extremely low (Fig. 4). Published compositional data for pilsenite from the "microprobe" era are remarkably few (*e.g.*, Bao 1994, Simon & Alderton 1995, Spiridonov 1995, De Souza Lima *et al.* 1996, Mikulski 1998, Gu *et al.* 2001), stressing the relative rarity of pilsenite compared to other binary tellurides of Bi.

We have described "selenian pilsenite" from Lega Dembi, Ethiopia (Cook & Ciobanu 2001b) and include an analytical dataset on this material later in the present contribution. The compositions approach Bi_4Te_2Se. Together with comparable data for ~Bi_4Te_2Se compositions from China and Korea (Gu *et al.* 2001, Shin *et al.* 2005), we choose to reappraise this "selenian pilsenite" as a derivative of joséite-B rather than pilsenite and discuss these compositions under that mineral below.

Contrary to the well-constrained Bi:Te ratio typical of pilsenite, Gu *et al.* (2001) chose to regard a distinct suite of compositions (~Bi_5Te_3; Bi:Te up to 1.80) from the Huangshaping deposit as bismuthian pilsenite (rather than bismuthian tsumoite, *cf.* Bayliss 1991, Dobbe 1993, or an independent unnamed Bi_5Te_3 phase), on the basis of the observation that compositions "gradually change into pilsenite within the same grain".

Tellurobismuthite

Tellurobismuthite, Bi_2Te_3 (as redefined by Frondel 1940), is a common mineral that never appears to contain significant sulfur, but it does display a range of Se-for-Te substitution, extending up to approximately $Bi_2(Te_{2.7}Se_{0.3})$. Many early authors (*e.g.*, Wiese & Muldawer 1960, LaChance & Gardner 1961, Nakajima 1963, Misra & Bever 1964) considered a continuous solid-solution series ($Bi_2Te_{3-x}Se_x$), with constant variation of *a* and *c* with mol.% Bi_2Se_3. Misra & Bever (1964) discussed a transition from a disordered arrangement of Te and Se atoms, *i.e.*, occupying the *Y*(1) and *Y*(2) sites at random, to an ordered Bi_2Te_2Se compound with the *Y*(1) layer completely filled with Se atoms, and the *Y*(2) sites with Te atoms. Dumas *et al.* (1987) showed the phase diagram to have a more complex subsolidus pattern, "with two terminal solid solutions α and α', and a zone of demixion", centered on Bi_2Te_2Se. In their phase diagram, solid solution α (Bi_2Te_3) is limited to a range a little larger than that observed in natural specimens (see also Carle *et al.* 1995). Most recently, Sokolov *et al.* (2004) have presented data for the Bi_2Te_3–Bi_2Te_2Se segment of the system, showing that the tellurobismuthite solid-solution extends up to 14 mol.% Bi_2Se_3 ($Bi_2Te_{2.58}Se_{0.42}$). At higher Se, Bi_2Te_2Se (kawazulite) will coexist.

Published electron-microprobe data for tellurobismuthite (*e.g.*, Lipovetskiy *et al.* 1977, 1979, Zav'yalov & Begizov 1977, Arutyunyan & Eremin 1978, Harańczyk 1978, Spiridonov *et al.* 1978, Miller 1981, Gamyanin *et al.* 1982, Harris *et al.* 1983, Oen & Kieft 1984, Eshimov & Khamrabayeva 1987, Stankovič & Kozumplíkova 1987, McQueen 1990, McQueen & Solberg 1990, Çağatay *et al.* 1991, Dobbe 1991, Maglambayan *et al.* 1998, Mikulski 1998) are plotted in Figure 4. Spiridonov *et al.* (1978) reported substantial Sb-for-Bi substitution in tellurobismuthite from northern Kazakhstan, up to $(Bi_{1.12}Sb_{0.88})_2Te_{2.98}$, fully consistent with experimental data for the ternary system Bi–Sb–Te (*e.g.*, Caillat *et al.* 1992).

We have investigated tellurobismuthite from the small Au–Ag–Cu–Te–Se deposit of Glava, Värmland, Sweden (Oen & Kieft 1984), in which it is the most common telluride in a complex association (Figs. 5a, b) of several dozen tellurides and selenides. The dataset (Table 3, Fig. 6) shows a pronounced Se-enrichment in tellurobismuthite, up to ~$Bi_2(Te_{2.65}Se_{0.35})$. Tellurobismuthite of such composition coexists with kawazulite, confirming the aforementioned data of Sokolov *et al.* (2004). We have also examined tellurobismuthite from the Orivesi (Kutemajärvi) gold deposit in central Finland (Fig. 5d). The data (Table 4, Fig. 6) point to close-to-ideal Bi_2Te_3, but with the persistent presence of 0.7 to 0.9 wt.% Sb.

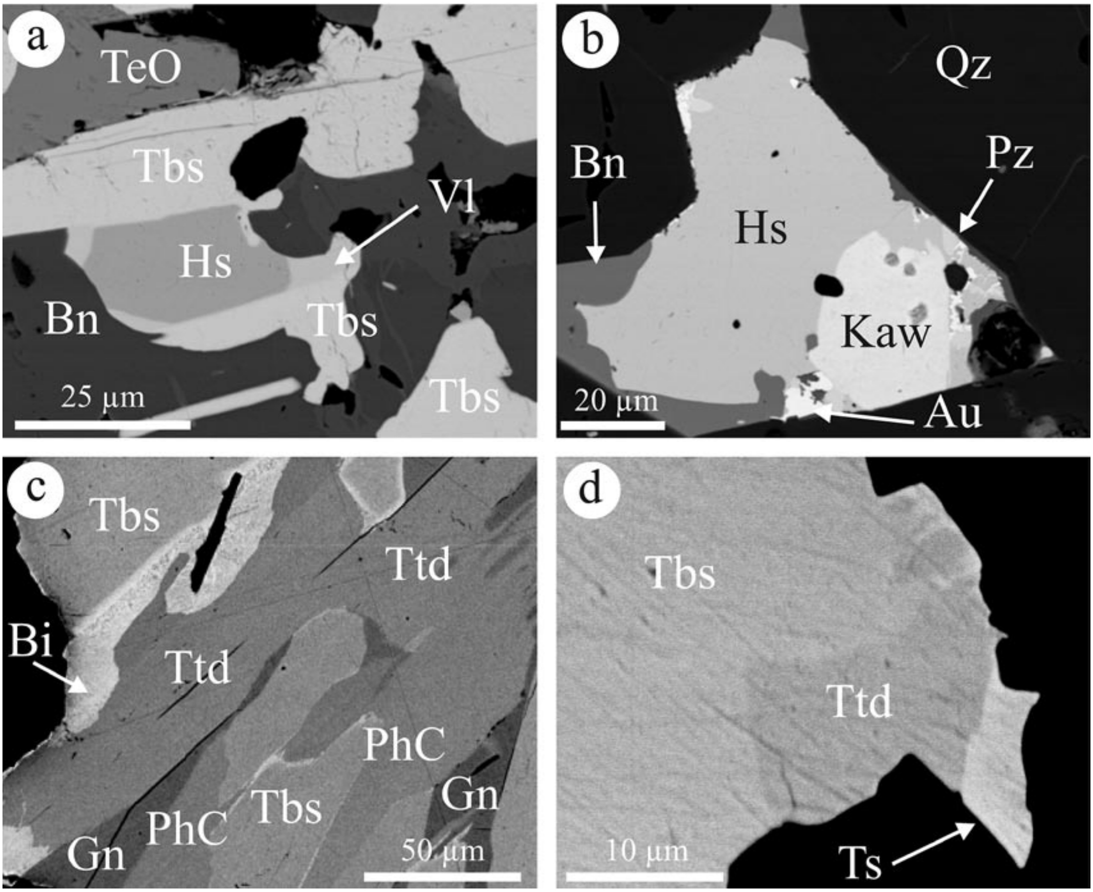

FIG. 5. Back-scattered electron images. (a) and (b) Association of tellurides from the Glava Au–Ag–Cu–Te–Se deposit, south-central Sweden. Tbs: tellurobismuthite, Hs: hessite, Pz: petzite, Vl: volynskite, Au: gold, Bn: bornite, TeO: tellurite. (c) Association of tetradymite (Ttd), tellurobismuthite (Tbs), unnamed $PbBi_4Te_4S_3$ (Phase "C"; PhC), native bismuth (Bi) and galena (Gn) from the Clogau mine, Dolgellau gold belt, North Wales, U.K. [Section E1309, The Natural History Museum, London]. (d) Association of tellurobismuthite (Tbs), Se-bearing tetradymite (Ttd) and tsumoite (Ts) from gold ores of the Orivesi (Kutemajärvi) deposit, central Finland.

The systems Bi–S and Bi–Se

In comparison to the binary system Bi–Te, minerals within the systems Bi–S and Bi–Se are less numerous. The following natural minerals are recognized: bismuthinite (Bi_2S_3), nevskite (BiSe, though rarely without sulfur) and ikunolite (Bi_4S_3), guanajuatite [$Bi_2(Se,S)_3$] and paraguanajuatite (Bi_2Se_3), and laitakarite (Bi_4Se_3). These will be discussed below.

The system Bi–Se (*e.g.*, Okamoto 1994) has many of the features of the system Bi–Te. Lind & Lidin (2003) have recently identified an extensive range of phases with compositions between Bi_2Se_3 and Bi_4Se_3. These compounds, for which the authors developed a general structural model, were said to be either commensurate or incommensurate, and crystallize as layered structures with either rhombohedral or trigonal symmetry.

Synthetic work in the system Bi–S typically produced only the single binary phase Bi_2S_3 (*e.g.*, Schunk 1969). In addition to Bi_4S_3, the literature contains references to other stoichiometries in the system Bi–S, including BiS, Bi_2S and Bi_3S_2 (*e.g.*, Zachariáš *et al.* 2001). Compositions approximating to Bi_3S_5 and Bi_3S_4 are reported from Kazakhstan (Pavlova & Kotelinikov 1988, Pavlova *et al.* 1988). Such phases require more comprehensive documentation, including quantitative microanalysis and X-ray data.

TABLE 3. ELECTRON-MICROPROBE DATA ON SELENIAN TELLUROBISMUTHITE AND KAWAZULITE, GLAVA DEPOSIT, SWEDEN

	Cu	Fe	Pb	Sb	Bi	S	Se	Te	Total	Formula	S/(S+Se)
Selenian tellurobismuthite											
GL5.57	-	-	-	0.34	52.83	-	0.49	46.12	99.78	$(Bi_{2.03}Sb_{0.02})_{\Sigma 2.05}(Te_{2.90}Se_{0.05})_{\Sigma 2.95}$	
GL5.61	-	-	0.98	0.33	52.08	-	0.68	45.54	99.60	$(Bi_{2.00}Sb_{0.05}Pb_{0.04})_{\Sigma 2.06}(Te_{2.87}Se_{0.07})_{\Sigma 2.94}$	
GL5.39	-	-	-	-	52.18	-	1.39	44.62	98.19	$Bi_{2.02}(Te_{2.84}Se_{0.14})_{\Sigma 2.98}$	
GL5.40	-	-	0.10	-	52.17	-	1.50	44.34	98.11	$Bi_{2.02}(Te_{2.82}Se_{0.16})_{\Sigma 2.98}$	
GL5.30	-	-	-	-	52.04	-	1.91	43.76	97.71	$Bi_{2.02}(Te_{2.78}Se_{0.16})_{\Sigma 2.98}$	
GL5.41	-	-	-	-	53.84	-	2.25	43.83	99.92	$Bi_{2.03}(Te_{2.73}Se_{0.23})_{\Sigma 2.97}$	
GL5.16	-	-	0.99	0.57	52.08	-	2.71	42.90	99.25	$(Bi_{1.99}Sb_{0.01}Pb_{0.04})_{\Sigma 2.03}(Te_{2.63}Se_{0.34})_{\Sigma 2.97}$	
Kawazulite											
GL5.51	-	-	-	0.06	55.39	0.67	8.28	34.30	98.64	$Bi_{2.01}(Te_{2.04}S_{0.16}Se_{0.79})_{\Sigma 2.99}$	0.19
GL5.53	-	-	-	-	55.86	0.71	8.07	34.27	98.90	$Bi_{2.02}(Te_{2.03}S_{0.17}Se_{0.77})_{\Sigma 2.98}$	0.18
GL5.56	-	-	-	0.07	56.14	0.21	9.17	34.15	99.67	$Bi_{2.04}(Te_{2.03}S_{0.05}Se_{0.88})_{\Sigma 2.96}$	0.05

The formula of samples of tellurobismuthite and kawazulite is calculated on basis of five atoms.

TABLE 4. ELECTRON-MICROPROBE DATA ON TELLUROBISMUTHITE, TSUMOITE AND SELENIAN TETRADYMITE, ORIVESI Au DEPOSIT, CENTRAL FINLAND

	Cu	Fe	Pb	Sb	Bi	S	Se	Te	Total	Formula	S/(S+Se)
Tellurobismuthite											
4a.8	-	-	-	0.75	51.70	-	0.81	46.41	99.67	$(Bi_{1.97}Sb_{0.05})_{\Sigma 2.02}(Te_{2.90}Se_{0.08})_{\Sigma 2.98}$	
4a.10	-	-	-	0.76	52.09	-	0.93	46.14	99.92	$(Bi_{1.98}Sb_{0.05})_{\Sigma 2.03}(Te_{2.88}Se_{0.09})_{\Sigma 2.97}$	
4a.21	0.09	-	-	0.85	51.51	-	1.10	46.06	99.60	$(Bi_{1.96}Sb_{0.06})_{\Sigma 2.02}(Te_{2.87}Se_{0.11})_{\Sigma 2.98}$	
Tsumoite											
4a.6	0.12	-	0.48	0.61	55.55	-	0.80	41.36	98.92	$(Bi_{0.44}Sb_{0.01})_{\Sigma 0.45}(Te_{0.54}Se_{0.01})_{\Sigma 0.55}$	
4a.7	0.19	-	0.55	0.67	56.24	-	0.69	41.13	99.46	$(Bi_{0.44}Sb_{0.01}Pb_{0.01})_{\Sigma 0.46}(Te_{0.53}Se_{0.01})_{\Sigma 0.54}$	
Selenian tetradymite											
4a.4	0.08	-	-	1.10	56.87	2.29	5.25	35.12	100.70	$(Bi_{1.97}Sb_{0.06})_{\Sigma 2.03}(Te_{1.98}S_{0.51}Se_{0.48})_{\Sigma 2.97}$	0.52
4a.15	-	-	-	1.03	56.28	2.59	4.38	34.87	99.15	$(Bi_{1.96}Sb_{0.06})_{\Sigma 2.03}(Te_{1.98}S_{0.59}Se_{0.40})_{\Sigma 2.97}$	0.60
4a.20	-	-	-	0.95	56.77	2.7	4.24	35.51	100.16	$(Bi_{1.95}Sb_{0.06})_{\Sigma 2.01}(Te_{2.00}S_{0.61}Se_{0.39})_{\Sigma 2.99}$	0.61
4a.25	-	-	-	1.01	55.60	2.56	4.51	35.17	98.84	$(Bi_{1.93}Sb_{0.06})_{\Sigma 1.99}(Te_{2.01}S_{0.58}Se_{0.41})_{\Sigma 3.01}$	0.59

The formula of samples of tellurobismuthite, tsumoite and tetradymite is calculated on basis of five atoms.

