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CRYSTALLOGRAPHY, MINERAL CHEMISTRY AND CHEMICAL NOMENCLATURE OF GOLDFIELDITE, THE TELLURIAN MEMBER OF THE TETRAHEDRITE SOLID-SOLUTION SERIES

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ABSTRACT

This comprehensive review on goldfieldite, $Cu_{10}Te_4S_{13}$, and tellurian phases of the tetrahedrite solid-solution series (tetrahedrite$_{ss}$), contains a summary of crystallographic properties and compositional data. A new classification scheme for these minerals is proposed. Furthermore, the association of these minerals to specific ore environments is discussed. The bond angles and the optical properties of goldfieldite and tetrahedrite are very similar. The cell dimension of goldfieldite is intermediate between that of tennantite and tetrahedrite; thus it is strongly controlled by the ionic radius of Te. As expected, Cu vacancies in goldfieldite reduce the size of the unit cell. The best electron-microprobe analyses are obtained when S is standardized on tetrahedrite, bismuthinite or stibnite. The preferred procedure for calculating structural formulae of tellurian examples of the tetrahedrite$_{ss}$ from electron-microprobe results is based on total numbers of atoms, as this distributes possible analytical errors over all elements. Owing to the occurrence of vacancies in goldfieldite, the calculation should be based on 29 atoms per formula unit (*apfu*) for minerals with 2 or less Te *apfu* [$Te/(Te + As + Sb + Bi + Te) < 0.5$]. For more Te-rich compositions, formula calculation on the basis of $29 - 4[Te/(Te + As + Sb + Bi) - 0.5]$ *apfu* is recommended. A review of available electron-microprobe data on goldfieldite and tellurian members of the tetrahedrite$_{ss}$ supports previous observations on the substitutions. For up to 2 Te *apfu*, substitution of Te^{4+} for $(As, Sb, Bi)^{3+}$ is coupled with Cu^+ for $(Fe,Zn)^{2+}$ substitution, whereas higher levels of Te result in vacancies (reduced Cu contents). A nomenclature grid for goldfieldite and the other Cu-dominant examples of the tetrahedrite$_{ss}$ is proposed on the basis of their semimetal content. The name "goldfieldite" is reserved for those compositions of the tetrahedrite$_{ss}$ that contain more than 3 *apfu* of Te. For those minerals with 2 to 3 *apfu* of Te, modifying adjectives such as arsenoan, stiboan or bismuthoan should be used, according to the second most abundant element. The remaining tellurian minerals of the tetrahedrite$_{ss}$ should be named according to the most abundant semimetal (tennantite for the As-rich member, tetrahedrite for the Sb-rich one) preceded by "tellurian", provided that at least 1 *apfu* of Te is present. Most of these tellurian minerals of the tetrahedrite$_{ss}$ are found in high-sulfidation epithermal Au deposits, regardless whether they are As- or Sb-rich. A few cases have been reported from porphyry Cu and volcanogenic massive sulfide deposits.

Keywords: goldfieldite, tetrahedrite solid-solution series, electron-microprobe data, substitutions, structural formula, nomenclature, ore deposits.

SOMMAIRE

Cette évaluation compréhensive de la goldfieldite, $Cu_{10}Te_4S_{13}$, et des phases riches en tellure de la solution solide dite tétraédrite$_{ss}$, contient un sommaire des propriétés cristallographiques et des intervalles de composition. Nous proposons un nouveau schéma de classification pour ces minéraux. De plus, nous discutons de l'association de ces minéraux avec des contextes de minéralisation spécifiques. Les angles des liaisons et les propriétés optiques de la goldfieldite et de la tétraédrite sont très semblables. Le paramètre réticulaire de la goldfieldite est intermédiaire entre celui de la tennantite et celui de la tétraédrite; il est donc fortement dépendent du rayon ionique du Te. Tel que prédit, les lacunes dans la position Cu réduisent le paramètre réticulaire. Les meilleures données obtenues par microsonde électronique sont attendues lorsque la standardisation pour le soufre s'effectue sur la tétraédrite, la bismuthinite ou la stibnite. Le protocole recommandé pour le calcul d'une formule structurale de cristaux de la série tétraédrite$_{ss}$ riche en Te à partir des résultats de microsonde est fondé sur le nombre total d'atomes, ce qui distribue les

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erreurs analytiques possibles sur tous les éléments. Vu la présence de lacunes dans la goldfieldite, le calcul devrait supposer 29 atomes par unité formulaire (*apuf*) pour les cas où le Te équivaut à 2 *apuf* ou moins [Te/(Te + As + Sb + Bi + Te) < 0.5]. Dans le cas de compositions plus enrichies en Te, le calcul de la formule se fait sur une base de 29 – 4[Te/(Te + As + Sb + Bi) – 0.5] *apuf*. Un examen des données disponibles de microsonde électronique portant sur la goldfieldite and et les membres enrichis en tellure de la série tétraédrite$_{ss}$ étaye les observations antérieures à propos des schémas de substitution. Où le Te équivaut à 2 *apuf* ou moins, la substitution de Te^{4+} à l'ensemble (As, Sb, $Bi)^{3+}$ est couplée au remplacement de Cu^+ par l'ensemble $(Fe,Zn)^{2+}$; en revanche, les niveaux plus élevés de Te mènent à des lacunes (teneur réduite en Cu). Nous présentons une grille de nomenclature pour la goldfieldite et les autres minéraux à dominance de Cu de la série tétraédrite$_{ss}$ selon leur teneur en semimétal. Le nom "goldfieldite" est réservé pour les compositions de la série tétraédrite$_{ss}$ contenant plus de 3 *apuf* de Te. Pour les compositions contenant entre 2 et 3 *apuf* de Te, nous proposons les qualificatifs arsenical, stibié, ou bismuthifère, selon lequel des trois éléments As, Sb ou Bi est le plus enrichi. Les autres cas porteurs de Te de la série tétraédrite$_{ss}$ devraient porter le nom du minéral selon l'élément semimétallique le plus abondant (tennantite pour le membre arsenical, tétraédrite pour le membre stibié) précédé par "tellureux", moyennant au moins 1 *apuf* de Te. La plupart des exemples de la série tétraédrite$_{ss}$ enrichis en tellurium proviennent des gisements d'or épithermaux à sulfidation élevée, qu'ils soient riches en As ou en Sb. Quelques cas ont été signalés dans les gisements de cuivre de type porphyrique et les gisements volcanogéniques de sulfures massifs.

(Traduit par la Rédaction)

Mots-clés: goldfieldite, solution solide de la tétraédrite, données de microsonde électronique, substitutions, formule structurale, nomenclature, gîtes minéraux.

INTRODUCTION

Goldfieldite, ideally $Cu_{10}Te_4S_{13}$, as shown by Kalbskopf (1974) and Johnson & Jeanloz (1983), is the tellurian end-member of the tetrahedrite–tennantite solid-solution series (henceforth tetrahedrite$_{ss}$). The pure end-member has not been found as natural mineral; a maximum of 3.4 Te (out of a possible 4) atoms per formula unit (*apfu*) has been reported (Trudu & Knittel, in press). Goldfieldite, tellurian tetrahedrite and tennantite have been reported to occur in various types of ore deposit, including epithermal gold deposits, porphyry-Cu deposits, and volcanogenic massive sulfide deposits.

Goldfieldite was first described by Sharwood (1907) and later identified by Ransome *et al.* (1909) in ores from the Mohawk mine at Goldfield, Nevada. Thompson (1946) summarized the controversy regarding the interpretation of this mineral, which was thought to be possibly a mixture of different known minerals (*e.g.*, tetrahedrite + calaverite, or famatinite + bismuthinite + calaverite or sylvanite), even if it appeared to be homogeneous. For a goldfieldite specimen from the Claremont mine at Goldfield, he obtained an X-ray pattern analogous to that of tetrahedrite and hence, proved it to be a member of the tetrahedrite solid-solution series.

In his classifications of sulfosalts, Nowacki (1969) regarded goldfieldite as a variety of tetrahedrite and believed that Te substituted for S. Kato & Sakurai (1970a) were the first to infer that Te substitutes for As and Sb. Kalbskopf (1974) independently came to the same conclusion and suggested the end-member formula $Cu_{10}Te_4S_{13}$. Charlat & Lévy (1974) speculated that in goldfieldite, Te can be both a cation, substituting for As and Sb, and an anion, replacing S. Kase (1986) proposed that substitution of Te^{4+} for the trivalent semimetals (As, Sb and Bi) is compensated by an increase of monovalent atoms (mainly Cu with minor Ag) from 10 to 12 *apfu* at the expense of a decrease of the divalent elements (Fe and Zn) from 2 to 0 *apfu* leading to the formula $Cu_{12}(As,Sb,Bi)_2Te_2S_{13}$. For higher concentrations of Te, the charge balance in tetrahedrite$_{ss}$ is maintained through vacancies in one of the sites occupied by monovalent metal atoms (Kalbskopf 1974, Dmitriyeva *et al.* 1987). These relationships have been confirmed for natural goldfieldite (Trudu & Knittel 1991, in press, Shimizu & Stanley 1991).

De Medicis & Giasson (1971a) investigated the system Cu–S–Te at 340°C, but did not report the occurrence of goldfieldite. In contrast, Karup-Møller (in prep.) found goldfieldite at 350° and 450°C in his experimental investigation of the same system.

We have collected results of over four hundred electron-microprobe analyses of natural tellurian tetrahedrite$_{ss}$ plus a few from synthetic material. These data form the basis for this review, in which we also summarize and discuss the crystallography, optical properties and mineral chemistry of natural and synthetic tellurian tetrahedrite$_{ss}$. We propose a new scheme of classification based on mineral chemistry and discuss the occurrence of these minerals in different types of ore deposits.

CRYSTALLOGRAPHIC PARAMETERS

Goldfieldite, as all minerals of the tetrahedrite$_{ss}$, is cubic, a derivative of the sphalerite structure, space group $I\bar{4}3m$ (Wuensch 1964) with two formula units per cell. The formula of a half unit cell of tetrahedrite$_{ss}$ is generally given as: $M^{+}_{10}M^{2+}_{2}X^{3+}_{4}S_{13}$, where M^+ = Cu, Ag; M^{2+} = Fe, Zn, Mn, Cd, and Hg, and X = Sb, As, Bi, Te.

Half of the twelve M sites are tetrahedrally coordinated ($M1$), and the remainder are in a triangular planar

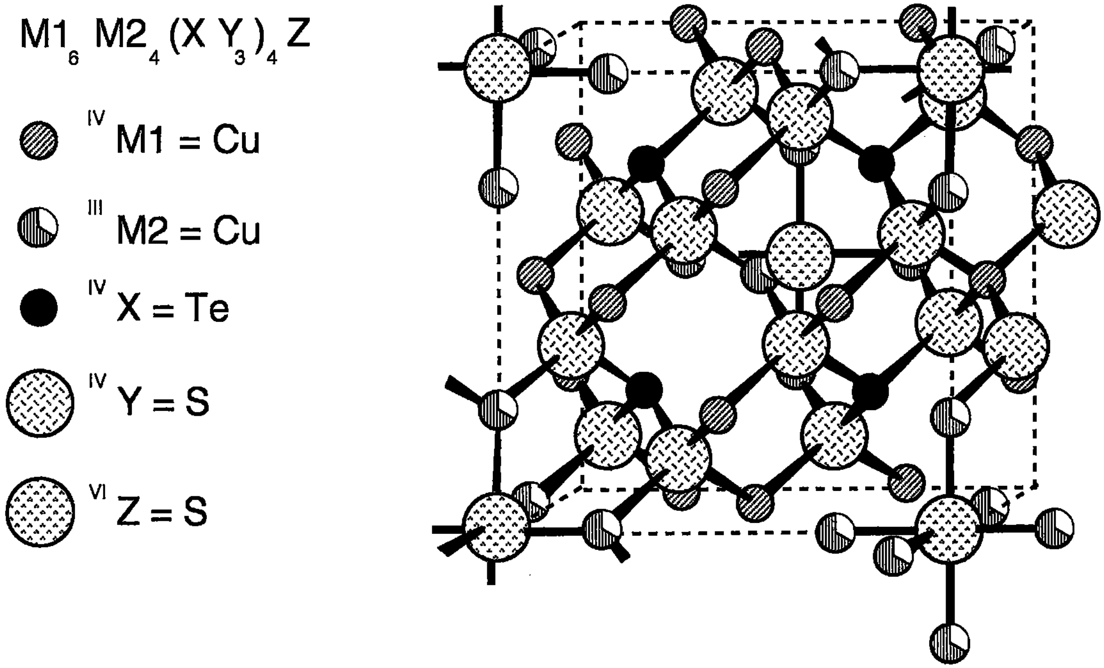

FIG. 1. Half unit-cell of pure goldfieldite, modified after Pauling & Newman (1934) and Charnock *et al.* (1989a). The *M*2 sites are depicted only 2/3 full to account for two vacancies.

coordination (*M*2). The *X* atoms occupy four 3-coordinated sites, forming a trigonal pyramid. This arrangement creates a void in the structure, the site of a lone pair of electrons originating from the *X* atoms (Moore 1981, Johnson & Burnham 1985). In end-member goldfieldite ($Cu_{10}Te_4S_{13}$), two of the *M*2 sites are vacant, and the others are occupied by monovalent atoms (predominantly Cu) to balance the charge resulting from the replacement of trivalent As, Sb and Bi by tetravalent Te (Kalbskopf 1974, Dmitriyeva *et al.* 1987). Amongst the anions, twelve (usually labeled *Y*) are in 4- fold coordination, and the 13th atom (normally referred to as *Z*) is octahedrally coordinated. A half unit-cell of goldfieldite is drawn in Figure 1; as they are supposed to be statistically occupied, the *M*2 sites are all represented as ⅔ full.

Radii for five elements relevant to this study ($^{IV}Cu^+$, $^{IV}Fe^{2+}$, $^{IV}Zn^{2+}$, Se^{2-} and S^{2-}) were given by Shannon (1981). This author also showed that the radius of S^{2-} in sulfides is independent of its coordination number. However, no radii are available for the other elements that may be incorporated in the structure. Owing to this lack of data, we must rely on radii measured in oxides and halides by Shannon (1976). Furthermore, for each element, ionic radii are available only for some of the valence and coordination numbers of interest to this study.

Estimates of ionic radii required for the interpretation of variations in bond lengths and cell dimensions in tellurian members of the tetrahedrite$_{ss}$ are based on the following observations (*e.g.*, Shannon 1976): (1) for each atomic species, the ionic radius decreases linearly with oxidation state and increases with coordination number, and (2) for Cu, Fe, and Zn, radii measured in sulfides are about 0.1 Å smaller than those in oxides. In

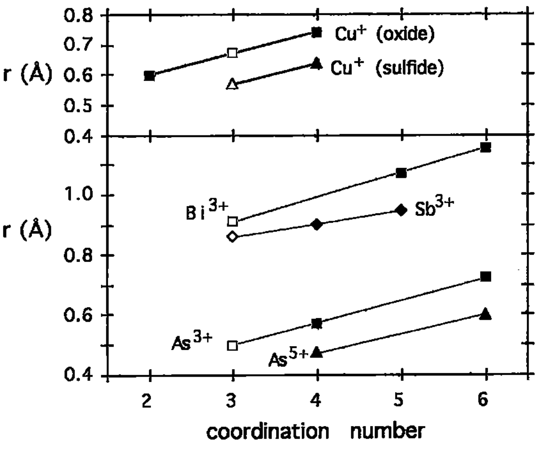

FIG. 2 . Plot of coordination number *versus* ionic radius, r, in Ångström (Å), for Cu and As, Sb and Bi. Measured radii from Shannon (1976, 1981) are shown by filled symbols, and estimated values by open symbols.