THE SUBSYSTEM Bi_2S_3–Bi_2Se_3–Bi_2Te_3 (THE "TELLUROBISMUTHITE" ISOSERIES)

Minerals within this subgroup (Table 1) are among the most abundant Bi–Te–Se–S phases in nature: tetradymite and tellurobismuthite, in particular, are common accessories in many telluride-bearing precious metal deposits. The historical background for tetradymite, tellurobismuthite and related phases has been comprehensively described by Peacock (1941). Tetradymite (Bi_2Te_2S), kawazulite (Bi_2Te_2Se), skippenite (Bi_2Se_2S), tellurobismuthite (Bi_2Te_3) and paraguanajuatite (Bi_2Se_3) have trigonal symmetry and the $R\overline{3}m$ space group. Tellurobismuthite, Bi_2Te_3, has been discussed in the section above. Tellurantimony, Sb_2Te_3 (Thorpe & Harris 1973) is also a fully isostructural member of the isoseries. A compilation of published compositional data for minerals in the subsystem Bi_2S_3–Bi_2Se_3–Bi_2Te_3 is given in Figure 7.

The simple sulfide, bismuthinite (Bi_2S_3), and guanajuatite, the dimorph of paraguanajuatite, are both orthorhombic with space group *Pbnm*, and are thus classified within the structurally distinct stibnite group (bismuthinite, stibnite, antimonselite, guanajuatite). Thus Bi_2S_3 does not crystallize with trigonal symmetry (Kupčík & Veselá-Nováková 1970). Bismuthinite is one of the two end members of the bismuthinite–aikinite homeotypic series (*e.g.*, Harris & Chen 1976, Makovicky & Makovicky 1978, Topa *et al.* 2002). It is nevertheless instructive to observe that bismuthinite, a widespread mineral, commonly found associated with other Bi–Te–Se–S minerals, may in some cases contain Se, up to concentrations of several wt.%, *i.e.*, $0.10 < Se:(S + Se) < 0.20$ [*e.g.*, Falun, Sweden: Karup-Møller (1970), Tennant Creek, N.T., Australia: Henley *et al.* (1975), Suttsu mine, Japan: Shimizu *et al.* (1995), Nevskii, Russia: Yefimov *et al.* (1988), Mozgova *et al.* (1992)], especially where it is associated with other selenides and selenosalts. Extreme Se-enrichment appears more rarely, although Kucha & Mochnacka (1986) reported Bi_2S_2Se (12.27 wt.% Se) from southwestern Poland. Incorporation of tellurium in the bismuthinite structure rarely exceeds a few tenths of a wt.%.

A second characteristic of bismuthinite is the tendency to incorporate Sb where it is available. Hayase (1955) introduced the name "horobetsuite" for compositions in the central part of the Bi_2S_3–Sb_2S_3 solid-solution series (30 to 70 mol.% Sb_2S_3), after their occurrence in the Horobetsu deposit, Japan. Springer (1969) showed that substitution of Sb for Bi in bismuthinite can occur up to 42 mol.% in natural specimens [Hayase (1955) had earlier proposed that solid solution up to 55 mol.% Sb_2S_3 was possible]. Rablovský & Krištín (1975) reported the presence of "horobetsuite" from the Dúbrava deposit, Slovakia, including one sample with a composition $(Sb_{1.38}Bi_{0.48})_{\Sigma 1.86}S_3$, suggesting more extensive solid-solution in natural samples than previously reported. Other occurrences (*e.g.*, Slim-Shimi *et al.* 1990, Chovan *et al.* 1998) also are documented.

Paraguanajuatite and guanajuatite

Paraguanajuatite and guanajuatite are dimorphs. Both were initially reported from the same type-locality (Santa Catarina mine near Guanajuato, Mexico; see Earley 1950, Ramdohr 1948, 1950). The compositions of both minerals occupy a wide field along the Se end of the Bi_2S_3–Bi_2Se_3 join, extending from almost pure Bi_2Se_3 to compositions where Se and S are approximately equal. Berry & Thompson (1962) gave the formula for guanajuatite as $Bi_2(Se,S)_3$. More rarely, Te substitution is recognized in paraguanajuatite, giving, for example, the tellurian sulfurian paraguanajuatite of

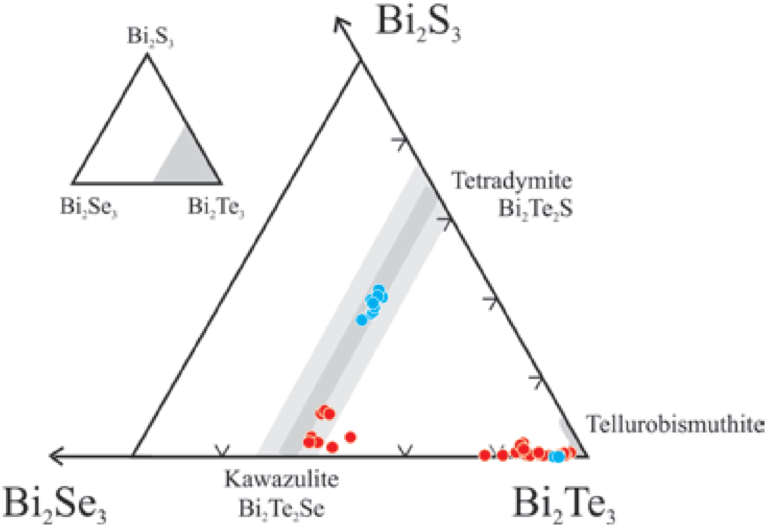

FIG. 6. Compositional plots for new data in the subsystem Bi_2Te_3–Bi_2Se_3–Bi_2S_3 from the Glava Au–Ag–Cu–Te–Se deposit, south-central Sweden (Se-bearing tellurobismuthite and kawazulite; red circles) and from the Orivesi (Kutemajärvi) deposit, central Finland (tellurobismuthite and Se-bearing tetradymite; blue circles).

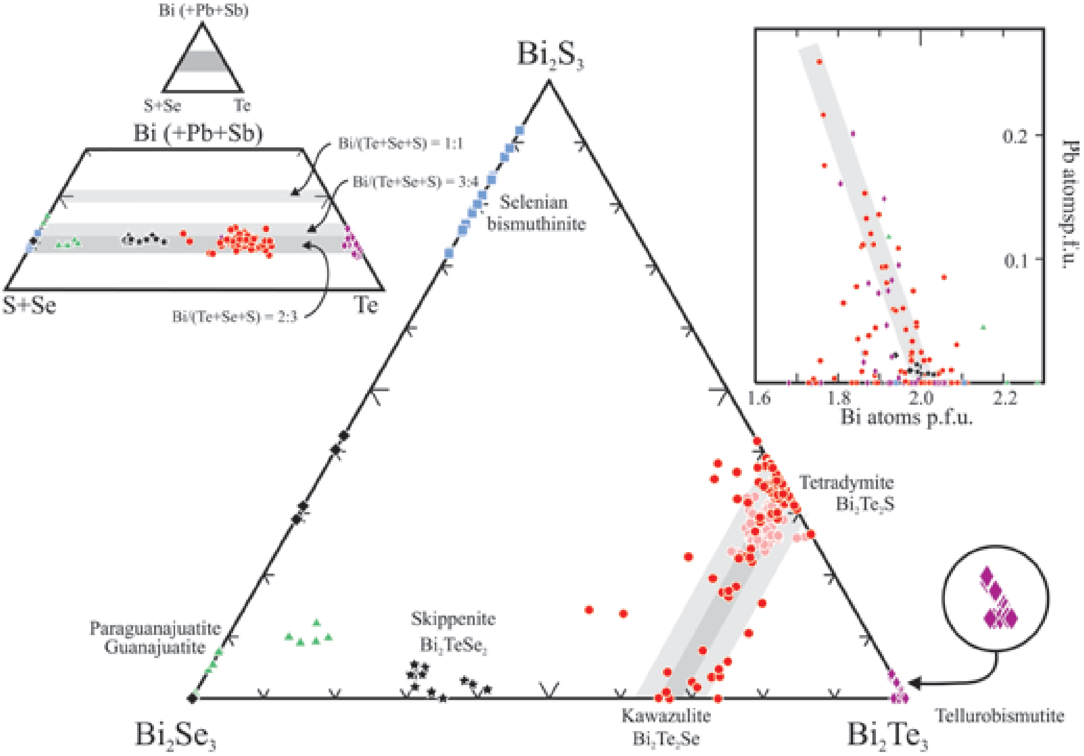

FIG. 7. Projection of literature data of minerals in the Bi_2S_3–Bi_2Se_3–Bi_2Te_3 subsystem. Inset at upper left shows variation in terms of Bi(+ Pb + Sb)–Te–(S + Se); inset at upper right shows Pb substitution. Purple diamonds: tellurobismuthite; red circles: tetradymite–kawazulite; black stars: skippenite; blue squares: selenian bismuthinite. Guanajuatite and paraguanajuatite are indicated by black rhombs and green triangles, respectively. Literature sources: Muthmann & Schröder (1898), Aksenov *et al.* (1968b), Kato (1970), Guha & Darling (1972), Czamanske & Hall (1975), Lipovetskiy *et al.* (1977, 1979), Zav'yalov & Begizov (1977, 1978, 1985), Arutyunyan & Eremin (1978), Harańczyk (1978), Shimazaki & Ozawa (1978), Spiridonov *et al.* (1978, 1995), Miller (1981), Bortnikov *et al.* (1982), Gamyanin *et al.* (1982), Sztrókay & Nagy (1982), Harris *et al.* (1983), Nagy (1983), Nysten & Annersten (1984), Oen & Kieft (1984), Yushko *et al.* (1984), Criddle & Stanley (1986, 1993), Kovalenker (1986), Ren (1986), Eshimov & Khamrabayeva (1987), Johan *et al.* (1987), Chovan & Michálek (1988), Shimizu *et al.* (1988, 1995), Yefimov *et al.* (1988, 1990), Kovalenker *et al.* (1989, 1990), Nikitin *et al.* (1989), McQueen (1990), McQueen & Solberg (1990), Dobbe (1991), Banás *et al.* (1993), Bonev & Neykov (1990), Çağatay *et al.* (1991), Francis *et al.* (1992), Lowry *et al.* (1994), Marcoux *et al.* (1996), De Souza Lima *et al.* (1996), Ueno *et al.* (1996), Cioflica *et al.* (1997), Kravchenko & Bondarenko (1997), Spry *et al.* (1997), Maglambayan *et al.* (1998), Mikulski (1998), Voicu *et al.* (1999), Cook & Ciobanu (2001a), Vanhanen (2001), Gu *et al.* (2001), Moloshag *et al.* (2002). Selected data for selenian bismuthinite are taken from Karup-Møller (1970) (Falun, Sweden), Shimizu *et al.* (1995) (Suttsu mine, Japan), and Yefimov *et al.* (1988) and Mozgova *et al.* (1992) (Nevskoe, Russia). Pink circles are tetradymite data from Cook & Ciobanu (2004).

Shimizu *et al.* (1988). Published data are not plentiful for either mineral (Aksenov *et al.* 1968a, Yushko *et al.* 1984, Shimizu *et al.* 1988, Yefimov *et al.* 1988, Nikitin *et al.* 1989), and unfortunately do not permit a comparison of the compositional ranges of one dimorph *versus* the other. Guanajuatite is recognized as the high-temperature form of Bi_2Se_3 (Atabaeva *et al.* 1973).

Investigations of the system Bi_2Se_3–Bi_2S_3 indicate extensive solid-solution from Bi_2Se_3 (*e.g.*, Novotný *et al.* 1984) and, in some studies, the presence of intermediate compounds with compositions close to Bi_2Se_2S and Bi_2SeS_2. Godovikov *et al.* (1966) indicated the existence of a solid solution from Bi_2S_3 up to 68% Bi_2Se_3, and from Bi_2Se_3 up to 17% Bi_2S_3 at temperatures above 500°C. This miscibility gap (Fig. 7) increases with decreasing temperature down to 300°C (Liu *et al.* 1995).

Tetradymite

Despite the fact that tetradymite is widespread, there is some continuing (though commonly conveniently forgotten) uncertainty about the structural formula, which is now almost universally accepted as Bi_2Te_2S (*e.g.*, Bayliss 1991). Nevertheless, sulfur-rich tetradymite appears more chemically stable than stoichiometric Bi_2Te_2S, and the formula $Bi_{14}Te_{13}S_8$ given by Pauling (1975) appears valid for most examples of natural tetradymite. Ciobanu & Cook (2000) described compositions resembling both the natural γ (Pauling 1975) as well as the synthetic β (Te-rich) type (Glatz 1967). An extensive compositional range is supported by experimental work in the system Bi_2S_3–Bi_2Te_3 at higher temperature: 43–66 mol.% Bi_2Te_3 (Yusa *et al.* 1979), 47–68 mol.% Bi_2Te_3 (Cortellini & Chang 1980), both at 500°C. Yusa *et al.* (1979) were able to synthesize $Bi_2Te_{1.9}S_{1.1}$ and showed tetradymite to be stable up to 638°C (or 609 ± 3°C according to Cortellini & Chang 1980).

A relatively large body of analytical data exists for tetradymite (*e.g.*, Sarkar & Deb 1969, Guha & Darling 1972, Lipovetskiy *et al.* 1977, 1979, Harańczyk 1978, Shimazaki & Ozawa 1978, Spiridonov *et al.* 1978, Zav'yalov & Begizov 1978, 1985, Bortnikov *et al.* 1982, Sztrókay & Nagy 1982, Nagy 1983, Kovalenker 1986, Ren 1986, Eshimov & Khamrabayeva 1987, Chovan & Michálek 1988, Bonev & Neykov 1990, Willgallis *et al.* 1990, Dobbe 1991, Francis *et al.* 1992, Banás *et al.* 1993, Spiridonov 1995, De Souza Lima *et al.* 1996, Cook & Ciobanu 2004, Marquez-Zavalia & Craig 2004). This database has allowed us to show the extent of natural compositions (Fig. 7), which mark a broad line between ideal tetradymite and kawazulite, expressing simple Se-for-S substitution. The data also express the extent of non-stoichiometry typical for tetradymite (-kawazulite), yet do not show any preferred tendency toward Te-rich or Te-poor compositions in natural specimens.

Lead may enter the tetradymite structure. Some higher Pb contents in published compositions (*e.g.*, Plimer 1974) may, nevertheless, be attributable to submicrometric inclusions of galena, an association typical for the mineral (*e.g.*, in the Larga deposit, Romania; Cook & Ciobanu 2004). In association with the Pb–Bi tellurosulfides $PbBi_4Te_4S_3$ and aleksite (Fig. 5c), we have documented (Cook *et al.* 2007) the presence of plumboan tetradymite that gives a range of compositions extending up to $PbBi_4Te_4S_3$, prompting us to consider the presence of intergrown lattice-scale homologues.

Kawazulite

Although kawazulite, ideally Bi_2Te_2Se, is a relatively widespread mineral, compositional data are relatively sparse (Kato 1970, Guha & Darling 1972, Miller 1981, Kovalenker 1986, Pavlova & Kotelnikov 1988, Willgallis *et al.* 1990, Dobbe 1991, Shimizu *et al.* 1995, Cook & Ciobanu 2001a). Nevertheless, continuous solid-solution between tetradymite and kawazulite is well established.

New, additional compositional data for the kawazulite–tetradymite solid-solution series from other deposits, such as Orivesi (Kutemajärvi), Finland, and Glava, Sweden (Figs. 5a–b, d, 6), confirm the above compositional trends, and also the tendency for only limited compositional variation in a given deposit. In general, deviation from the Bi_2Te_2S–$BiTe_2Se$ join (Fig. 7) may be due either to analytical error, or to limited Se-for-Te substitution, as proposed by Bayliss (1991).

Skippenite

Appreciably rarer than tetradymite–kawazulite is skippenite, ideally Bi_2Se_2Te [but more generally $Bi_2Se(Se,Te,S)_2$ or $Bi_2(Se,Te,S)_3$, Bayliss 1991]. The mineral (Mineral B of Miller 1981) is known only from a few localities (Johan *et al.* 1987, Kovalenker *et al.* 1989, Spiridonov *et al.* 1995). Published data indicate extensive solid-solution toward kawazulite, *e.g.*, unnamed Mineral C of Miller (1981), who gave the formula $Bi_4Se_3Te_3$. Bindi & Cipriani (2004) have given new structural data for the mineral.