TABLE 1. IONIC RADII FOR MAJOR AND MINOR ELEMENTS REFERRED TO IN THIS WORK

Atom	oxidation state	CN	IR	SR
Cu	+1	II	0.60	-
Cu	+1	III	0.67*	**0.57***
Cu	+1	IV	0.74	**0.635**
Fe	+2	IV	0.77	**0.66**
Zn	+2	IV	0.74	**0.64**
As	+3	III	**0.495**	-
As	+3	IV	0.57	-
As	+3	VI	0.72	-
As	+5	IV	0.475	0.465
As	+5	VI	0.60	-
Te	+4	III	**0.66**	-
Te	+4	IV	0.80	0.80
Sb	+3	III	**0.86***	-
Sb	+3	IV	0.90	-
Sb	+3	V	0.94	-
Sb	+5	IV	-	0.64
Sb	+5	VI	0.74	-
Bi	+3	III	-	**0.91***
Bi	+3	V	1.10	1.07
Bi	+3	VI	1.17	1.15
S	−2	IV	1.56	**1.70**
Se	−2	IV	1.84	**1.84**

* Values calculated following the procedure described in the text and shown in Figure 2. The number of digits is given as in the original reference. CN: coordination number, IR: ionic radii reported by Shannon (1976), SR: radii in sulfides reported by Shannon (1981). The data applicable to tetrahedrite$_{ss}$ appear in bold face.

TABLE 2. MEASURED AND CALCULATED BOND-LENGTHS IN SYNTHETIC GOLDFIELDITE, ARSENOAN GOLDFIELDITE, TENNANTITE AND TETRAHEDRITE

Bond	IR$_{cation}$	oxid. state	CN	f_i•100	IR$_{anion}$	ΣIR'i	measured bond-length	Δ (calc. − meas.)
*M*1–*Y*	Cu: 0.635	1	IV	8.61	S: 1.70	2.335	2.37(2) sGfd	−0.035(2)
							2.313(9) aGfd	0.022(9)
							2.337(8) Ten	−0.002(8)
							2.342(6) Tet	−0.007(6)
*M*2–*Y*	Cu: 0.57	1	III	8.61	S: 1.70	2.27	2.16(5) sGfd	0.11(5)
							2.240(10) aGfd	0.030(10)
							2.258(9) Ten	0.012(9)
							2.272(7) Tet	−0.002(7)
*M*2–*Z*	Cu : 0.57	1	III	8.61	S: 1.70	2.27	2.13(3) sGfd	0.14(3)
							2.182(7) aGfd	0.088(7)
							2.204(8) Ten	0.066(8)
							2.234(5) Tet	0.036(5)
X–*Y*	Te: 0.66	4	III	3.92	S: 1.70	2.36	2.41(3) sGfd	−0.05(3)
	(3 Te + 1 As)		III		S: 1.70	(2.319)	2.364(9) aGfd	−0.045(9)
	As: 0.495	3	III	6.06	S: 1.70	2.195	2.246(5) Ten	−0.051(5)
	Sb: 0.86	3	III	8.61	S: 1.70	2.56	2.446(3) Tet	0.114(3)

All values are in Ångström units. The oxidation state (oxid. state) of S is invariably 2−, but its coordination numbers (CN) are IV and VI for the *Y* and *Z* sites, respectively. f_i: fractional ionic character (see text). IR: ionic radius. sGfd: data on synthetic goldfieldite from Kalbskopf (1974). aGfd: data on arsenoan goldfieldite from Dmitriyeva *et al.* (1987). Ten: data on tennantite from Wuensch (1964). Tet: data on tetrahedrite from Wuensch *et al.* (1966).

contrast, semimetals have nearly the same ionic radius in both types of crystals (Table 1).

Ionic radii for oxides (Shannon 1976) and sulfides (Shannon 1981) for Cu, Fe, Zn, As, Te, Sb, Bi, S and Se in the oxidation states and coordinations relevant to this investigation are listed in Table 1. Figure 2 shows the graphic extrapolation of the radii of Cu, As, Sb and Bi in 3-fold coordination. The radius of $^{III}Cu^+$ in sulfides was calculated as the equivalent value measured in oxides minus 0.1 Å (Fig. 2).

Because the radii for As, Te, Sb and Bi are very close (±0.03 Å or better) in oxides and sulfides (*cf.* $^{IV}As^{5+}$, $^{IV}Te^{4+}$, $^{V}Bi^{3+}$ and $^{VI}Bi^{3+}$ in Table 1), data obtained from oxides (*e.g.*, for Sb) and sulfides (*e.g.*, Bi) may be used interchangeably. The extrapolation method used to estimate the radius of As is similar to that employed for Cu. Interestingly, although the radius of S^{2-} is different in oxides and sulfides, no such change is observed for Se.

Bond lengths and angles

Crystal-structure data has been reported so far only by Kalbskopf (1974), who gathered powder-diffraction data from synthetic material, and by Dmitriyeva *et al.* (1987), who studied a single crystal from the Yelshishche deposit in Bulgaria. Bond lengths reported in these studies, as well as data for tetrahedrite (Wuensch 1964) and tennantite (Wuensch *et al.* 1966), are summarized in Table 2. The effect of Zn and Fe in the *M*2 site on the bond lengths of tennantite and tetrahedrite was neglected, because the radii of Fe and Zn differ from that of Cu by only 0.02 Å. The analytical uncertainties in the bond lengths measured by Kalbskopf (1974) are relatively large (±0.02 to ±0.05 Å), because they were calculated from powder-diffraction data, whereas the single-crystal data of Dmitriyeva *et al.* (1987), Wuensch (1964) and Wuensch *et al.* (1966) are associated with substantially lower uncertainties (±0.003 to 0.010 Å).

There are four distinct bonds in the tetrahedrite$_{ss}$ structures. Atoms in the *M*1 and *X* sites are bonded to 4-coordinated *Y* anions, whereas the atoms in the *M*2 sites are bonded to those in both the *Y* and *Z* sites. As the bond length in theory is equal to the sum of the radii of the two atoms linked together, Table 2 also compares theoretical bond-lengths based on the data of Table 1 with the direct measurements of bond lengths in tetrahedrite$_{SS}$. Increasing covalency (Gamble 1974) and delocalization of electrons (Shannon 1976) lead to measured bond-lengths that are smaller than the sum of ionic radii.

The *M*1–*Y* bond-length should be about the same in all Cu-dominated minerals of the tetrahedrite$_{ss}$, because substitution in the *X* position does not affect these sites. The data in Table 2 support this interference, considering the uncertainties of the measurements. There is also good agreement between bond lengths calculated from ionic radii (2.34 Å) and measured bond-lengths (2.31–2.37 Å).

The *M*2–*Y* bond lengths for tennantite, tetrahedrite, and the arsenoan goldfieldite of Dmitriyeva *et al.* (1987) are very similar, though a decrease from tetrahedrite to

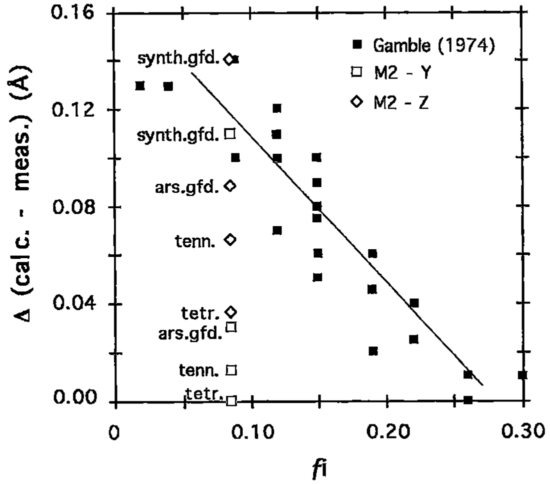

FIG. 3. Plot of fractional ionic character (f_i) *versus* the difference between calculated and measured bond-lengths (in Å). The line represents the linear regression through the data of Gamble (1974), which is represented by filled squares. See text for further explanation. synth. gfd.: synthetic goldfieldite (Kalbskopf 1974), ars. gfd.: arsenoan goldfieldite (Dmitriyeva *et al.* 1987), tenn.: tennantite (Wuensch *et al.* 1966), tetr.: tetrahedrite (Wuensch 1964).

tennantite to arsenoan goldfieldite is indicated. In contrast, the synthetic goldfieldite has a significantly shorter *M*2–*Y* bond-length (2.16 ± 0.05 Å *versus* 2.240 ± 0.010 Å); however, Kalbskopf (1974) proposed that a relatively large error might be attached to that value owing to an increased temperature-factor.

All measured *M*2–*Z* bond lengths are shorter than the calculated values. Measured bond-lengths shorter than the sum of the ionic radii of the elements concerned were observed by Gamble (1974) to be inversely proportional to the fractional ionic character (f_i) in sulfides, selenides and tellurides (Fig. 3), with f_i defined as:

$$f_i\,(A - B) = 1 - \exp\,[-0.25\,(\chi_A - \chi_B)^2] \qquad (1)$$

(Pauling 1948), where *A* and *B* are the two atoms involved in the bond, and χ, their electronegativities, as calculated by Pauling (1948). However, use of the smaller radii observed in sulfides (Shannon 1981; Table 1 of this paper) led to good agreement between calculated and observed bond-lengths for *M*1–*Y* and *M*2–*Y* bonds in tetrahedrite, tennantite and arsenian goldfieldite. Only the shorter bond-length in goldfieldite would be consistent with the relationship observed by Gamble (1974). Hence, the shorter bond-lengths in goldfieldite might be due to the vacancies in the *M*2 site, rather than to decreasing ionic character of the bond.

The *X*–*Y* bond lengths show some contradictory results. The measured Te–S and As–S distances in synthetic goldfieldite, arsenoan goldfieldite and tennantite are longer than those calculated, a fact in contrast with Gamble's (1974) observation. These discrepancies may be the result of analytical errors related to the chemical composition the mineral, errors in the determination of the bond lengths, possible changes in coordination of the semimetals as a result of vacancies in the structure, or inapplicable ionic radii.

The possibility of an analytical error was discussed by Wuensch *et al.* (1966) in their study of the structure of tennantite; the mineral they used could have contained minor amounts of Sb, thus increasing the bond length. A similar error could not have affected synthetic goldfieldite. Substantial errors in measurements of the bond lengths are unlikely, though Kalbskopf (1974) reported a relatively large uncertainty of ±0.03 Å for the measured Te–S bond length in synthetic goldfieldite. This leaves the possibility that the estimated ionic radius for $^{\mathrm{III}}$Te is slightly too low at 0.66 Å.

Vacancies are reported only in goldfieldite, but they should not affect the coordination of Te (Kalbskopf 1974). If they did, these would result in an increase in the radius of Te, which would make the difference between calculated and measured bond-lengths positive (Table 2), in agreement with Gamble's (1974) general prediction for all minerals.

Thus, with the data currently available, no viable hypothesis can be proposed to explain why the measured bond-lengths for synthetic goldfieldite, natural arsenoan goldfieldite and tennantite exceed the calculated values. More accurate measurements can possibly help to solve this problem. The *X*–*Y* bond lengths in tetrahedrite are in agreement with Gamble's (1974) prediction, though we used the radii applicable to sulfides.

There are very limited published data regarding the bond angles in goldfieldite. Kalbskopf (1974) reported that in pure goldfieldite, the S–Te–S angle is 95.7 ± 0.7°, which is very close to the corresponding value (95.1 ± 0.2°) for tetrahedrite measured by Wuensch (1964), as are reported values for the two S(*Y*)–Cu(*M*1)–S(*Y*) angles in arsenoan goldfieldite (Dmitriyeva *et al.* 1987).

Cell dimensions

Currently available data for the cell dimensions of goldfieldite are summarized in Table 3, which also lists reference values for synthetic tetrahedrite and natural tennantite. The prediction of cell dimensions as a function of the different types of substitutions in tetrahedrite$_{ss}$ was first attempted by Charlat & Lévy (1975) and subsequently refined by Mozgova *et al.* (1979) and Johnson *et al.* (1986, 1987). However, only Johnson *et al.* (1986, 1987) provided details on the type of statistical analysis used. Te-for-(As,Sb) substitution is only taken into account by the equation given by Mozgova *et al.* (1979):

TABLE 3. UNIT-CELL SIZE OF GOLDFIELDITE, TETRAHEDRITE AND TENNANTITE

Mineral	Formula	a_o (Å)	Reference
Synthetic crystals			
Goldfieldite	$Cu_{10}Te_4S_{13}$	10.263(5)	Kalbskopf (1974)
Tetrahedrite	$Cu_{12}Sb_4S_{13}$	10.319(1)	Hall (1972)
Tetrahedrite	$Cu_{10}(Fe,Zn)_2Sb_4S_{13}$	10.383(1)	Hall (1972)
Natural crystals			
Arsenoan goldfieldite	$Cu_{11.2}As_{1.1}Sb_{0.9}Te_{1.8}S_{13.9}$	10.304	PDF (29-531)
Arsenoan goldfieldite	$Cu_{11.3}As_{1.2}Te_{3.3}S_{13.2}$	10.247(2)	Dmitriyeva *et al.* (1987)
Stiboan goldfieldite	$Cu_{11.4}As_{0.5}Sb_{1.7}Te_{1.9}S_{12.9}$	10.35	Spiridonov *et al.* (1984)
Stiboan goldfieldite	$Cu_{11.4}As_{0.6}Sb_{0.7}Te_{2.9}S_{12.4}$	10.320(5)	Tsepin *et al.* (1977)
Selenian goldfieldite	$Cu_{11.9}As_{1.5}Sb_{0.4}Te_{2.1}S_{10.7}Se_{2.3}$	10.38	Spiridonov & Okrugin (1985)
Tennantite§		10.186	PDF (11-102)
Tennantite	$Cu_9Fe_{0.7}Zn_{1.1}As_{3.8}S_{14.4}$*	10.235(5)	Wuensch et al. (1966)
Tetrahedrite	$Cu_{10}Fe_{0.3}Zn_{1.7}Sb_{4.0}S_{13}$**	10.391(1)	Wuensch (1964)

§ Chemical composition is not available. * Chemical composition is unreliable and at variance with spectrometric data on the same material; composition probably close to $Cu_{9.8}Zn_{1.8}Fe_{0.2}As_{3.9}S_{13}$ (Wuensch *et al.* 1966). ** Results of old analysis; Springer (1969) reported the following composition for material from this locality: $Cu_{10}Zn_{1.8}Fe_{0.2}Sb_4S_{13}$.

$$a_0 = 10.319 + 0.031\ \mathrm{Fe} + 0.028\ \mathrm{Zn} + 0.096\ \mathrm{Hg} + 0.007\ \Sigma Me/\mathrm{S} - 0.040\ \mathrm{As} + 0.093\ \mathrm{Bi} - 0.003\ \mathrm{Te} + \mathrm{Ag}/(21.9–1.01\ \mathrm{Ag}) \tag{2}$$

This equation is valid only for tetrahedrite$_{ss}$ with less than 3.7 *apfu* Ag and for minerals with a total of 29 *apfu* (Mozgova *et al.* 1979). The first condition is easily met, as the highest Ag content recorded in goldfieldite is 2.2 *apfu* (Kovalenker *et al.* 1980), but the second excludes crystals with more than 2 Te *apfu* owing to vacancies in the *M*2 site. The validity of Equation 2 has been tested against the measured size of the unit cell of goldfieldite reported in Table 3 (PDF #29–531; Spiridonov *et al.* 1984) with the following results: cell dimensions calculated from mineral-chemistry data are smaller than those measured [10.280 Å *versus* 10.304 Å for the arsenoan goldfieldite of PDF #29–531, and 10.32 Å *versus* 10.35 Å for the stiboan goldfieldite of Spiridonov *et al.* (1984)]. In contrast, Basu *et al.* (1981) claimed that Equation 2 can predict cell sizes within the analytical uncertainty of the measured value.

As expected, the cell size of synthetic goldfieldite is intermediate in size between that of tennantite and that of tetrahedrite in spite of the two vacancies present. However, there is still some debate about the exact cell-dimension of tennantite. Wuensch *et al.* (1966) questioned the purity of the natural crystal they analyzed, because it yielded a value of 10.235 ± 0.005 Å, which is too large if compared to the value of 10.19 Å previously reported. L.G. Berry (as cited in PDF #29–531) reported a value of 10.186 Å for natural tennantite containing up to 4.77 wt.% Ag; as the Ag-for-Cu substitution in the tetrahedrite$_{ss}$ causes an increase in the cell edge (Hall 1972), it can be predicted that a pure tennantite end-member ($Cu_{10}[Fe,Zn]_2As_4S_{13}$) should have a cell size slightly smaller than 10.186 Å.