Bi_2SeS_2 and Bi_2TeS_2

In the sulfur-rich portion of the subsystem Bi_2S_3–Bi_2Se_3–Bi_2Te_3, there are no trigonal phases with the ideal compositions of Bi_2SeS_2 and Bi_2TeS_2. "Csiklovaite" was proposed as a species with formula $Bi_2Te(S,Se)_2$ by Koch (1948) from the Csiklova (Ciclova) skarn deposit, Romania. It had earlier been discovered and analyzed, but not named, by Sztrókay (1946). *Csiklovaite* was said to be isomorphous with tetradymite, with which it coexists. A phase with similar composition had been described from a limited number of other occurrences (Plimer 1974, Harańczyk 1978). "Csiklovaite" was officially discredited following the work of Bayliss (1991), who conducted an X-ray powder-diffraction study on eight specimens of material used in the original description (Koch 1948). "Csiklovaite" was shown to be composed of tetradymite ($Bi_2S_{1.1}Se_{0.1}Te_{1.8}$) containing fine lamellar intergrowths of bismuthinite and galenobismutite. Bayliss concluded that a mixture of 60% tetradymite and 40% bismuthinite would account for the chemical formula proposed by Koch (1948). Bayliss further noted that a phase with the composition $Bi_2Te(S,Se)_2$ had never been synthesized in experiments in the system Bi–S–Te–Se (Glatz 1967, Kuznetsov & Kanishcheva 1970, Evdokimenko & Tsepin 1971; see also Cortellini & Chang 1980).

THE SUBSYSTEM Bi_4S_3–Bi_4Se_3–Bi_4Te_3 (THE “JOSÉITE” ISOSERIES)

Five mineral species are recognized (laitakarite, ikunolite, pilsenite, joséite-A and joséite-B; Table 1). All share a trigonal symmetry and the $R\bar{3}m$ space group. Compositional variation is expressed on Figure 8. Pilsenite, Bi_4Te_3, has been discussed above. Compositions (Fig. 8) are invariably close to end-member Bi_4Te_3, with no compositional data to support solid solution toward joséite-B or Bi_4Te_2Se.

Laitakarite

Laitakarite, $Bi_4(Se,S)_3$, is commonly found together with other minerals of the subsystem Bi_4S_3–Bi_4Se_3–Bi_4Te_3. Published data (*e.g.*, Vorma 1960, Karup-Møller 1970, Stanley & Vaughan 1982, Zav’yalov & Begizov 1983c, Kovalenker & Geynke 1984, Nechelyustov *et al.* 1984, Kovalenker 1986, Nenasheva *et al.* 1988, Yefimov *et al.* 1988, Meisser 1994, Holtstam & Söderhielm 1999, Wagner & Jonsson 2001) show that laitakarite almost always contains variable amounts

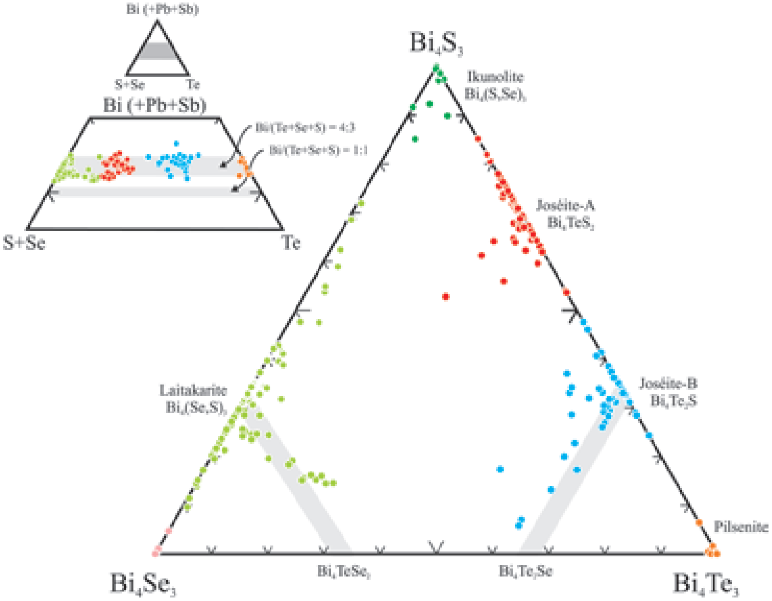

FIG. 8. Projection of published literature data of minerals in the subsystem Bi_4S_3–Bi_4Se_3–Bi_4Te_3. Inset at upper left shows variation in terms of Bi(+ Pb + Sb)–Te–(S + Se). Orange circles: pilsenite, blue circles: joséite-B, red circles: joséite-A, dark green circles: ikunolite, light green circles: laitakarite, pale red circles: Bi_4Se_3 of Piestrzyński (1992). Other literature sources: Peacock (1941), Grasselly (1948), Vorma (1960), Markham (1962), Dunin-Barkovskaya *et al.* (1968), Mintser *et al.* (1968), Godovikov *et al.* (1970, 1971b), Karup-Møller (1970, 1973), Kerimov & Velizade (1974), Groves & Hall (1978), Nechelyustov *et al.* (1978, 1984), Zav’yalov *et al.* (1978, 1984), Boldyreva *et al.* (1979), Finashin *et al.* (1979), Pringle & Thorpe (1980), Zav’yalov & Begizov (1981b, 1983b), Bortnikov *et al.* (1982), Sztrókay & Nagy (1982), Stanley & Vaughan (1982), Nagy (1983), Kovalenker & Geynke (1984), Lithoshko *et al.* (1984), Soeda *et al.* (1984), Yushko *et al.* (1984), Bonev (1986), Criddle & Stanley (1986, 1993), Imai & Chung (1986), Kovalenker (1986), Ren (1986), Eshimov & Khamrabayeva (1987), Nenasheva *et al.* (1988), Yefimov *et al.* (1988), Nekrasov *et al.* (1989), Bergman & Sundblad (1991), Kojonen *et al.* (1991), Kontoniemi *et al.* (1991), Verryn *et al.* (1991), Dobbe (1993), Kato *et al.* (1994), Luukkonen (1994), Meisser (1994), Cioflica *et al.* (1995, 1997), Simon & Alderton (1995), Sheppard *et al.* (1995), Spiridonov (1995, 1996), Zhan *et al.* (1995), De Souza Lima *et al.* (1996), Horner *et al.* (1997), Lawrence *et al.* (1998), Mikulski (1998), Holtstam & Söderhielm (1999), Wagner & Jonsson (2001), Gu *et al.* (2001), Alechevskiy (2002), Moloshag *et al.* (2002) and Fomin *et al.* (2004).

TABLE 5. ELECTRON-MICROPROBE DATA ON TELLURIAN LAITAKARITE AND SELENIAN JOSÉITE-B, LEGA DEMBI DEPOSIT, ETHIOPIA

	Pb	Bi	S	Se	Te	Total	Formula
Laitakarite							
1	2.76	77.26	0.36	21.33	0.21	101.91	$(Bi_{3.89}Pb_{0.14})_{\Sigma 4.03}(Se_{2.84}S_{0.12}Te_{0.02})_{\Sigma 2.97}$
Tellurian laitakarite							
7	2.21	78.79	2.37	11.55	7.38	102.30	$(Bi_{3.96}Pb_{0.11})_{\Sigma 4.08}(Se_{1.54}S_{0.78}Te_{0.61})_{\Sigma 2.92}$
6	2.14	77.49	2.40	11.94	7.51	101.48	$(Bi_{3.90}Pb_{0.11})_{\Sigma 4.01}(Se_{1.59}S_{0.79}Te_{0.62})_{\Sigma 2.99}$
9	2.48	77.93	2.27	11.99	7.57	102.22	$(Bi_{3.92}Pb_{0.13})_{\Sigma 4.04}(Se_{1.59}S_{0.74}Te_{0.62})_{\Sigma 2.96}$
8	2.23	78.13	2.31	11.86	7.91	102.44	$(Bi_{3.91}Pb_{0.11})_{\Sigma 4.02}(Se_{1.57}S_{0.76}Te_{0.65})_{\Sigma 2.98}$
10	1.26	74.87	1.31	10.47	12.19	100.10	$(Bi_{3.96}Pb_{0.07})_{\Sigma 4.03}(Se_{1.46}S_{0.45}Te_{1.06})_{\Sigma 2.97}$
12	1.44	75.50	1.33	10.60	12.46	101.33	$(Bi_{3.94}Pb_{0.08})_{\Sigma 4.02}(Se_{1.47}S_{0.45}Te_{1.07})_{\Sigma 2.99}$
11	1.29	74.37	1.17	10.59	12.96	100.38	$(Bi_{3.93}Pb_{0.07})_{\Sigma 4.00}(Se_{1.48}S_{0.40}Te_{1.12})_{\Sigma 3.00}$
14	0.29	75.38	0.83	9.14	14.50	100.14	$(Bi_{4.09}Pb_{0.02})_{\Sigma 4.11}(Se_{1.31}S_{0.29}Te_{1.29})_{\Sigma 2.89}$
Selenian joséite-B							
5	-	74.60	0.50	5.14	21.46	101.71	$Bi_{4.12}(Te_{1.94}S_{0.18}Se_{0.75})_{\Sigma 2.88}$
3	-	71.59	0.43	4.30	24.35	100.67	$Bi_{3.99}(Te_{2.22}S_{0.16}Se_{0.63})_{\Sigma 3.01}$

The formula of laitakarite and joséite-B samples is calculated on the basis of seven atoms.

of S, typically within the range $Bi_4Se_{2.0–2.5}S_{0.5–1.0}$. Isolated examples attain $Bi_4Se_{1.5}S_{1.5}$. Compositions reported by Stanley & Vaughan (1982) are unique in that they extend up to Bi_4SeS_2 (= Se-rich ikunolite). The mineral almost never corresponds to pure Bi_4Se_3. Nenasheva *et al.* (1988) examined the modification of the crystal structure as a function of chemical composition, confirming solid solution.

Most previously reported natural compositions of laitakarite plot close to the Bi_4Se_3–Bi_4S_3 join, with Te substitution for Se being typically less than 0.2 atoms per formula unit (*apfu*; Fig. 8). An exception is the dataset of Wagner & Jonsson (2001) from Boliden, Sweden, showing up to as much as 0.78 *apfu* Te.

New electron-microprobe data for "laitakarite" from the Lega Dembi Au deposit, Ethiopia (Figs. 9a–b, Table 5), have confirmed the earlier suggestion of two of us (Cook & Ciobanu 2001b) that in some cases, there may be extensive solid-solution fields within the entire lower half of the Bi_4S_3–Bi_4Se_3–Bi_4Te_3 triangle (Fig. 10). Our new compositional data, which show little overlap with previously published data, depict a broad range of "tellurian laitakarite" compositions that could be considered as members of a solid solution between laitakarite and a point on the Bi_4Se_3–Bi_4Te_3 join (Bi_4Se_2Te?). Alternatively, these compositions, and possibly some of the Te-rich compositions of Wagner & Jonsson (2001), could be members of a solid-solution join beween joséite-A and Bi_4Se_2Te, rather than laitakarite. Mechanisms of substitution between Te on the one hand, and (S + Se) on the other, are poorly understood. Several wt.% Pb appear characteristic for laitakarite (0.15–0.25 *apfu*.; Fig. 9, inset).

A re-investigation by two of us (CLC and NJC) of type specimens from Orijärvi, southwest Finland (Laitakari 1934, Vorma 1960) has revealed that the type material contains laitakarite of varying composition. Most abundant is sulfur-bearing laitakarite with compositions in the range $Bi_4Se_{1.91–2.49}S_{0.51–1.09}$ (Fig. 10). A lesser amount of a discrete close-to-end-member Bi_4Se_3 mineral, also present, is typically associated with native bismuth. These two phases have been found to be distinct both chemically and in reflected light (corroborated by measurement of reflectance spectra). We note with interest that Piestrzyński (1992) reported a sulfur-free Bi_4Se_3 mineral from the Polish Kuperschiefer. This phase contains 1.4 to 3.9 wt.% Cu and minor Ag, and it is closely associated with covellite and selenian chalcocite. The Bi_4Se_3 phase, conspicuously without Pb, occurs intergrown with clausthalite in an ore type rather atypical for most natural occurrences of laitakarite. An additional occurrence of "end-member" Bi_4Se_3 has recently been reported by Fojt & Škoda (2005), associated with clausthalite in the Zalesi uranium deposit, Czech Republic, and compositionally distinct from the laitakarite in the same ores.

Ikunolite

Ikunolite has only been recognized from a relatively small number of localities (*e.g.*, Kato 1959, Markham 1962, Nechelyustov *et al.* 1978, Finashin *et al.* 1979, Bortnikov *et al.* 1982, Imai & Chung 1986). Although appreciably less common than bismuthinite, the mineral is nevertheless stable in several telluride- and selenide-bearing deposits. In our experience, it is most stable

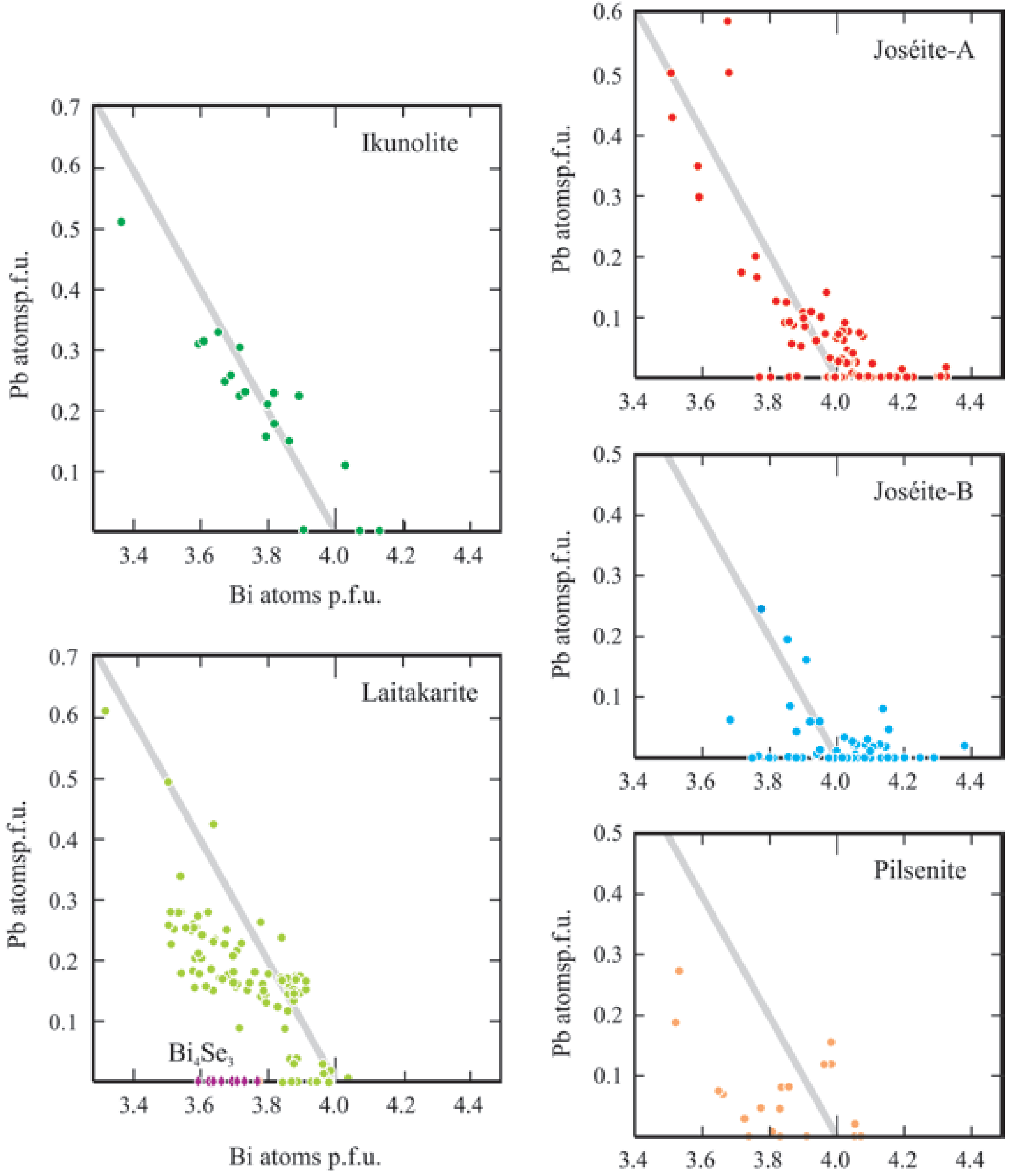

FIG. 9. Variation of Pb *versus* Bi in the analyses for minerals of the Bi_4S_3–Bi_4Se_3–Bi_4Te_3 subsystem (based on seven atoms in formula). Dataset and symbols as in Figure 8. Note the persistent presence of Pb in most laitakarite and ikunolite samples.

where pyrrhotite is the stable Fe-sulfide. Ikunolite may occur together with laitakarite, joséite-A or joséite-B, hedleyite, native bismuth and bismuthinite (Fig. 11d).