On the basis of the available data (Table 3), there is a considerable contraction (about 0.1 Å) in the cell edge as the proportion of vacancies increases in goldfieldite. The largest cell-edge reported, 10.38 Å, measured by Spiridonov & Okrugin (1985), pertains to the selenian variety. It is evident that the increase in the cell dimension with respect to that of pure goldfieldite is due to the Se-for-S substitution (*cf.* Table 1).

OPTICAL PROPERTIES AND SPECTROSCOPIC RESULTS

Quantitative measurements of the reflectance of goldfieldite were reported by Spiridonov *et al.* (1984): values in the range of 29.5 to 31% were measured for the As-bearing variety. High Te contents in goldfieldite marginally increase its reflectance, but large amounts of Sb have the opposite effect. These authors concluded that this mineral is indistinguishable from tetrahedrite, as both are grey with a pinkish to brownish hue. In contrast, unpublished observations suggest that the Te content of goldfieldite may affect its color. One of the present authors (UK) notes that Te-rich tetrahedrite$_{ss}$ is distinctly pinkish where in contact with Te-free tetrahedrite$_{ss}$, in particular in oil immersion. At the La Mejicana base- and precious-metal epithermal deposit (Argentina), two types of goldfieldite were recognized (A. Losada-Calder6n, pers. commun.): a low-Te (<2 *apfu*) variety, which occurs at deeper levels and is texturally associated with gold, shows a greenish tint resembling tennantite, and a high-Te (>2 *apfu*) variety, which is present at shallower levels, is grey, like normal goldfieldite. The presence of Se, as shown by material from the Ozernoye Au deposit, in Kamchatka, Russia, does not seem to affect the color of the mineral.

Spiridonov *et al.* (1984) measured also the Vickers microhardness (load = 30 g) of goldfieldite and obtained values decreasing from 334 for tetrahedrite with a very low Te content (0.54 wt.%) to 205 for goldfieldite (Te = 14.98 wt.%).

At present, there are only two studies concerned with the spectroscopic examination of goldfieldite. In a recent laser Raman investigation of some geologically important sulfides, Mernagh & Trudu (1993) observed Raman bands at 354 and 324 cm^{-1}, which represent an intermediate position between those of tennantite and of tetrahedrite. They interpreted these results as typical one-mode behavior, with frequencies decreasing continuously from lighter (tennantite) to heavier (tetrahedrite and goldfieldite) minerals of the same group.

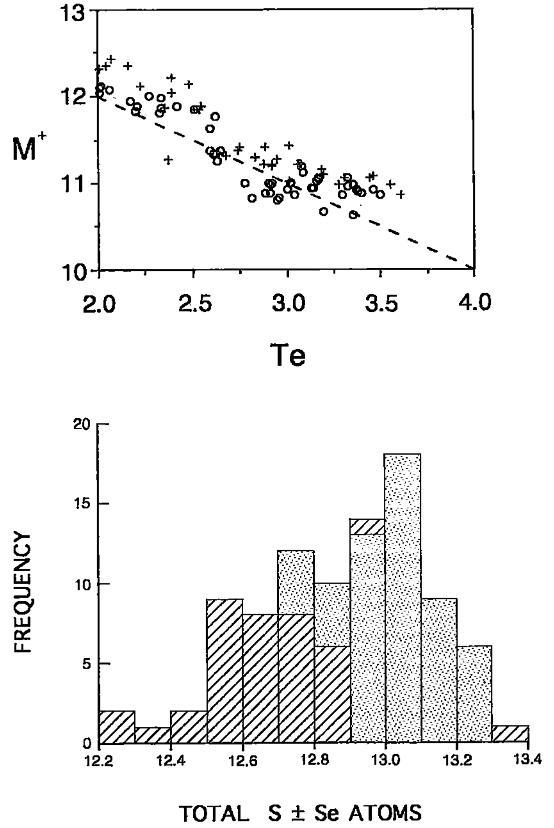

FIG. 4. Plots showing the effect of the choice of the reference material for S calibration on the analytical data. All the data in this diagram are from the Tirad porphyry Cu–Au prospect, northwestern Luzon, Philippines (Trudu and Knittel, in press). Legend: analyses with S calibration carried out on tetrahedrite, stibnite and bismuthinite (circles in upper diagram and stippling in lower diagram), and on arsenopyrite (crosses in upper diagram and hatching in lower diagram). All concentrations are expressed in *apfu*.

In the second study, a ^{121}Sb Mössbauer investigation of several Sb-bearing minerals, Hedges & Stephens (1977) determined that the Sb in goldfieldite is 3-coordinated, confirming the result of Kalbskopf (1974).

CALIBRATION OF ELECTRON-MICROPROBE DATA

The quality of electron-microprobe data on goldfieldite, generally obtained in the wavelength-dispersion mode, surprisingly seems to depend on the choice of the reference materials used for calibration, in particular for analysis of the samples for S. Figure 4 shows that calibration of S on an arsenopyrite standard gave low values for S in goldfieldite, resulting in too high a number of atoms per formula unit, when formulae were calculated on the basis of 13 S. Calibration on stibnite, bismuthinite and tetrahedrite produced markedly better results (Fig. 4). A similar behavior in electron-microprobe data was reported by Harris (1990) for Ni–Hg sulfides: HgS analyzed with S standardized on NiS at 20 kV yielded values up to 7 wt. % higher than expected, whereas the opposite effect took place when NiS was analyzed with S standardization on HgS. Harris (1990) ascribed these poor results to the correction programs, which inadequately dealt with the absorption edge of the standards.

Analytical problems with Cu in tetrahedrite that is not fully substituted have been discussed by Lind & Makovicky (1982). However, the available data suggest that tellurian tetrahedrite$_{ss}$ is in general fully substituted.

It is not known whether Se, the other anion possibly present in goldfieldite, should be calibrated under conditions similar to those of S. Se-bearing goldfieldite is very rare. The only published data pertain to materials from the Ozernoye Au deposit in Kamchatka, Russia. Spiridonov & Okrugin (1985) did not mention which Se standard they used. For Te and most of the other elements, standardization on pure metal produced good results (Trudu & Knittel, in press). This shows that matrix effects have a negligible effect on the measured concentrations of the cations, as already pointed out by Harris (1990).

Altogether, 19 elements have been reported to occur in tellurian tetrahedrite$_{ss}$, but only the following are routinely detected: S, Cu, Fe, Zn, As, Se, Ag, Sb, Te and Bi. Of these, Bi and Se tend to be neglected in routine analysis of goldfieldite. Bi substitutes for Te, and its theoretical end-member will be used in the new classification scheme for goldfieldite (see below). Neglecting to analyze for Se, even if present in amounts as low as 1 wt.%, can lead to the erroneous assumption that low S is caused by a poor calibration of the electron microprobe. It must be kept in mind that low concentrations of Se may not appear on an elemental spectrum of goldfieldite, because critical X-ray absorption lines of Se partially overlap those of As, which is usually present in larger amounts than Se in this mineral.

Elements of secondary importance, Au and Pb, and minor or trace amounts of Hg, Mn, Cd, Sn, Co, V and Ge have been reported only occasionally.

CALCULATION OF THE STRUCTURAL FORMULA

Structural formulae for tetrahedrite$_{ss}$ are usually calculated on the basis of 13 anions (S + Se) or 29 total atoms. Seal *et al.* (1990) suggested that a calculation procedure based on 4 semimetal atoms (As, Sb, Bi, Te) be adopted, although they admit that small analytical errors for the semimetals can cause larger errors in recasting the number of sulfur and metal atoms. This problem is also inherent in the calculation of the structural formula on the basis of 13 anions, in particular, if Se is not sought, but is present in substantial amounts. In addition, analytical data for S may be problematical, as outlined above. It is even less suitable to calculate the structural formula for goldfieldite based on 12 metal (Cu, Ag, Zn, Fe, *etc.*) atoms (*e.g.*, Charlat & Lévy 1975) because vacancies occur for more than 2 atoms of Te (*apfu*). The same reason should make the calculation procedure based upon a fixed number of total atoms suspect, as this varies from 29 for Te $\leq$ 2 *apfu* to 27 *apfu* for end- member goldfieldite.

Keeping in mind all these considerations, we prefer to calculate the structural formula of goldfieldite and other tellurian minerals of the tetrahedrite$_{ss}$ using the method based on the total number of atoms. This procedure has the advantage of spreading the analytical error over all the elements sought. In order to take into account the occurrence of vacancies for Te > 2 *apfu*, we suggest that: 1) for Te/(Te + As + Sb + Bi) $\leq$ 0.5, the calculation be based on 29 *apfu*, as no vacancies occur in the crystal structure; 2) for Te/(Te + As + Sb + Bi) > 0.5, the formulae are to be calculated on the basis of

$$29 - 4\,[\mathrm{Te}/(\mathrm{Te} + \mathrm{As} + \mathrm{Sb} + \mathrm{Bi}) - 0.5]\ apfu.$$

TABLE 4. LIST OF SOURCES OF ELECTRON-MICROPROBE DATA ASSEMBLED FOR THIS STUDY, AND NUMBER OF DATASETS OBTAINED FROM EACH SOURCE*

Borisova *et al.* (1986)	5	Kovalenker *et al.* (1990)	35
Dmitriyeva *et al.* (1987)	1	Lévy (1967)	1
Frenzel *et al.* (1975)	1	Loginov *et al.* (1983)	4
Igumnova (1986)	7	Mozgova & Tsepin (1983)	8
JCPDS (1990)	1	Novgorodova *et al.* (1978)	19
Karup-Møller (1992) (synthetic)	14	Noviello (1989)	3
Kase (1986)	10	Sakharova *et al.* (1984)	6
Kato & Sakurai (1970a)	1	Shimizu & Stanley (1991)	11
Kato & Sakurai (1970b)	1	Spiridonov (1984)	1
Knittel (unpubl. data)	28	Spiridonov (1987)	3
Knittel (1989)	11	Spiridonov *et al.* (1984)	6
Kovalenker *et al.* (1989)	27	Spiridonov & Okrugin (1985)	3
Kovalenker & Rusinov (1986)	91	Springer (1969)	2
Kovalenker & Troneva (1980)	8	Trudu & Knittel (in press)	32
Kovalenker *et al.* (1980)	18	Tsepin *et al.* (1977)	1
Kovalenker *et al.* (1989)*	20	Willgallis *et al.* (1990)	2
Total			354

* excluding seven compositions already reported in Kovalenker & Rusinov (1986). The complete database may be obtained as an EXCEL file from the second author.

MINERAL CHEMISTRY

We have assembled a database containing all results of electron-microprobe analyses of tellurian members of the tetrahedrite$_{ss}$ group available to us, using an arbitrary cut-off of 0.3% Te (in all, 354 compositions, as shown in Table 4). No attempt was made to evaluate the quality of these data, because various types of errors can affect them, *e.g.*, counting statistics, matrix correction, use of inappropriate standards, *etc.*, but we have excluded all compositions with totals outside the range 97–102%. In the following discussion, we will, however, point out inconsistencies in some data sets.

In the following sections, we summarize what is known about the distribution of the elements on the different structural positions. Where no information is available, we will discuss the possibilities based on Goldschmidt's rules of substitution, as summarized in Faure (1991), and with reference to other studies of tetrahedrite-group minerals.

The M sites

In tetrahedrite$_{ss}$, there are two sites occupied by metals, *M*1 and *M*2, which are 4- and 3-fold coordinated, respectively. Cu is the main occupant of the *M* sites; it may be replaced by variable amounts of Fe, Zn, Ag, Mn, Cd and Hg. In the tellurian members of the tetrahedrite$_{ss}$, X-ray-diffraction studies (Kalbskopf 1974, Dmitriyeva *et al.* 1987) have shown that up to two vacancies occur in the *M*2 site where the Te contents exceed 2 *apfu*, as previously discussed.

The crystallographic positions of the metals (Fe, Zn, Ag, Mn, Cd and Hg) substituting for Cu in the tetrahedrite$_{ss}$, and thus in goldfieldite, must be re-assessed in light of the findings of Charnock *et al.* (1989a, b), who used extended X-ray absorption fine structure (EXAFS) and Mössbauer spectroscopy, and Makovicky *et al.* (1990), who studied synthetic tetrahedrite by Mössbauer spectroscopy. These studies in part arrived at different conclusions relevant to tellurian tetrahedrite$_{ss}$.

Copper, the most abundant metal in goldfieldite, occupies both the *M*1 and *M*2 site. Its oxidation state has been the source of speculation; however, X-ray photoelectron spectroscopy of about twenty sulfides and sulfosalts, including tetrahedrite, by Nakai *et al.* (1976), as quoted by Kase (1986), indicates that Cu tends to be monovalent in these minerals. Reported concentrations of Cu in the tellurian members of the tetrahedrite$_{ss}$ vary from 5.88 to 12.74 *apfu*, but values of less than *ca.* 9.5 Cu *apfu* were obtained only for Au-rich goldfieldite (Figs. 5, 6; Kovalenker & Troneva 1980), which probably is not really goldfieldite but a mixture of different minerals (see discussion below). Problems of electron-microprobe analysis of tetrahedrite not fully substituted with Cu were discussed by Lind & Makovicky (1982), but the trend displayed in Figure 6 suggests that Cu invariably is in excess of 10 *apfu*, where this is required by coupled substitution as a result of Te incorporation.

The Cu contents are a function of two types of substitutions, Ag ± Au for Cu, and Te for (As, Sb, Bi). The plot shown as Figure 5 indicates that the first type of substitution is of minor importance, as the concentration of the precious metals rarely exceeds 0.5 *apfu*. The data of Charnock *et al.* (1989a, b) indicate that Ag-for-Cu substitution occurs at the *M*2 site in both natural and synthetic tetrahedrite. Figure 6 shows the relationships between concentrations of monovalent metals (mainly Cu) and Te; Cu increases from 10 to 12 *apfu* as Te concentrations reach up to 2 *apfu*. For higher amounts of Te, the Cu content decreases to 10 *apfu*, as vacancies in the *M*2 site appear (Kase 1986,

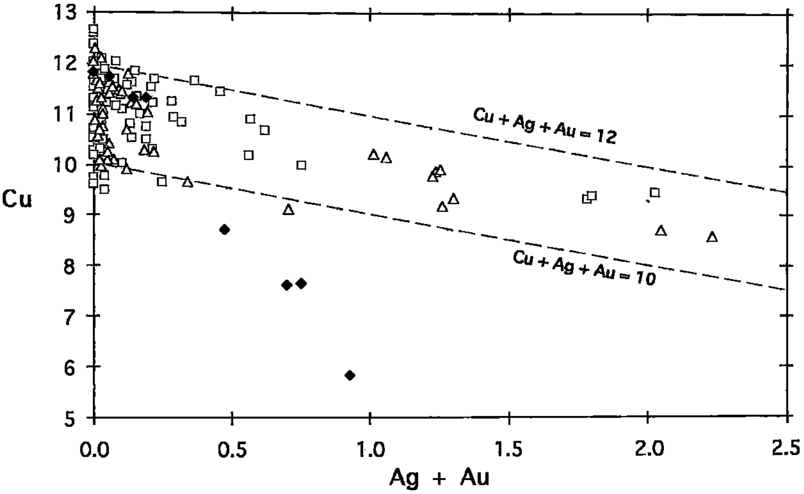

FIG. 5. Plot of the level of Ag + Au *versus* Cu in tellurian tetrahedrite$_{ss}$. All the values are in *apfu*. The dashed lines indicate the range of possible substitutions. Compositions of alleged auriferous goldfieldite (Kovalenker & Troneva 1980) are shown as filled diamonds. Triangles represent samples from the Kochbulashk deposit (Novgorodova *et al.* 1978, Kovalenker *et al.* 1980, Kovalenker & Rusinov 1986); squares depict all other samples (see Table 4).