Compositional data show a range of compositions from end-member Bi_4S_3 to $Bi_4S_{2.5}Se_{0.5}$. It is uncertain whether there is complete solid-solution with laitakarite, or if there is a partial miscibility-gap between Bi_4S_2Se and Bi_4Se_2S. The only dataset falling in this range is the laitakarite of Stanley & Vaughan (1982). Compositional data for ikunolite (Fig. 9) indicate very limited Te-for-(Se,S) substitution in most natural specimens. There are numerous data-points plotting between ikunolite and joséite-A, but we would favor an explanation based on the presence of submicroscopic intergrowths rather than solid solution between the two minerals. Like other minerals in the Bi_4Se_3–Bi_4Se_3–Bi_4Te_3 isoseries, both joséite minerals show significant Pb-for-Bi substitution, at levels comparable with those in laitakarite (Fig. 8, inset).

Joséite-A and joséite-B

Until publication of a paper by Gamyanin (1968), showing the distinct optical and X-ray-diffraction character of joséite-A and joséite-B, and the two review papers by Zav'yalov & Begizov (1978, 1983b), "joséite" was the source of some confusion involving the inappropriate or confusing use of "joséite" for a whole range of compositions, *e.g.*, $Bi_7Te_2(S,Se)_2$ (joséite of Genth 1886), $Bi_7(Te_{0.74}S_{5.26})_{\Sigma 6}$ (Bi telluride of Koch 1948) or $Bi_7(Te_{2.68}S_{2.29})_{\Sigma 5}$ (joséite-B of Boldyreva *et al.* 1979). Zav'yalov & Begizov (1978) gave electron-microprobe and X-ray data for joséite-A (Bi_4TeS_2) and joséite-B (Bi_4Te_2S; so-called "tellurojoseite" in the earlier Russian literature) showing that these are distinct phases, with only partial solid-solution between them. The same authors later comprehensively reviewed published data on these phases (Zav'yalov & Begizov 1983b), showing that many of the names given to phases in the older literature bear little relation to their true identity. In doing so, Zav'yalov & Begizov established, once and for all, the discrete nature of both joséite phases in the subsystem Bi_4S_3–Bi_4Se_3–Bi_4Te_3 and their distinction from other tellurosulfides of Bi. Moreover, the reviews by Zav'yalov & Begizov contributed to the characterization of the new minerals *ingodite* and *rucklidgeite* and to the recognition of the stoichiometric groups identified in the present paper.

Published compositions of both joséite-A and joséite-B are abundant and show a considerable range along the Bi_4Te_3–Bi_4S_3 join, clustering around the ideal compositions (Fig. 8). The data also show a considerable degree of Se-for-(S,Te) substitution in some specimens. In joséite-B, such a substitution can extend up to a selenian end-member, Bi_4Te_2Se, (*e.g.*, in the Dataushan deposit; Gu *et al.* 2001; see also Shin *et al.* 2005). Selenium substitution in joséite-A may approach Bi_4TeSSe, adding indirect evidence for the joséite-A – Bi_4Se_2Te join that we speculated upon above. We should not, however, rule out the analysis of fine-grained intergrowths in some of the datasets as an explanation for the strong variation in Se/Te seen in both joséite-A and joséite-B.

New data for the Lega Dembi deposit, Ethiopia (Table 5, Figs. 10, 11), echo these findings, with compositions (which we earlier referred to as "selenian pilsenite"; Cook & Ciobanu 2001b) also approaching Bi_4Te_2Se. Selenium seems to replace only S, analogous to the substitution trend observed between tetradymite and kawazulite. Note that Bi_4Te_2Se is an end member of a solid-solution series, and phases in which the amount of Se exceeds that of S, such as the $Bi_4(Te,Se,S)_3$ and Bi_4Te_2Se phases recognized in Dataushan and Lega Dembi, probably correspond to what would be a new mineral, once the necessary corroborative data for Bi_4Te_2Se become available. In the case of the selenian derivatives of joséite-A, the extent of solid solution is unclear, and may possibly extend beyond Bi_4TeSSe to the aforementioned tellurian laitakarite. As mentioned above, there appears to be extensive (but incomplete ?) solid-solution between ikunolite and joséite-A. "Joséite-C", $Bi_{4.1}Te_{0.7}S_{2.2}$ of Godovikov *et al.* (1971a), an unnamed phase from China, [$(Bi_{3.5}Te_{0.5})S_2Te$; Ren (1986)], and "joséite-C" of Alechevskiy (2002) lie along the Bi_4S_3–Bi_4TeS_2 join. Other joséite-like phases in the literature (*e.g.*, joséite phases I to V of Rabone 1989) are more difficult to readily assign to known phases.

As is common in other members of the Bi_4S_3–Bi_4Se_3–Bi_4Te_3 isoseries, Pb-for-Bi substitution in joséite-A and joséite-B (Fig. 9) is widespread, although generally more limited than in laitakarite or ikunolite.

Bayliss (1991) suggested that Bi-for-Te substitution ("disorder") may play a role in the "joséite" isoseries, contributing to the considerable solid-solution among members of the series, even though he noted that the majority of phases in this system have generally good or excellent "4:3" stoichiometry. Our compilation backs these claims and suggests that minerals in the Bi_4S_3–Bi_4Se_3–Bi_4Te_3 isoseries tend to have ordered structures. A modest variation in Bi/(Te + Se + S) is, however, noted in all minerals of the isoseries (Fig. 8).

The Subsystem BiS–BiSe–BiTe: Phases with Bi:(Te,Se,S) ≈ 1 (the "Tsumoite" Isoseries)

Ingodite [Bi(S,Te)] and nevskite [Bi(Se,S)] can be considered as ternary phases in the systems Bi–Te–S and Bi–Se–S, respectively. Both species display a similar degree of nonstoichiometry, as has already been shown for tsumoite (see above). Published data for nevskite and ingodite remain relatively few (Fig. 12). In the case of ingodite, data in the original description (Zav'yalov & Begizov 1981a) can be compared with additional data in a later paper, showing the extent of solid solution (Zav'yalov *et al.* 1984). The same seems to apply to nevskite (Nechelyustov *et al.* 1984, Yefimov *et al.* 1988, Zhukova & Ordnets 1988). The other phases in this rather loosely defined subgroup are sulphotsumoite (Zav'yalov & Begizov 1983a) and the recently accepted

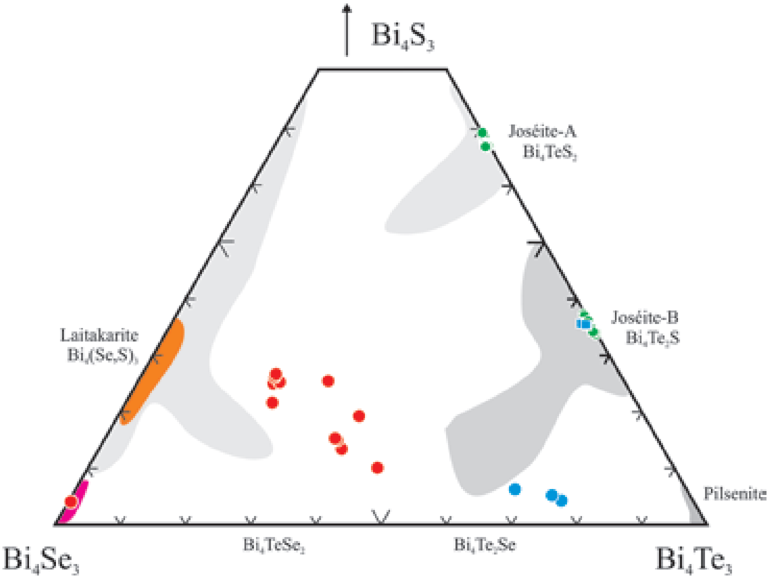

FIG. 10. Compositional plots for new data on the system Bi_4Te_3–Bi_4Se_3–Bi_4S_3. Grey shaded fields are from the literature, data given on Figure 8 for laitakarite, joséite-A, joséite-B and pilsenite. The bimodal composition of laitakarite in the type material from the Orijärvi deposit, southwest Finland (Bi_4Se_3 and $Bi_4(Se,S)_3$, simplified from Ciobanu *et al.* 2002), is shown by the orange- and pink-colored fields. Other symbols are: compositions of Te-bearing laitakarite (red circles) and Se-bearing joséite-B from the Lega Dembi deposit, Ethiopia (blue circles); joséite-A and joséite-B from Carrock Fell, Cumbria, U.K. (green circles) and joséite-B from the Maiskoe Au-deposit, Ukraine (blue squares).

telluronevskite (Řídkošil *et al.* 2001), neither of which is so far known to occupy a broad compositional range beyond Bi_3TeS_2 and Bi_3TeSe_2, respectively.

Ingodite

Zav'yalov & Begizov (1981a) formally described ingodite as Bi(Te,S) (ideally Bi_2TeS), although the existence of the phase had been mentioned in several earlier studies (Zav'yalov & Begizov 1978). Their data and subsequent information from other occurrences (*e.g.*, Ren 1986, Shimizu *et al.* 1999) illustrate a degree of nonstoichiometry [(Bi/(Se + S + Te) between 0.95 and 1.08] and also variable but roughly equal Te and S contents (Te:S ratio between 0.45 and 0.55). Although relatively few analyses for ingodite have been made, a number of compositions described as joséite, yet having Bi/(Te + S) ≈ 1, can be readily assigned to ingodite (*e.g.*, Turlychkin 1987). Bayliss (1991) re-appraised compositional and X-ray powder-diffraction data given by Zav'yalov & Begizov (1981a) and Zav'yalov *et al.* (1984) and concluded that ingodite should be attributed a formula Bi(S,Te). Compositions in which Te > S (*e.g.*, no. 77 of Zav'yalov & Begizov 1981a) are, in fact, tsumoite, Bi(Te,S), according to Bayliss. Zav'yalov *et al.* (1984) reported a number of compositions of Pb-bearing ingodite, the majority of which most closely resemble "phase C" of Lipovetskiy *et al.* (1977), discussed below and by Cook *et al.* (2007).

To illustrate the apparent nonstoichiometry, as well as the difficulties involved in microanalysis, we have re-examined ingodite from the Carrock Fell mine, Cumbria, U.K (polished specimens E817 and E819 from samples BM 39768 and BM 35459, respectively, Natural History Museum, London, U.K., summarized in Cooper & Stanley 1990). Ingodite is intimately associated with joséite-A, joséite-B, tetradymite, bismuthinite and hedleyite (Fig. 13). Microanalytical data (Table 6, Fig. 14) illustrate the variation in Bi/(Te + S) from 0.88 to 1.08 [between $\sim Bi_5(S,Te)_6$ and $\sim Bi_6(S,Te)_5$] and significant differences also in Te:S value. The Se contents in ingodite are negligible. Although much of the ingodite in sample E817 (BM 39768) is close to stoichiometric Bi(S,Te), and has been confirmed as such by X-ray powder diffraction (C.J.S., unpubl. data; see also Criddle & Stanley 1993), much of the coarser, deformed ingodite in specimen E819 (BM 35459) is chemically inhomogeneous, with composi-

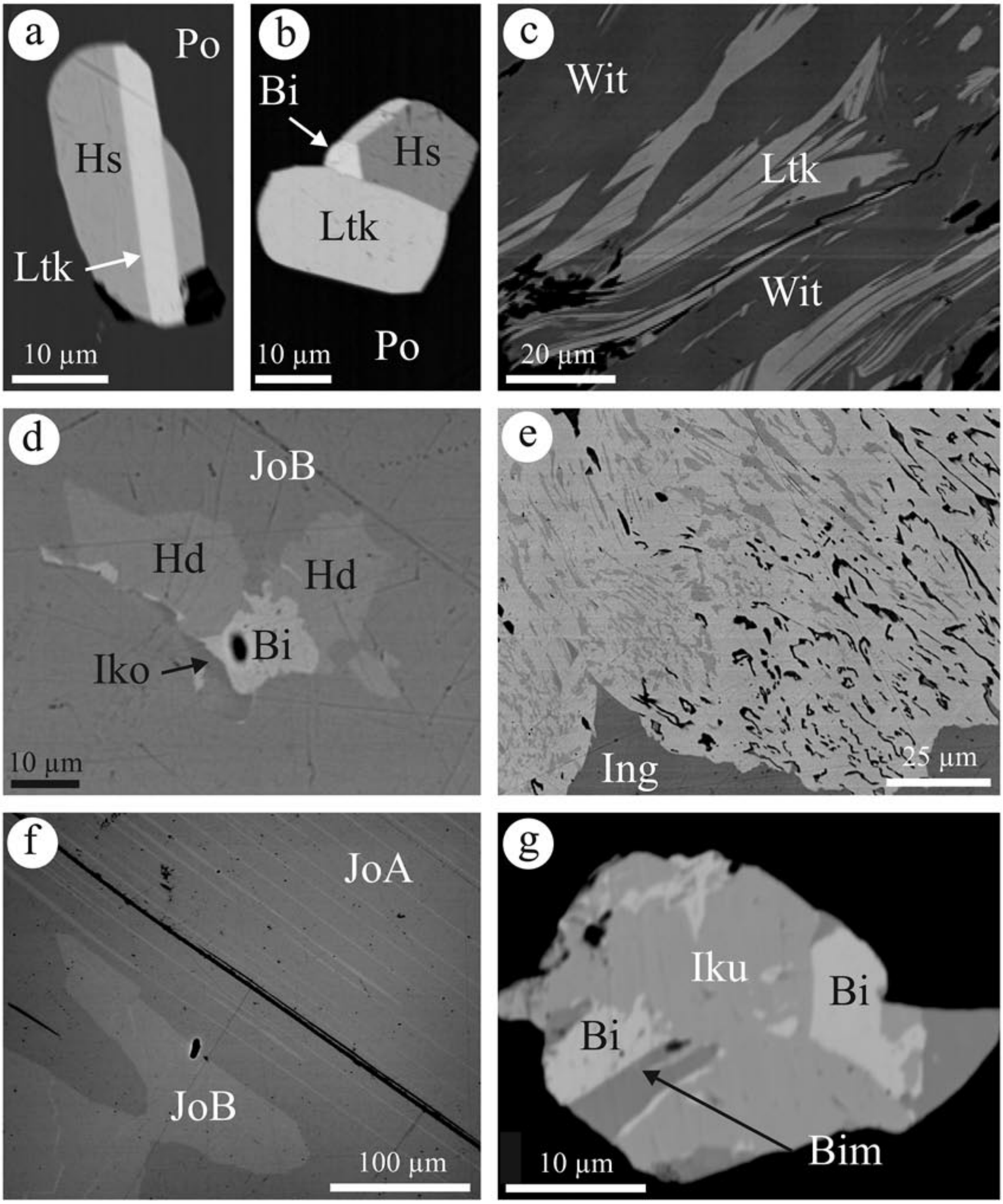

FIG. 11. Back-scattered electron images. (a) and (b) Inclusions of Te-bearing laitakarite (Ltk) within pyrrhotite (Po) in gold ores, Lega Dembi mine, Ethiopia. Hs: hessite, Bi: native bismuth. (c) Deformed lamellar intergrowths of laitakarite (Ltk) and wittite (Wit) from the Falun deposit, Bergslagen, central Sweden [Section E312, Specimen BM 1956,130, Natural History Museum, London]. (d) Coarse-grained joséite-B (JoB) with inclusions of hedleyite (Hed), native bismuth (Bi) and ikunolite (Iku) in the Maiskoe Au deposit, Ukraine. (e) Blebs of joséite-A (medium gray) exsolved in coarse, deformed joséite-B (light gray), Carrock Fell mine, Cumbria, U.K. Ing: ingodite. [Section E819, BM 35459, Natural History Museum, London]. (f) Coexisting coarse joséite-A, with lamellar exsolution of joséite-B (light gray) and coarser areas of joséite-B from Carrock Fell mine, Cumbria, U.K. [Section E820, BM 88363, Natural History Museum, London]. (g) Assemblage consisting of ikunolite (Iku), native bismuth (Bi) and bismuthinite (Bim) from the Sergeevske gold deposit, Ukraine.

TABLE 6. ELECTRON-MICROPROBE DATA ON INGODITE AND ASSOCIATED MINERALS, CARROCK FELL

	Ag	Cu	Pb	Fe	Cd	Bi	Sb	Te	Se	S	Total	Formula
						E817 (BM 39768)						
ingodite												
p.4*	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	72.63	b.d.l.	21.03	b.d.l.	5.96	99.62	$Bi_{2.98}(Te_{1.41}S_{1.59}Se_{0.01})_{\Sigma 3.01}$
p.1*	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.08	73.44	b.d.l.	19.95	0.08	6.16	99.70	$Bi_{3.00}(Te_{1.33}S_{1.64}Se_{0.01})_{\Sigma 3.00}$
p.8*	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	77.92	b.d.l.	15.48	b.d.l.	6.26	99.67	$Bi_{3.24}(Te_{1.06}S_{1.70})_{\Sigma 2.76}$
p.10*	0.12	b.d.l.	b.d.l.	b.d.l.	b.d.l.	77.93	b.d.l.	15.33	0.12	6.45	99.95	$Bi_{3.21}(Te_{1.03}S_{1.73}Se_{0.01})_{\Sigma 2.79}$
mean (n=8)	0.07	b.d.l.	b.d.l.	b.d.l.	0.05	74.99	b.d.l.	18.16	0.06	6.16	99.48	$Bi_{3.09}(Te_{1.23}S_{1.66}Se_{0.01})_{\Sigma 2.91}$
S.D.	0.06				0.04	2.63		2.55	0.04	0.18		
joséite-B	b.d.l.	b.d.l.	b.d.l.	0.07	b.d.l.	75.52	b.d.l.	21.36	b.d.l.	2.83	99.77	$Bi_{4.09}(Te_{1.90}S_{1.00})_{\Sigma 2.91}$
bismuthinite	0.22	0.15	b.d.l.	b.d.l.	b.d.l.	80.58	0.12	0.27	b.d.l.	18.26	99.60	
						E819 (BM 35459)						
ingodite												
p.34*	b.d.l.	b.d.l.	0.61	b.d.l.	b.d.l.	66.81	b.d.l.	25.77	0.08	5.73	98.99	$(Bi_{2.72}Pb_{0.03})_{\Sigma 2.75}(Te_{1.72}S_{1.52}Se_{0.01})_{\Sigma 3.25}$
p.17*	b.d.l.	b.d.l.	0.67	b.d.l.	0.10	67.14	b.d.l.	26.19	b.d.l.	5.70	99.79	$(Bi_{2.72}Pb_{0.03})_{\Sigma 2.75}(Te_{1.74}S_{1.51})_{\Sigma 3.25}$
p.30*	b.d.l.	b.d.l.	0.66	b.d.l.	0.10	68.82	b.d.l.	23.77	b.d.l.	6.43	99.77	$(Bi_{2.74}Pb_{0.03})_{\Sigma 2.77}(Te_{1.55}S_{1.67})_{\Sigma 3.23}$
p.29*	b.d.l.	b.d.l.	0.34	b.d.l.	0.05	69.98	0.05	23.29	b.d.l.	5.95	99.65	$(Bi_{2.86}Pb_{0.03})_{\Sigma 2.89}(Te_{1.55}S_{1.58})_{\Sigma 3.13}$
p.32*	b.d.l.	b.d.l.	1.40	b.d.l.	0.04	71.52	b.d.l.	21.01	0.08	5.66	99.71	$(Bi_{2.97}Pb_{0.06})_{\Sigma 3.03}(Te_{1.43}S_{1.53}Se_{0.01})_{\Sigma 2.97}$
p.38*	b.d.l.	b.d.l.	2.74	b.d.l.	0.14	74.84	b.d.l.	17.45	b.d.l.	5.46	100.64	$(Bi_{3.17}Pb_{0.12})_{\Sigma 3.29}(Te_{1.21}S_{1.50})_{\Sigma 2.71}$
mean (n=12)	0.02	0.01	0.95	b.d.l.	0.01	68.86	0.01	23.76	0.05	5.81	0.01	$(Bi_{2.82}Pb_{0.04})_{\Sigma 2.86}(Te_{1.59}S_{1.55}Se_{0.01})_{\Sigma 3.14}$
S.D.	0.04	0.03	0.65		0.03	2.55	0.02	2.84	0.05	0.23		
max	0.42	0.23	2.74		0.14	74.84	0.07	26.19	0.11	6.43		
min	b.d.l.	b.d.l.	0.34		b.d.l.	66.81	b.d.l.	17.45	b.d.l.	5.46		
joséite-B												
mean (n=6)	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.03	75.80	0.06	21.63	0.04	2.85	100.40	$(Bi_{4.08}Sb_{0.01})_{\Sigma 4.09}(Te_{1.90}S_{1.00}Se_{0.01})_{\Sigma 2.91}$
S.D.					0.05	0.49	0.05	0.23	0.04	0.02		
tetradymite												
mean (n=7)	0.06	0.03	0.45	b.d.l.	0.03	59.86	0.04	33.92	0.07	5.05	98.83	$(Bi_{2.00}Pb_{0.02})_{\Sigma 2.02}(Te_{1.86}S_{1.10}Se_{0.01})_{\Sigma 2.97}$
S.D.	0.06	0.04	0.53		0.03	0.19	0.05	0.81	0.04	0.24		
bismuthinite												
mean (n=3)	0.03	0.24	0.32	b.d.l.	0.04	80.95	0.13	0.07	0.03	18.40	99.42	$(Bi_{2.00}Pb_{0.01}Cu_{0.02})_{\Sigma 2.03}S_{2.97}$
S.D.	0.05	0.21	0.32		0.06	1.05	0.06	0.08	0.03	0.21		
						E820 (BM 88363)						
joséite-A												
mean (n=6)	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.06	83.33	b.d.l.	11.65	0.06	6.34	101.30	$Bi_{4.05}(Te_{0.93}S_{2.00}Se_{0.01})_{\Sigma 2.95}$
S.D.					0.05	0.64		0.14	0.04	0.05		
joséite-B												
mean (n=6)	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	77.69	b.d.l.	20.69	0.05	3.05	98.37	$Bi_{4.13}(Te_{1.80}S_{1.06}Se_{0.01})_{\Sigma 2.86}$
S.D.						0.32		0.25	0.04	0.05		

* result of a single representative analysis; S.D.: standard deviation. The formulas are calculated on the basis of five atoms (bismuthinite, tetradymite), six atoms (ingodite), or seven atoms (joséite-A, joséite-B).

tions deviating from Bi(S,Te). Significantly, we observe compositions ~$Bi_5(S,Te)_6$ immediately adjacent to BiTe, distinguishable in back-scattered electron images (Fig. 13d). Although it may be convenient to describe the bulk material as ingodite solid-solution (or disordered ingodite), we do not exclude the possibility that other (structurally distinct) phases are present. Specifically, and because of the marked tendency toward Te < S in the Bi-rich "ingodite" (Fig. 14), we suspect that baksanite, $Bi_6Te_2S_3$ (see below) may be present, neces-

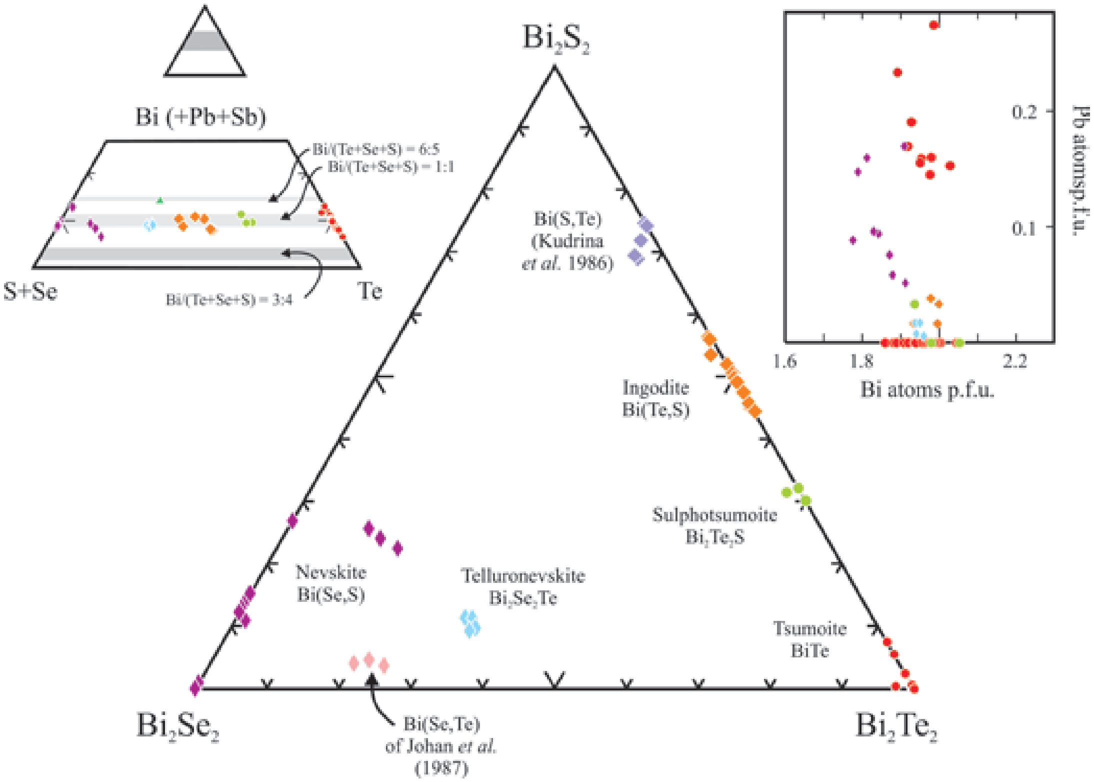

FIG. 12. Projection of published literature data for minerals and unnamed phases with Bi/(S + Se + Te) ~ 1, expressed in terms of Bi_2Te_2–Bi_2Se_2–Bi_2S_2. Literature sources for ingodite, nevskite, sulphotsumoite and telluronevskite from Aksenov *et al.* (1968b), Godovikov *et al.* (1970), Zav'yalov *et al.* (1978), Zav'yalov & Begizov (1981a), Nechelyustov *et al.* (1984), Criddle & Stanley (1986, 1993), Ren (1986), Yefimov *et al.* (1988), Zhukova & Ordynets (1988), Řídkošil *et al.* (2001). Source of tsumoite data is given in caption to Figure 4. Unnamed Bi(Se,Te) from Johan *et al.* (1987); unnamed Bi(S,Se) from Kudrina *et al.* (1986).

sitating supplementary single-crystal examination of this classic material.

Ingodite is described as the second most abundant Bi–Te–(S) phase after tetradymite in the Băiţa Bihor skarn deposit, Romania, as well as others in the Upper Cretaceous "banatitic" province (Ilinca & Makovicky 1999). Compositional ranges are said to be restricted within individual samples, but the entire population varies across a broad range, with Bi/(Te + S) from ~0.7 to 1.25 and Te/S from ~0.4 to 0.6. Ilinca & Makovicky (1999) stated that their compositions contain Pb and plot along the same line as reported by Zav'yalov *et al.* (1984), *i.e.*, from $Pb_{0.02}Bi_2Te_{0.86}S_{1.12}$ to $Pb_{0.24}Bi_{1.38}Te_{1.42}S_{0.95}$.

Nevskite

Nevskite, Bi(Se,S), was defined by Nechelyustov *et al.* (1984). Additional microanalytical data have subsequently been published (*e.g.*, Yefimov *et al.* 1988). Variable Bi/(Se + S + Te) between 0.96 and 1.12 and variation in Se/(Se + S + Te) within a wide range (0.61–1.00) appear characteristic of this phase. Zhukova & Ordnets (1988) have also presented data for nevskite; one sample contains negligible sulfur, therefore suggesting the existence of a BiSe "end member" (Fig. 12). This inference is supported by the BiSe composition reported by Yushko *et al.* (1984). The Te contents of nevskite seem to be negligible, except in the dataset of Yefimov *et al.* (1988). A degree of Pb-for-Bi substitution [0.03 < Pb/(Pb + Bi) < 0.09] seems to be typical of nevskite.