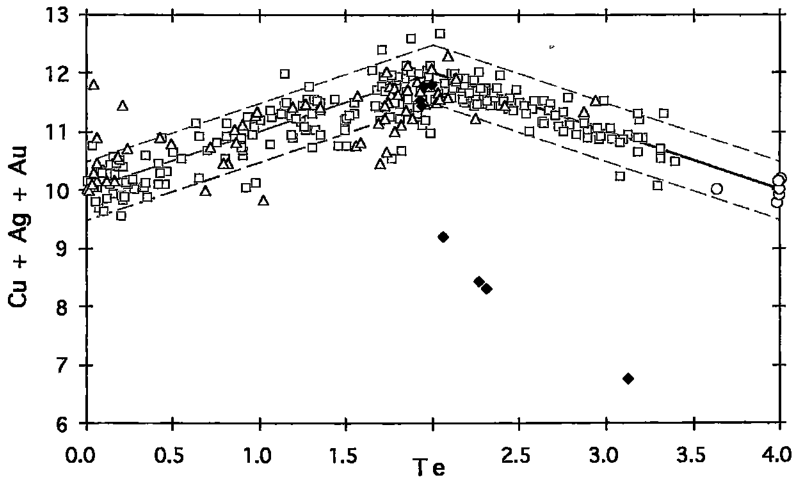

FIG. 6. Plot of Te content *versus* that of monovalent metals M^+ (Cu, Ag, Au) in tellurian tetrahedrite$_{ss}$ minerals. All the values are in *apfu*. The solid line shows the trend of the ideal Te *versus* M^+ relationship, whereas the dashed lines enclose the data that deviate by less than 0.5 *apfu* from the ideal relationships. The circles refer to synthetic compositions. Other symbols as in Figure 5.

Trudu & Knittel 1991) to balance the increase in charges caused by the substitution of Te for trivalent semimetals.

Figure 7 shows the relationship between monovalent (mainly Cu) and divalent (mainly Fe and Zn) cations in tellurian tetrahedrite$_{ss}$. The plot confirms the substitution of divalent by monovalent atoms to balance the excess charges resulting from incorporation of tetravalent Te (up to 2 Te *apfu*).

Iron occurs in tellurian tetrahedrite$_{ss}$ only if the Te content is less than 2 *apfu*, owing to charge-balance

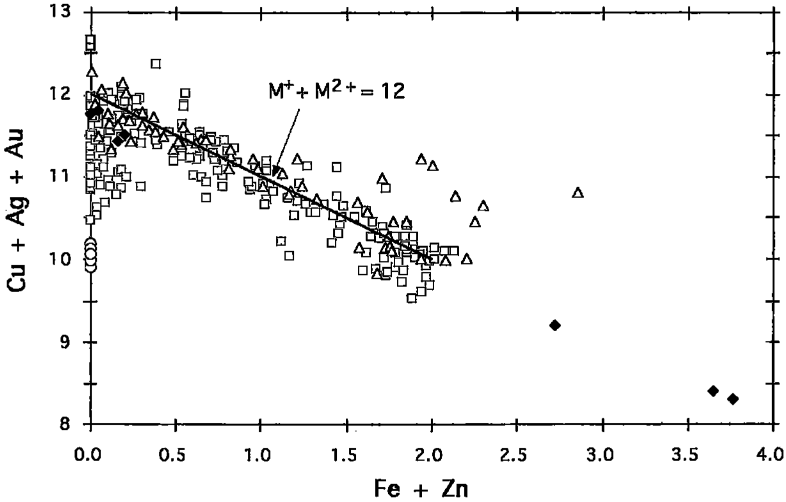

FIG. 7. Plot of divalent M^{2+} (Fe, Zn) *versus* M^{+} (Cu, Ag, Au) metals in tellurian tetrahedrite$_{ss}$ minerals. All the values are in *apfu*. Symbols as in Figure 6.

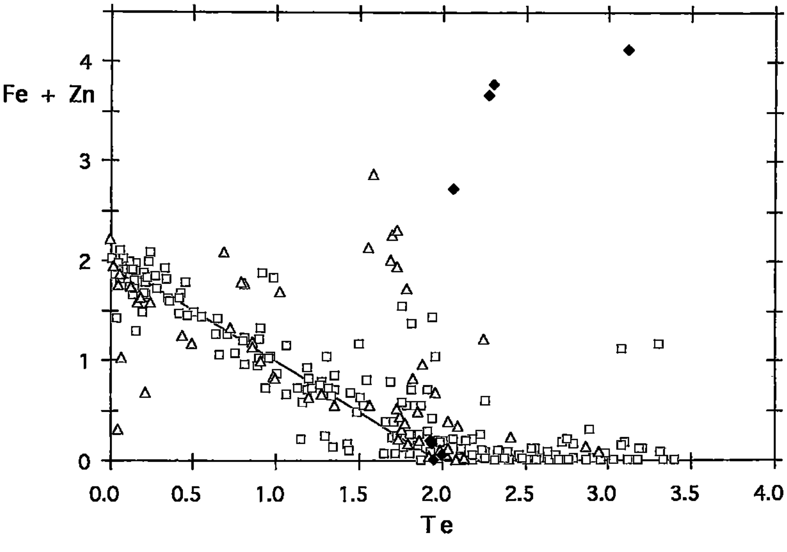

FIG. 8. Plot of proportion of divalent ions M^{2+} (Fe, Zn) *versus* Te in tellurian tetrahedrite$_{ss}$. All the values are in *apfu*. The solid line in the diagram shows the trend of the ideal Te *versus* M^{2+} relationship. Symbols as in Figure 5.

constraints (Fig. 8). Charnock *et al.* (1989b) investigated the oxidation state and coordination of Fe in the tetrahedrite$_{ss}$ and concluded that divalent and trivalent Fe occur in the *M*1 and *M*2 sites, respectively, but the lower oxidation state predominates in natural minerals. In synthetic tetrahedrite$_{ss}$, the presence of trivalent Fe is proportional to the excess of monovalent cations (Cu + Ag > 10 *apfu*) resulting in a change in trend for the ideal M^{2+} *versus* M^{+} substitution. This is not the case for tellurian tetrahedrite$_{ss}$, as most compositions do plot close to the line of ideal substitution. In contrast to these findings, on the basis of their study of synthetic tetrahedrite, Makovicky *et al.* (1990) found that at low iron contents, iron is predominantly ferric, whereas between $Cu_{11}Fe_1Sb_4S_{13}$ and $Cu_{10}Fe_2Sb_4S_{13}$, iron is predominantly ferrous. Whether these findings are relevant to tellurian tetrahedrite$_{ss}$ is uncertain, because Cu in excess of 10 *apfu* is compensated by Te^{4+} (Fig. 5). Furthermore, Makovicky *et al.* (1990) concluded that probably all iron resides at the *M*2 site, regardless of its oxidation state.

The *zinc*-for-iron substitution in tetrahedrite$_{ss}$ was studied experimentally by Cambi *et al.* (1965). As Zn only occurs in the divalent state, it must substitute for Fe in the *M*1 site with 4-fold coordination. A histogram of Fe/(Fe + Zn) in goldfieldite (Fig. 9) shows that there is complete solid-solution between pure Fe and Zn end-members; however, most compositions analyzed are either Zn- or Fe-rich. This could be a function of the composition of the hydrothermal fluids from which these crystals precipitated.

The *silver* content of tellurian tetrahedrite$_{ss}$ rarely exceeds 1 *apfu*; even in those few cases in which it does (*e.g.*, Kovalenker *et al.* 1980), the values are erratic. Harris (1990) cautioned that Ag enrichment can take place during electron-microprobe analysis of Ag-rich tetrahedrite owing to migration of Ag toward the analyzed spot.

Using EXAFS spectroscopy, Charnock *et al.* (1988) have ascertained that in tetrahedrite$_{ss}$, Ag occurs in the 3-coordinated *M*2 site, where it substitutes for Cu. Figure 5 supports this substitution, as previously discussed. However, the lack of data and the low concentrations of Ag in the tellurian tetrahedrite$_{ss}$ prevent us from evaluating the effect of Ag-for-Cu substitution on the cell dimension. It must be pointed out that samples of Ag-rich natural tetrahedrite are characterized by an anomalously small unit-cell (Hall 1972, Riley 1974).