Sulphotsumoite

Sulphotsumoite, Bi_3Te_2S, was accepted as a distinct mineral in 1982 (Zav'yalov & Begizov 1983a). The mineral has been little recognized from other localities, in part no doubt owing to the difficulty in identifying the phase by microanalysis, and distinguishing it from

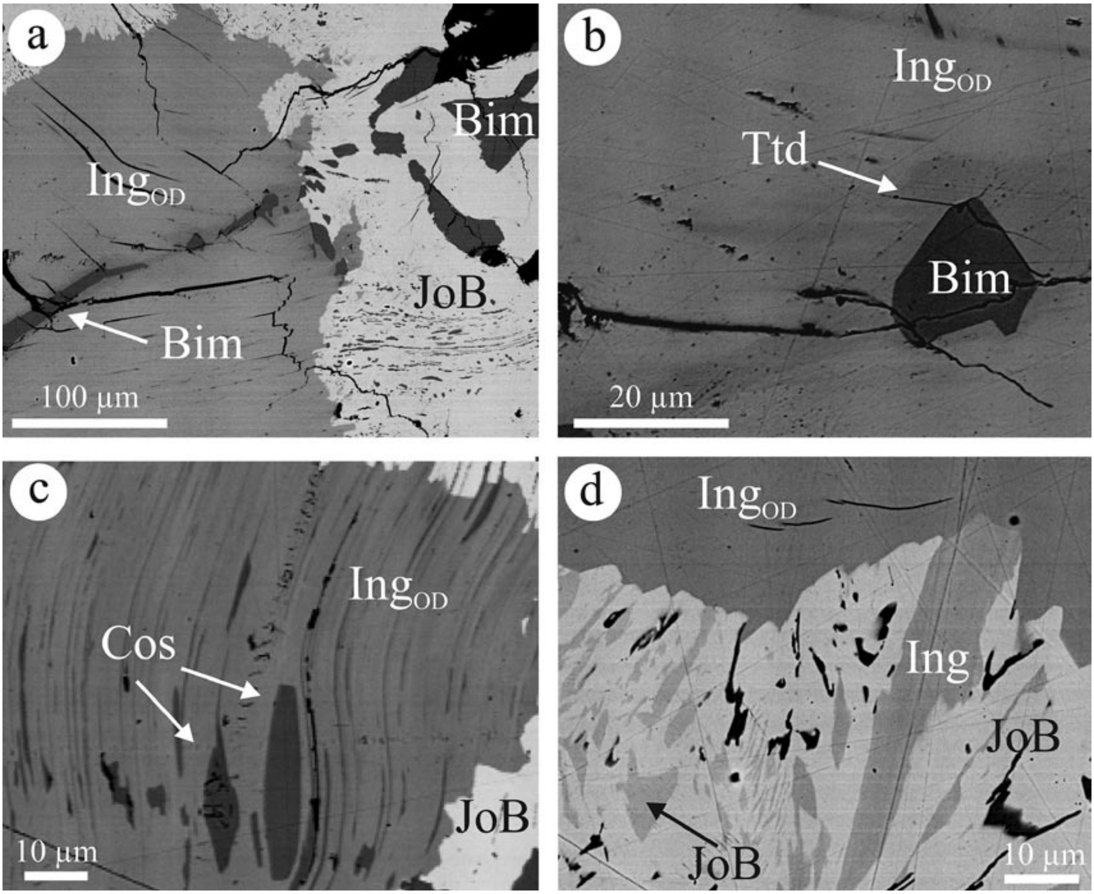

FIG. 13. Back-scattered electron images showing the occurrence of ingodite from Carrock Fell, Cumbria, U.K. [Section E819, BM 35459, Natural History Museum, London]. (a) Coarse disordered ingodite (Ing_{OD} ~$Bi_5(S,Te)_6$) in a matrix of joséite-A (JoA). Note irregular boundaries and deformation of the assemblage. Bismuthinite (Bim) occurs within joséite-A. (b) Detail of central part of (a) showing bismuthinite (Bim) as an exsolution product from ingodite (Ing_{OD}). Tetradymite (Ttd) forms a halo around the bismuthinite, indicating a secondary, overprinting event. (c) Detail of ingodite (Ing_{OD}) displaying deformed lamellar textures, with inter-lamellar exsolution of cosalite (Cos). (d) At margin of the coarse, disordered ingodite (Ing_{OD} ~$Bi_5(S,Te)_6$), we note ordered ingodite with a perfect Bi(S,Te) stoichiometry within joséite-A (JoA), that is also exsolving joséite-B (JoB).

ingodite. Apart from the type locality (Burgagylkan, Magadan District, Russian Far East), for which the two published compositions led to the empirical formulae $Bi_{3.08}Te_{1.94}(S_{0.92}Se_{0.06})_{\Sigma 0.98}$ and $Bi_{2.97}Te_{2.06}S_{0.97}$, the only published data that we are aware of are those given by Spiridonov (1995) and Gu *et al.* (2001).

Telluronevskite

Telluronevskite was recently accepted with the ideal formula Bi_3TeSe_2 and the empirical formula $Bi_{2.92}Pb_{0.02}Te_{1.01}Se_{1.73}S_{0.32}$. The mineral has been reported only from the type locality (Vihorlat Mountains, Slovakia; Řídkošil *et al.* 2001). Compositions of an unnamed Bi(Se,Te) phase given by Johan *et al.* (1987) fall between telluronevskite and nevskite (Fig. 11).

Other compositions

During re-examination of "wehrlite" type material, Sztrókay & Nagy (1982) and Nagy (1983) identified a phase with the composition Bi_3TeS_2; the latter author proposed the name "sztrokayite". The phase coexists with tsumoite, tellurobismuthite, joséite-B, tetradymite and bismuthinite. The status of "sztrokayite" remains in doubt; it may correspond to ingodite or be an additional, S-dominant member of the subgroup. Compositions published by Kudrina *et al.* (1986) seem to be similar to that of Sztrókay & Nagy (1982) and are similarly S-dominant (Fig. 12).

We have encountered numerous, sub-10-µm grains with compositions consistently close to Bi_3Te_2Se, with only negligible S contents, in samples from the telluride- and selenide-bearing core portions of the Ocna de Fier Fe–Cu–(Zn–Pb) skarn deposit, Romania (Cook & Ciobanu 2001a), coexisting with tsumoite, tellurobismuthite and kawazulite. Details of this phase, which would represent the selenian analogue of sulphotsumoite, will be reported elsewhere upon completion of the analytical work.

THE SUBSYSTEM Bi_3S_4–Bi_3Se_4–Bi_3Te_4, RUCKLIDGEITE AND POUBAITE

Two phases are currently recognized in the subsystem, rucklidgeite, $(Bi,Pb)_3Te_4$, and poubaite, $(Bi,Pb)_3(Se,Te)_4$ (Fig. 15).

Rucklidgeite was originally defined as $(Bi,Pb)_3Te_4$ by Zav'yalov & Begizov (1977). It was later established that the Pb content is variable, up to one *apfu*, and probably not essential (Kase *et al.* 1993). Lead-free members of a limited rucklidgeite solid-solution series (Bi_3Te_4–$PbBi_2Te_4$; inset to Fig. 15) have been described from several localities (Rucklidge 1969, Lipovetskiy *et al.* 1977, 1979, Zav'yalov & Begizov

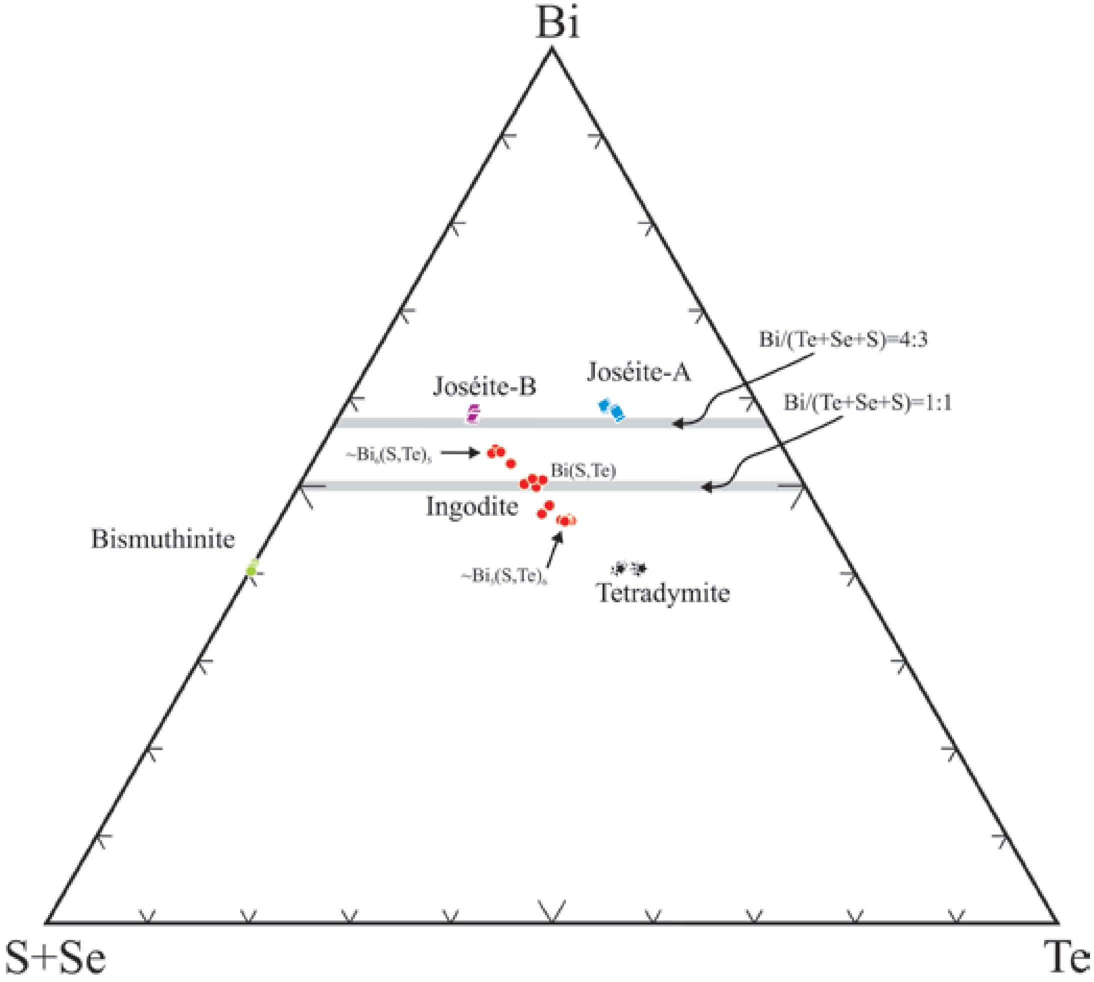

FIG. 14. Compositional plots for Carrock Fell ingodite and co-existing tetradymite, bismuthinite, joséite-A and joséite-B. Note the wide compositional field for ingodite, extending from ~$Bi_5(S,Te)_6$ (tight cluster of points) through ideal Bi(S,Te) to compositions approaching ~$Bi_6(S,Te)_5$ (*i.e.*, baksanite). See text for further discussion.

1977, Harańczyk 1978, Harris *et al.* 1983, Pašava *et al.* 1986, Sakharova *et al.* 1986, Spiridonov *et al.* 1989, McQueen 1990, McQueen & Solberg 1990, Kase *et al.* 1993, Maglambayan *et al.* 1998, Moloshag *et al.* 2002). Both Zav'yalov & Begizov (1977) and Kase *et al.* (1993) noted that Ag and minor Sb might also enter rucklidgeite. This is in agreement with the presence of Ag in a significant proportion of published compositions for the mineral (*e.g.,* Criddle & Stanley 1986). The apparent tendency for rucklidgeite to accommodate other metals (unlike most other minerals under discussion in this contribution) is amplified by the report of "Cu-rich rucklidgeite" by Pašava *et al.* (1986).

Recently, the present authors (Cook & Ciobanu 2004) contrasted low-Pb rucklidgeite (0.02 Pb *apfu*) in veins above porphyry-style mineralization containing Pb-bearing rucklidgeite [$(Pb_{0.82–0.87}Bi_{2.11–2.16})_{\Sigma 3}(Te,Se,S)_4$], in the same Larga–Trîmpoiele hydrothermal system, Apuseni Mountains, Romania. Only minor S, but up to 0.3 *apfu* Se, were determined in the latter Pb-bearing variety.

The possibility of an extensive solid-solution series derived from rucklidgeite, with general formula $Bi_3(Te,Se,S)_4$, has been raised in the description of several possibly related compositions (Fig. 15). Unnamed $Bi_3(Te,S)_4$ has been described by Zav'yalov *et al.* (1978), Kojonen *et al.* (1991), Spiridonov (1995) and Moloshag *et al.* (2002). In addition, $Bi_3(Te_{1.67–2.21}Se_{0.67–1.65}S_{0.70–1.14})_{\Sigma 4}$ is described from the Suttsu mine, Japan (Shimizu *et al.* 1995). The absence of Pb was, however, noted by these authors to support their contention that this is not a derivative of rucklidgeite.

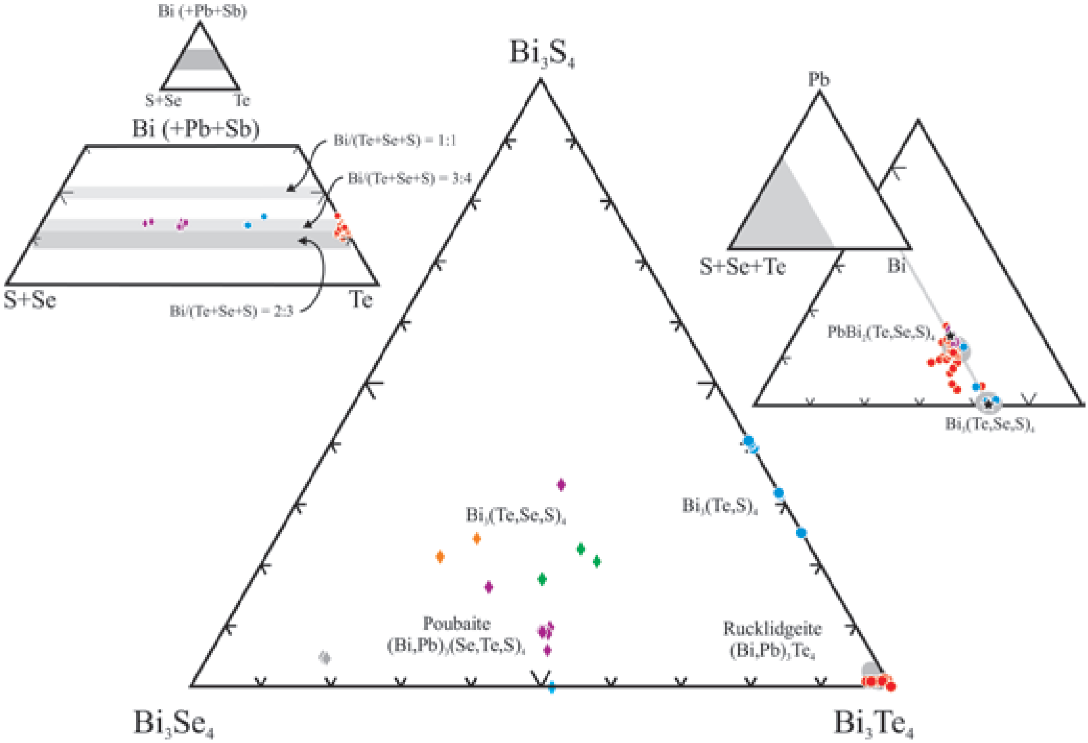

FIG. 15. Summary plots for rucklidgeite (red circles) and poubaite (purple rhombs) in the subsystem Bi_3Te_4–Bi_3Se_4–Bi_3S_4. Inset (upper right) shows correlation between Pb and Bi in rucklidgeite between Bi_3Te_4 and $PbBi_2Te_4$. Rucklidgeite data from Rucklidge (1969), Lipovetskiy *et al.* (1977, 1979), Zav'yalov & Begizov (1977), Harańczyk (1978), Harris *et al.* (1983), Sakharova *et al.* (1986), Criddle & Stanley (1986, 1993), Pašava *et al.* (1986), Spiridonov *et al.* (1989), McQueen (1990), McQueen & Solberg (1990), Kase *et al.* (1993), Maglambayan *et al.* (1998), Moloshag *et al.* (2002). Poubaite data from Čech & Vavřín (1978, 1979), Johan *et al.* (1987). Unnamed $Bi_3(Te,S)_4$ of Zav'yalov *et al.* (1978), Kojonen *et al.* (1991), Spiridonov (1995) and Moloshag *et al.* (2002) shown as blue circles. Unnamed $Bi_3(Te,Se,S)_4$ of Shimizu *et al.* (1995), probably a Pb-free poubaite, is shown as green rhombs. Unnamed $Bi_3(Te,Se,S)_4$ of Yefimov *et al.* (1989), also probably poubaite, is shown as orange rhombs. Mineral 'C' of Miller (1981) is marked by a blue rhomb. An unnamed Se-phase (Johan *et al.* 1987) is shown with gray rhombs. Grey areas on main plot and inset (right) are compositional fields for Pb-free and Pb-bearing rucklidgeite from Larga, Romania (Cook & Ciobanu 2004).

Poubaite, $(Bi,Pb)_3(Se,Te)_4$ [the formula has also been given as $PbBi_2Se_2(Te,S)_2$], is considered as being isostructural with rucklidgeite, sharing trigonal symmetry and the $R\bar{3}m$ space group. The mineral is rare: apart from the type locality (Oldřichov, Czech Republic; Čech & Vavřín 1978), we are aware of only two additional confirmed occurrences: Otish Mountains, Quebec (Johan *et al.* 1987) and a second, without analytical data, the Kawazu mine, Rendaiji, Honshu, Japan (Shikazono *et al.* 1990). The empirical formula of holotype poubaite is $Pb_{1.11}Bi_{1.94}Cu_{0.10}(Se_{1.97}Te_{1.37}S_{0.66})_{\Sigma 4.00}$. Other $Bi_3(Te,Se,S)_4$ compositions, though differing compositionally from type poubaite (*e.g.,* Čech & Vavřín 1979, Miller 1981, Yefimov *et al.* 1988) are also probably poubaite, as is possibly a further very Se-rich phase also mentioned by Johan *et al.* (1987). All are plotted on Figure 15. The synthetic compound $PbBi_2Se_4$ was studied by electron diffraction (Agaev & Semiletov 1968) and seems to be isostructural with Bi_3Se_4 (Sn_3As_4 type).

OTHER STOICHIOMETRIES

Baksanite, $Bi_6Te_2S_3$ was described (Pekov *et al.* 1996) from the type occurrence, the Baksan W–Mo skarn deposit, Tyrny'uaz, North Caucasus, Russian Federation [empirical formula, $(Bi_{5.77}Pb_{0.16}Sb_{0.22})_{\Sigma 5.95}(Te_{1.77}S_{3.27})_{\Sigma 5.04}$]. The mineral has not been subsequently described from other localities. Recently, a Pb-bearing variety, $(Bi_{4.94}Pb_{0.96})_{\Sigma 5.90}(Te_{2.03}S_{3.06})$, has been described in a sample from the same deposit by Bindi & Cipriani (2003). These authors confirmed the trigonal ($P\bar{3}m1$) symmetry of baksanite. A phase with a similar stoichiometry, $(Bi,Pb)_6(Se,S,Te)_5$, is mentioned in a recent publication by Semenyak *et al.* (2005).

Apart from the established stoichiometric groupings that we have discussed above, there exist numerous analytical data in the literature suggestive of additional, unnamed phases with alternative stoichiometries. Many of these can, however, be readily assigned to known phases. Examples include $Bi_8(Te_7S_5)_{\Sigma 12}$ and $Bi_8(Te_{7.15}S_{4.48})_{\Sigma 12.63}$ of Cioflica *et al.* (1997), which are most likely to be tetradymite. In other cases, the compositions can be assigned to minerals that were approved and named after the data were originally published (*e.g.,* ingodite, rucklidgeite, telluronevskite); such cases have been included in the datasets discussed above. Explanations for other data can be sought in poor analytical quality, interference from adjoining minerals, and other reasons. There do, nevertheless, remain a small number of compositions that may well pertain to possible new, as yet incompletely characterized minerals. Two stoichiometric groups stand out: $Bi_2(Te,Se,S)$ and $Bi_3(Te,Se,S)_2$.

In the first group, Bi_2Te has been reported by Gamanyin *et al.* (1980, 1982), Goncharov *et al.* (1984), Huang *et al.* (1991), Luukkonen (1994) and Gu *et al.* (2001). Some of the "wehrlite" compositions of Cabri & Laflamme (1976) and the "bismuthian tsumoite" of Dobbe (1993) have similar compositions. Sulfur- and selenium-bearing derivatives are $Bi_2(Te,Se,S)$ (Kontoniemi *et al.* 1991) and $Bi_6(Te,Se)_3$ (Gu *et al.* 2001). In the case of Bi_2Te, the observations of Gu *et al.* (2001) are to be noted: "…. the consistent "2:1" stoichiometry and slight difference in optical properties compared to hedleyite, joséite-B or pilsenite, lead us to infer that this may be an independent mineral". The small size of the grains (<10 µm) prevents further work aimed at establishing if this, and analogous $Bi_2(Te,Se)_3$ phases, are additional members of the group. Our own observations are similar: Bi_2Te is conspicuous within several of the Romanian skarn deposits, and in numerous other reduced gold deposits, but it rarely exceeds a few µm in diameter. We would further reason that the incidence of Bi_2Te in nature and in synthetic studies (Abrikosov & Bankina 1958, Okamoto & Tanner 1990) is sufficiently great to suggest that a discrete mineral with this composition exists.

The phase Bi_3Te_2 has been reported by Kukovsky & Lazarenko (1959, cited by Zav'yalov *et al.* 1978), Sarkar & Deb (1969), Cabri & Laflamme (1976), Strozkay & Nagy (1982) and Garuti & Rinaldi (1986). Sulfur-bearing derivatives include the phases Bi_3TeS, $Bi_3(Te_{1.33}S_{0.67})_{\Sigma 2}$ and $Bi_3(Te_{0.5}S_{1.5})_{\Sigma 2}$ reported by Godovikov *et al.* (1970, 1971a, b; minerals L, K and P, respectively) and $Bi_{2.97}(Te_{1.34}S_{0.69})_{\Sigma 2.03}$ (Alechevskiy 2002). To these can be added phases listed in the reviews of Zav'yalov & Begizov (1978, 1983b) that are considered similar, but not identical, to joséite-A or joséite-B. Such compounds are close to Bi_3TeS or are part of the series $Bi_3(Te,S)_2$, including $Bi_{2.90–3.07}(Te_{1.13–1.28}S_{0.62–0.77})_{\Sigma 1.88–2.01}$ of Ontoev *et al.* (1974). Lawrence (1998) mentioned a phase with the empirical formula $Bi_{10}Te_2S_5$.

In the course of our own investigations of bismuth tellurides in Băiţa Bihor and other Romanian skarns, we have also noted Bi_3Te_2 as well as $Bi_3Te(S,Se)$. In both cases, the compositions could be readily dismissed, invoking conventional thinking, as "disordered" members of the tsumoite – ingodite – nevskite series. The regularity of the stoichiometry, however, is an adequate reason not to discount the possibility of a subgroup of independent, stable minerals with this stoichiometry.

We have also studied "wehrlite" from a locality in the Ukrainian Transcarpathians (Ciobanu *et al.*, in prep.) and note three distinct phases with Bi_3X_2 stoichiometry: $Bi_3(S,Se)_{1.33}Te_{0.67}$, $Bi_3Te_{1.33}(S,Se)_{0.67}$ and $Bi_3Te(S,Se)$, strongly suggesting the existence of ordered phases, with separation of Te and (S,Se) into specific structural sites.

"Protojoséite" is considered a questionable species (Jambor 1984). Zav'yalov & Begizov (1983b) plotted published compositions of "protojoséite", which differ markedly from joséite-B and do not overlap with compositions of that mineral, with which it may coexist. The formula for "protojoséite" was given as $Bi_3(Te,S)_2$, but there is noticeable variation in Bi:(Te + S) value in the dataset given by Zav'yalov & Begizov (1983b), prompting the general formula $Bi_{3+x}Te_{1-x-y}S_{1+y}$, where $-0.02 < x < 0.14$ and $-0.05 < y < 0.17$. Although some authors have chosen to consider the phase as nonstoichiometric joséite-B (or even joséite-A), the distinct stoichiometry, close to 3:2 rather than 4:3, has contributed to its status as a distinct but insufficiently defined phase. X-ray data for "protojoséite" presented by Zav'yalov & Begizov (1983b) from the "type locality" of Băiţa Bihor, Romania, as well as additional material from the Malishevski Izumrydrye pit, Ural Mountains, are not unequivocal either. The X-ray spectra closely resemble those of joséite-B, although they are not identical. Bayliss (1991) assigned a $P\bar{3}m1$ structure to "protojoséite" and attributed to it the probable formula $Bi_5(Te,S)_4$, which is not consistent with the above analytical data.

Reported compositions that can be assigned to these two subgroups have been summarized in Figure 16. We have chosen to plot "protojoséite" in the potential Bi_3Te_2–Bi_3Se_2–Bi_3S_2 isoseries, in part because we have observed a $Bi_3(Te,S)_2$ phase in specimens from Băiţa Bihor that is clearly distinct from joséite-B.

Whereas it is not difficult to consider the binary phases Bi_2Te and Bi_3Te_2 as nonstoichiometric tsumoite or hedleyite [*cf.* overlap with datasets of "wehrlite" in Cabri & Laflamme (1976) and "bismuthian tsumoite" in Dobbe (1993)], it is harder to explain the compositions of the S- and Se-bearing compositions within these datasets simply as substituted nevskite and ingodite, given the consistent stoichiometry, with 60 and 66.6 mol.% Bi, respectively. The present authors wish to be neither judge nor jury concerning the true identity of the phases represented by these published compositions, but we would suggest that natural phases within the subsystems (isoseries) Bi_2Te–Bi_2Se–Bi_2S and Bi_3Te_2–Bi_3Se_2–Bi_3S_2 probably exist; note that both stoichiometries have been synthesized experimentally (*e.g.*, Okamoto & Tanner 1990, Okamoto 1994).

Vihorlatite, $Bi_{8+x}(Se,Te,S)_{11-x}$, was approved as a new mineral species in 2000. The type locality is given as Poruba, Vihorlat Mountains, Slovakia. A description was published by Skála *et al.* (2007), with the formula given as $Bi_{24}Se_{17}Te_4$. This would appear to be the first member of a Bi_8X_7 isoseries.

Other stoichiometries reported include the Bi_2Te_5 ($BiTe_2$?) phase of Aksenov *et al.* (1968a, c), interpreted as "disordered" tsumoite by Bayliss (1991), but surely requiring re-examination. Okamoto & Tanner (1990) reported such a composition as a metastable phase in the binary system Bi–Te. The same applies to $BiSe_2Te$ (Nekrasov 1996).

DISCREDITED AND NON-ACCEPTED MINERALS

The literature contains numerous references to additional "minerals" and, not uncommonly, the unfortunate practice of using non-approved names to describe mineral compositions different from those of known minerals can be seen. This eclectic group includes mixtures, insufficiently characterized minerals, possible nonstoichiometric "variants" of known minerals, and also a number of phases of uncertain status. Some have already been discussed. The following are included here for the sake of clarity and completeness.

"Grünlingite" was first mentioned from Carrock Fell, Cumbria, England by Rammelsberg (1853) and later defined by Muthmann & Schröder (1898) as having the composition Bi_4TeS_3. Examination of the "type" material by Peacock (1941) proved inconclusive, but the phase was considered very close, if not identical to "joséite". A similar composition was also described by Koch (1948) and subsequently analyzed by Grasselly (1948); these analyses also gave Bi_4TeS_3. The "type" material was re-examined by Zav'yalov & Begizov (1981a, b, 1983b), but the presence of a bismuth telluride with this stoichiometry was not confirmed. The conclusion reached was that a discrete phase with this composition does not exist, and the type material is a mixture of two or more sulfotellurides of bismuth (joséite-A, ingodite), possibly also with admixed bismuthinite. Subsequent electron-microprobe analysis of the material (summarized in Cooper & Stanley 1990) showed "grünlingite" to consist of a mixture of finely intergrown joséite-A, joséite-B, ingodite and bismuthinite. The samples also contain krupkaite, cosalite and native bismuth. Additional compositions of the same material were given in Table 6. Given the nonstoichiometry seen in joséite-A at higher temperatures ($Bi_{4-x}Te_{1+x}S_2$; Yusa *et al.* 1979), it is plausible that the "grünlingite" data may, in fact, represent the products of decomposition of nonstoichiometric, high-temperature joséite-A. Kudrina *et al.* (1986) published results of a single electron-microprobe analysis of a phase from the Bayanskoye deposit in northern Kazakhstan, which show a Bi: (Te + S + Se) stoichiometry between that of "grünlingite" (3:3) and joséite-A (4:3).

"Platynite", $PbBi_2(Se,Se)_3$ (Flink 1910), was long considered a questionable species (Nikitin *et al.* 1989, Bayliss 1991) and has subsequently been formally discredited as a mixture of laitakarite and selenian galena (Holtstam & Söderhielm 1999).

"Oruetite", Bi_8TeS_4, was described by Piña de Rubies (1919) from the Ronda massif, Spain, and later said to be identical to "grünlingite" (Garrido & Feo 1938). Although the name has been used more recently to describe a phase with such a composition (*e.g.*, Ontoyev *et al.* 1974), the original Spanish samples are recognized as inhomogeneous (*e.g.*, Peacock 1941). In

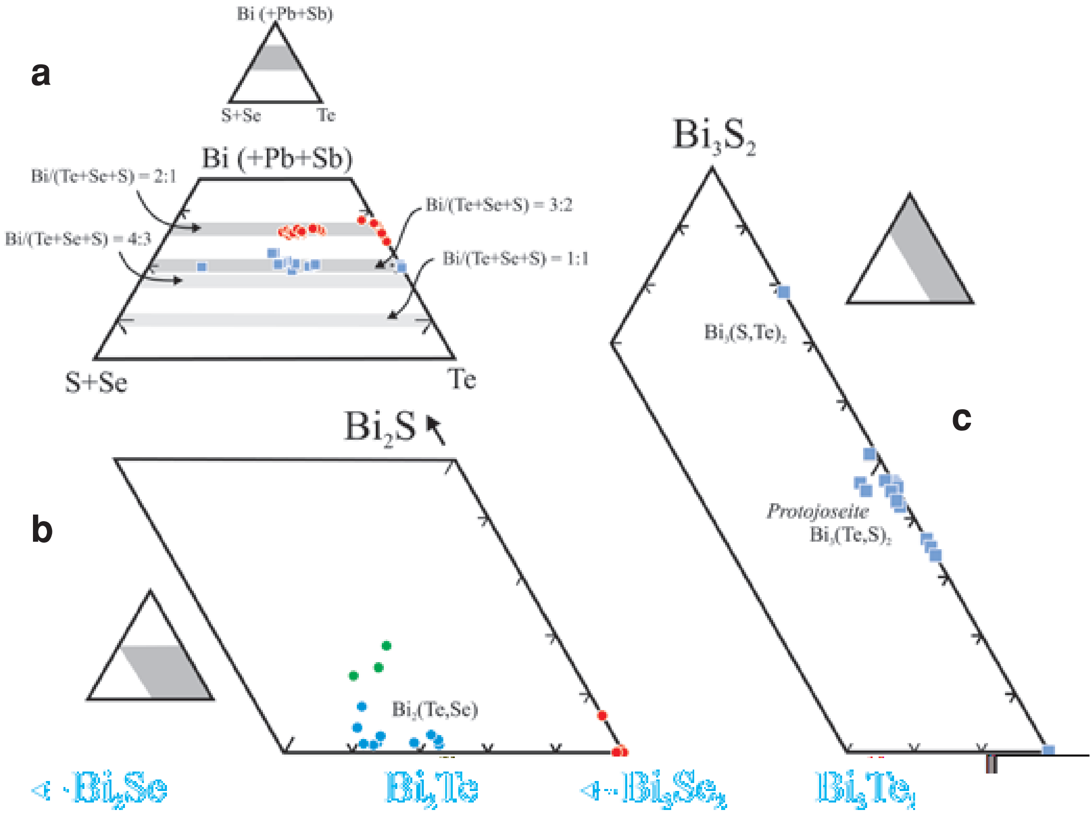

FIG. 16. Summary plot for unnamed phases in the subsystems Bi_2Te–Bi_2Se–Bi_2S and Bi_3Te_2–Bi_3Se_2–Bi_3S_2. (a) Plot of phases in both subsystems in terms of Bi(+ Pb + Sb)–(S + Se)–Te. (b) Bi_2Te–Bi_2Se–Bi_2S subsystem. Data for Bi_2Te from Gamyanin *et al.* (1980, 1982), Goncharov *et al.* (1984), Huang *et al.* (1991), Luukkonen (1994) and Gu *et al.* (2001); for $Bi_2(Te,Se,S)$ (green circles) from Kontoniemi *et al.* (1991) and for $Bi_2(Te,Se)$ (blue circles) from Gu *et al.* (2001). (c) Bi_3Te_2–Bi_3Se_2–Bi_3S_2 subsystem. Protojoseite from Zav'yalov & Begizov (1983b). Data for Bi_3Te_2 from Kukovsky & Lazarenko (1959) cited by Zav'yalov *et al.* (1978), Sarkar & Deb (1969) and Sztrozkay & Nagy (1982); data for $Bi_3(TeS)_2$ and $Bi_3(STe)_2$ from Godovikov *et al.* (1970, 1971b).

the system Bi–Te–Se–S, however, unless such material is clearly and unequivocally shown to be a mixture of known minerals and can be discredited (*e.g.*, "csiklovaite"; Bayliss 1991 or "platynite"; Holtstam & Söderhielm 1999), it can remain extremely difficult to definitively prove that phases with other compositions or stoichiometries do not (or cannot) exist, and accordingly expunge such names from the literature.

MINERALS WITH VARIABLE STOICHIOMETRY AND CONTAINING ESSENTIAL PB

A group of tellurosulfide minerals contains essential Pb as well as Bi, and both Te and S. Although part of the tetradymite group (Strunz & Nickel 2001) and sharing similar structures and mode of occurrence with other minerals in the groups discussed formally above, they qualify as sulfosalts (Moëlo & Makovicky 2006). Inasmuch as poubaite and plumboan rucklidgeite (see above) are commonly Pb-bearing, and other minerals (like tetradymite, laitakarite, joséite-A, joséite-B) may also contain significant Pb, a brief account of other minerals of the subgroup containing essential Pb belongs in the present contribution.

The Pb–Bi compounds are structurally distinct from the (ideally) Pb-free compounds. With the exception of the study by Zhukova & Zaslavskii (1971), however, single-crystal X-ray studies are lacking for these compounds. Aleksite, $PbBi_2Te_2S_2$ (Lipovetskiy *et al.* 1977, 1979, Spiridonov *et al.* 1989, Bevins & Stanley 1990, De Souza Lima *et al.* 1996, Ueno *et al.* 1996) and saddlebackite, $Pb_2Bi_2Te_2S_3$ (Clarke 1997), together with an additional compound, "phase C" of Lipovetskiy *et al.* 1977, 1979 ($PbBi_4Te_4S_3$), are suggested to belong to a single accretional chemical series with the general formula $Pb_nBi_4Te_4S_{n+2}$ (Cook *et al.* 2007). "Phase C", aleksite, $Pb_3Bi_4Te_4S_5$ and saddlebackite have previously been reported as synthetic products (Phases D, E, F and J) in experiments at 500°C (Liu & Chang 1994). Unit-cell data provided by Liu & Chang (1994) support the existence of a chemical series, but X-ray data on natural specimens are required to validate the hypothetical model proposed by Cook *et al.* (2007). In this model, the unit cell of aleksite comprises three seven-atom layers (each Te–Bi–S–Pb–S–Bi–Te), and "phase C" consists of a combination of one five-atom tetradymite unit (as in the simple Bi–Te–Se–S compounds above) and one seven-atom layer. Although no single-crystal data exist for saddlebackite, unit-cell data on phase J (Liu & Chang 1994) suggest that saddlebackite is a superstructure consisting of a single nine-atom layer, and $Pb_3Bi_4Te_4S_5$ may be regarded as a combination of one seven-atom and one nine-atom layer. Investigations of complex sulfosalt-telluride assemblages from Iilijärvi, southwest Finland (Ciobanu *et al.* 2002, Cook *et al.* 2007) have revealed possible additional Pb-rich members of this series, with compositions in the range between $Pb_5Bi_4Te_4S_7$ and $Pb_7Bi_4Te_4S_9$. Characteristic of all these minerals are fine intergrowths and lamellar banding, resulting in poor stoichiometry. This may readily be linked to the loss of periodicity and the difficulty of building thick Pb-filled slabs.

Kochkarite, $PbBi_4Te_7$ (Spiridonov *et al.* 1989) corresponds to the synthetic phase M of Liu & Chang (1994). Synthetic $PbBi_4Te_7$ (and $PbBi_2Te_4$) were obtained in experiments of the system $PbTe–Bi_2Te_3$ by Chami *et al.* (1983). The structure can be considered in terms of alternations of seven-atom (Te–Bi–Te–Pb–Te–Bi–Te) and five-atom (Te–Bi–Te–Bi–Te) layers (Petrov & Imamov 1970). Imai & Watanabe (2003) have satisfactorily determined the electronic structure of $PbBi_4Te_7$, based on such a "75" structure.

Although much of the early data favoring the seven-atom layer structure for $PbBi_2Te_4$ (rucklidgeite), with possible extension to aleksite and other tellurosulfides, is powder-diffraction data with typically high values (>15%) of *R* (Petrov & Imamov 1970, Imamov *et al.* 1970, Zhukova & Zaslavskii 1976), corroborative single crystal and HRTEM data are available for the directly analogous and well-characterized nGeTe•mBi$_2$Te$_3$ compounds (Kuypers *et al.* 1988, 1989, Frangis *et al.* 1989, Shelimova *et al.* 1996, 2000, 2001, 2004, Karpinsky *et al.* 1998, Kuznetsova *et al.* 2000, Konstantinov *et al.* 2001).

Karpinsky *et al.* (2002) identified three additional layered compounds, $PbBi_6Te_{10}$, $PbBi_8Te_{13}$ and $Pb_2Bi_6Te_{11}$, and proposed that these belong to a homologous series nPbTe•mBi$_2$Te$_3$, with $n = 1, 2$, and m ranging from 1 to 4.

Babkinite was introduced as a new mineral with the formula $Pb_2Bi_2(S,Se)_3$ (Bryzgalov *et al.* 1996). The type locality is the high-temperature Nevskii Sn–W deposit, Magadan District, Russia. Type babkinite gives the empirical formula $Bi_{1.95}Pb_{1.99}Ag_{0.01}Sb_{0.01}S_{1.74}Se_{1.30}$. The mineral has not been reported from other deposits.

An unnamed phase, $Pb_5Bi_5Te_3S_7$, was reported to be associated with kochkarite from Kochkar (Spiridonov *et al.* 1989). Selenium-bearing compounds with compositions close to $Pb_2Bi_2(S,Se)_3$ and $(Bi,Pb)_3(S,Se)_4$ were reported by Sakharova *et al.* (1993). A synthetic compound with composition close to $PbBi_4Te_3Se_4$, with orthorhombic symmetry, was studied by Kichambare *et al.* (1997).

DISCUSSION

In this contribution, we have contrasted the need for a functional system of nomenclature and classification based upon stoichiometry, with the inherent character of the Bi–Te–Se–S compounds to form a number of (complete or partial) solid-solution series: $Bi_2(Te,Se,S)_3$, $Bi_3(Te,Se,S)_4$, $Bi(Te,Se,S)$, $Bi_4(Te,Se,S)_3$, *etc.*, each derived from discrete variants in stacking sequence (= homologue types). Although Bi-for-Te(Se) substitution may yet be unequivocally demonstrated to play a significant role in natural specimens, we can still choose to regard each of the above as a discrete isoseries, each with unique integer values of N1 and N2 in the general series $Bi_{N1}(Te,Se,S)_{N2}$.

Many of the numerous compounds successfully synthesized in the systems Bi–Te and Bi–Se appear to have no natural analogues. It is fair to say, however, that it may be difficult or impossible to recognize many of these in nature, owing to overlapping ranges of substitution and solid solution, the potential for stacking disorder, precision of the electron-microprobe data and potential analytical error. This is compounded by the lack of single-crystal X-ray data. Such problems are particularly valid for the central parts of the system Bi–Se, where a large number of phases with individual combinations of stacking could theoretically exist in nature, for example, Bi_6Te_5, Bi_8Te_7, Bi_8Te_9, Bi_6Te_7 and Bi_4Te_5. Although closely related, each of these will be structurally distinct from BiTe, in the same way that Bi_2Te_3 or Bi_4Te_3 also are distinct from BiTe, and would therefore warrant distinct mineral status at a point in the future when they can be completely characterized. Pragmatists may argue that identification of large numbers of new mineral phases, virtually indistinguishable from one another in terms of composition, may disrupt any reasonable system of enforceable classification. Nevertheless, we note that precedents have already been set, for example, in the bismuthinite–aikinite series (*e.g.*, Makovicky *et al.* 2001). In this series, well-defined compounds with stoichiometric formulae are identified, but many natural samples give nonstoichiometric compositions. Electron-microprobe data are not sufficient to name such compounds. Instead, a substitution coefficient is used to give the position of the analysis within the series.

The application of high-resolution transmission electron microscopy to natural bismuth chalcogenides of various compositions is needed to clarify many of the issues outlined here, as is high-precision single-crystal X-ray data for natural minerals and problematic intermediate compositions. In their discussion of the correlation between composition and structure of laitakarite, Nenasheva *et al.* (1988) noted that two phases with slightly different stoichiometries (Bi_6Se_5, Bi_8Se_7), but otherwise similar to laitakarite, have larger unit-cells, and thus are probably distinct from laitakarite (or indeed nevskite).

In nature, $Bi_2(Te,Se,S)_3$ minerals, especially tetradymite and tellurobismuthite, are the most common statistically, closely followed by $Bi_4(Te,Se,S)_3$ minerals and, then, by Bi(Te,Se,S) and $Bi_3(Te,Se,S)_4$ minerals. These have relatively simple structures in common, involving low-integer combinations of Bi_2 and $Bi_2(Te,Se,S)_3$ units. We have made a plausible case for the existence of two additional isoseries, $Bi_2(Te,Se,S)$ and $Bi_3(Te,Se,S)_2$. Minerals of the $Bi_4(Te,Se,S)_3$ isoseries, with alternating Bi_2 and Bi_2Se_3 layers, are stable at Bi-rich compositions and commonly coexist with native bismuth. Other structures still richer in Bi, *e.g.,* $Bi_3(Te,Se,S)_2$ or $Bi_2(Te,Se,S)$, appear to be only rarely preserved in nature. Similarly, minerals of the $Bi_2(Te,Se,S)_3$ isoseries are more stable than others at the Te-rich end of the spectrum.

In this contribution, we have stressed that all phases in the system Bi–Te–Se–S, whether natural or synthetic, can be considered to belong to a single homologous series built by variations of Bi_2X_3 and Bi_2 units. When considering Pb-bearing compounds, we have introduced the concept of seven- and even nine-layered lamellae. Nevertheless, the introduction of seven- and even nine-layer units as structural defects into Bi_2Te_3 or Bi_2Se_3 can be considered as plausible (Frangis *et al.* 1989, 1990). Degrees of nonstoichiometry in synthetic Bi_2X_3 compounds may be explained in terms of lattice point-defects (antisite defects; *e.g.*, Horák *et al.* 1990), impurities and vacancies, but with increased amounts of excess Bi atoms, the incorporation of larger units can be invoked (*e.g.*, Horák *et al.* 1992, Plecháček *et al.* 2002). Investigators of synthetic compounds have also documented atomic-scale diffusion of Se in Bi_2Te_3 by antisite defects and thermal vacancies (*e.g.,* Scherrer *et al.* 1988, Chitroub *et al.* 2000). The significance of these findings for compositional variation in natural specimens is unknown.

The basic data on the tellurides and selenides of bismuth have largely come from inorganic chemists or physicists interested in the compounds for their thermoelectric properties. Geologists and mineralogists need to address many of the open questions regarding the internal structures of natural phases, documentation of solid solutions, the stabilities of these compounds, their association, paragenesis and conditions of formation, including their application as redox indicators. In a companion paper, we will address a number of these issues, at least in cases where reliable data can be established. In particular, we will address the common misconception that the tellurides of bismuth are typically "low-temperature" minerals.

In this review, we have illustrated the considerable advance in understanding these minerals that has been afforded by the application of modern investigative techniques. Nevertheless, very many uncertainties and incongruencies remain to be solved in the future. The evolution in our technical ability to fully characterize smaller and smaller grains may yet permit some of the outstanding problems to be resolved. Results of such investigations may necessitate a revision of the way in which these mineral groups are classified. As mentioned above, new ways to adequately describe the compositions of these minerals may need to be developed. Some revisions to the nomenclature may be required.

Lastly, given the frequent change of mineral names and formulae, redefinitions, uncertainty concerning various phases, and the common-place presence of microscopic to submicroscopic intergrowths among Bi–Te–Se–S minerals, the labeling of specimens in many museum collections should be doubted unless corroborative microanalytical data are available. We are convinced that many of the uncertainties illustrated in this contribution could be rectified if older, generally coarser material is made available for restudy.

CONCLUSIONS

1. We have demonstrated that the system of classification used for the bismuth chalcogenides on a stoichiometric basis is broadly correct, both with respect to the underlying structures and in practice. Four principal isoseries exist in nature and contain named minerals, Bi_2Te_3–Bi_2Se_3–Bi_2S_3, Bi_4Te_3–Bi_4Se_3–Bi_4S_3, BiTe–BiSe–BiS and Bi_3Te_4–Bi_3Se_4–Bi_3S_4. Each of these is, in turn, a stacking variant in a general homologous series $Bi_{N1}(Te,Se,S)_{N2}$, where N1 and N2 are integer values. Cases can be made for the existence of further isoseries in nature, Bi_2Te–Bi_2Se–Bi_2S, Bi_3Te_2–Bi_3Se_2–Bi_3S_2, Bi_3Te_4–Bi_3Se_4–Bi_3S_4, Bi_6Te_5–Bi_6Se_5–Bi_6S_5, *etc.*, although further characterization, based in particular on single-crystal X-ray-diffraction data, is essential to verify this.

2. Solid solution is not unlimited within each isoseries, but is closely governed by a series of substitution mechanisms, governed by structural continuity. The Se $\rightleftharpoons$ S substitution is prevalent in all series, with well-developed solid-solution series, *e.g.,* between tetradymite and kawazulite, joséite-B and unnamed Bi_4Te_2Se. The Te $\rightleftharpoons$ Se(S) substitution appears more restricted. Binary Bi-tellurides in each isoseries (tellurobismuthite, pilsenite, tsumoite, hedleyite) show only moderate Te $\rightleftharpoons$ Se substitution, and negligible Te $\rightleftharpoons$ S substitution.

There is no significant solid-solution between *e.g.*, tellurobismuthite and tetradymite, pilsenite and joséite-B. The Bi ⇌ Te(Se,S) substitution ("disordering" in the sense of Bayliss) may satisfactorily explain variations in Bi:(Te + Se + S) ratio in some minerals (hedleyite, tsumoite), but stacking disorder is also an efficient mechanism to account for apparent nonstoichiometry.

3. Several potential "new" mineral species can be identified in the known isoseries, *e.g.*, Bi_4Te_2Se, $Bi_4Te(Se,S)_2$, Bi_3Te_2Se and $Bi_3(Te,S,Se)_4$. A large number of additional "phases" have been synthesized or predicted in the binary systems Bi–Te and Bi–Se, and many of these have no natural analogues. Others may exist, but have not been detected, owing to their compositional proximity to named minerals, especially in the central region of the system with Bi/(Te + Se + S) values close to unity. There is a need for HRTEM and single-crystal X-ray work on natural specimens to resolve such issues.

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Lastly, we should mention that in this review, we have attempted to take into account all published compositional data on phases in the system. We recognize that there may still be valuable data in conference abstracts, in theses, and in publications, which we have either not been aware of, or which were inaccessible to us for reasons of language or other reasons. We, therefore, express our apologies to any authors who feel that their work has been ignored, and request that relevant information be forwarded to us.

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