Among the other metals reported in goldfieldite, *gold* is the most common (Borisova *et al.* 1986, Knittel & Johnson, unpubl. data, Kovalenker & Troneva 1980, Kovalenker *et al.* 1980, Sakharova *et al.* 1984, Trudu & Knittel, in press). In general, it occurs in concentrations below 1%, the only possible exception being goldfieldite from epithermal gold deposits in the C.I.S. (Kovalenker & Troneva 1980, Kovalenker *et al.* 1980), where amounts of up to 10.68 wt.% Au have been reported. Kovalenker & Troneva (1980) concluded that Au substitutes for Cu in tetrahedrite$_{ss}$. Spiridonov (1984) disputed the existence of Au-rich goldfieldite on the basis that the examples of auriferous goldfieldite with Au concentrations in excess of 1 wt.% contain quantities of Fe and Zn (up to 4.16 *apfu* in one sample; Fig. 8) that are incompatible with the maximum content of 2 *apfu* of divalent elements in tetrahedrite$_{ss}$. Furthermore, X-ray-diffraction patterns of auriferous goldfieldite by Kovalenker & Troneva (1980) indicate that analyzed grains are inhomogeneous (Spiridonov 1984) and may be considered as intergrowths of goldfieldite, Fe-sulfide and calaverite.

In Figures 5 and 6, the data of Kovalenker & Troneva (1980) for Au-rich goldfieldite display a trend different from the 1-to-1 substitution between Cu and the precious metals. Furthermore, the structural formulae calculated for these samples are not charge-balanced. These observations support Spiridonov's (1984) conclusion that the examples of auriferous (>1 wt.% Au) goldfieldite of Kovalenker & Troneva (1980) probably are mixtures of several minerals. Therefore, it appears that only a limited degree of Au incorporation is possible in goldfieldite; we infer that Au, which falls in the same column of the periodic table as Ag, probably occupies *M*2 sites and is monovalent.

Cadmium concentrations of less than 0.10 wt. % in tellurian tetrahedrite$_{ss}$ phases were reported by Spiridonov *et al.* (1984), Borisova *et al.* (1986) and Spiridonov (1987). In these minerals, the Cd-for-(Fe,Zn) substitution may be similar to that proposed for tetrahedrite by Johnson *et al.* (1986) and confirmed by Charnock *et al.* (1989a), in spite of the substantial difference in ionic radii between 4-coordinated divalent Fe and Zn (0.66 and 0.64 Å, respectively, from Table 1) and Cd (0.84 Å: Shannon 1981).

Manganese has been reported to occur only in tellurian tetrahedrite$_{ss}$ in concentrations up to 0.24 wt. % (Spiridonov *et al.* 1984, Shimizu & Stanley 1991) and is also uncommon in tetrahedrite$_{ss}$ in general. Basu *et al.* (1984) reported Mn concentrations as high as 5.74 wt.% from the Rajpura – Dariba deposit in Rajastan (India), characterized by low contents of Fe and Zn, indicating that Mn in goldfieldite occupies a tetrahedral position, substituting for divalent Fe and Zn as in tetrahedrite.

Mercury, not surprisingly, has been found in goldfieldite, as there is a pure mercurian end-member, schwazite of the tetrahedrite$_{ss}$ series. However, Hg in tellurian tetrahedrite$_{ss}$ has been reported only from the

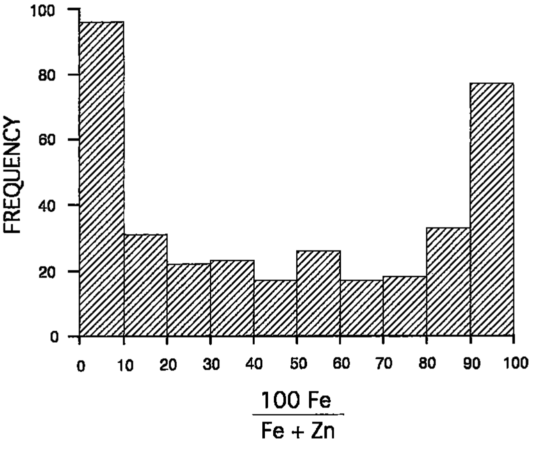

FIG. 9. Histogram of the ratio 100 [Fe/(Fe + Zn)] in tellurian tetrahedrite$_{ss}$.

Akturpak deposit in Russia (Kovalenker & Rusinov 1986). Kalbskopf (1971) showed that divalent Hg is 4-coordinated in mercurian tetrahedrite, thus substituting for other divalent metals such as Fe and Zn. In 4-coordination, Hg has a radius of 0.84 Å (Shannon 1981), the same as Cd.

The X site

The *X* site is of considerable interest, because it is where Te-for-(As,Sb,Bi) substitution takes place. Figure 10 shows the occupancy of this site; there is considerable scatter, if all data are considered (from 3.4 to 4.6 *apfu*), but the values cluster within the 3.9 to 4.2 *apfu* interval. The relatively large spread of the data, which does not occur in the data obtained by Springer (1969), Kase (1986) and Trudu & Knittel (in press), may, in some instances, be due to the standardization of S on unsuitable reference materials, as previously discussed.

Tellurium. In nature, tellurian tetrahedrite$_{ss}$ crystals contain up to 3.4 *apfu* of Te; there are no gaps in this solid solution (Figs. 6, 8, 11). Figure 11 presents a plot of the concentration of Te *versus* the sum of As, Sb and Bi concentrations. These data points show a very high correlation coefficient (0.97), supporting the assumption that Te substitutes for any of the three semimetals.

Arsenic, antimony and, to a lesser extent, *bismuth,* are the most common elements substituting for Te in goldfieldite. Johnson *et al.* (1986) inferred that Sb-for-Te substitution may be prevalent, but our data, plotted as Figure 12, indicates that there is no preferred substitution between any of As, Sb and Bi. Whereas virtually unlimited substitutions is observed among As, Sb and Te (up to a maximum of 3.5 Te *apfu*), the currently known maximum Bi contents is 1 *apfu* (Fig. 12c). This is not surprising, because a pure Bi-bearing tetrahedrite$_{ss}$ end-member has never been documented to occur in nature.

The Y and Z sites

In goldfieldite, the twelve *Y* and one *Z* sites are occupied by S and Se, and not by Te, as believed earlier (*e.g.*, Nowacki 1969). Figure 13 presents histograms of the total number of anions per formula unit; the upper diagram of Figure 13, based on all available data, shows a rather broad spread from 11.3 to 14.0 *apfu* S + Se, with most data clustering around 13 *apfu*. In the lower histogram, the data of Kase (1986) and Trudu & Knittel (in press) are displayed; these cover the entire range of the Te *versus* (As + Sb + Bi) substitution and were obtained under optimal analytical conditions. These data cluster in the very limited range of 13.0 ± 0.3 *apfu* S + Se. This suggests that the large spread in the complete dataset (including data of Knittel 1989) results from the use of an inappropriate S standard, as previously discussed.

S is replaced to a maximum of 2.8 *apfu* by Se (Fig. 14). Tellurian tetrahedrite with an elevated Se content was found only in samples from the Ozernoye epithermal Au deposit (Kamchatka, Russia: Kovalenker *et al.* 1989, Spiridonov & Okrugin 1985), and from the Wild Dog epithermal Au system on Bougainville Island (Papua New Guinea: Noviello 1989). As the experiments at 340°C by de Medicis & Giasson (1971b) on the system Cu–Te–Se failed to produce the Se-bearing homologues of goldfieldite, we cannot assess whether complete Se-for-S substitution exists in goldfieldite, as it does in sulfides (Bethke & Barton 1961).

Other elements

In addition to the aforementioned elements, V, Co, Ge, Sn and Pb have in cases been reported in trace amounts in goldfieldite. Vanadium so far has only been reported by Spiridonov *et al.* (1984), who found 0.02 wt.% V in goldfieldite from Uzbekistan, a value so

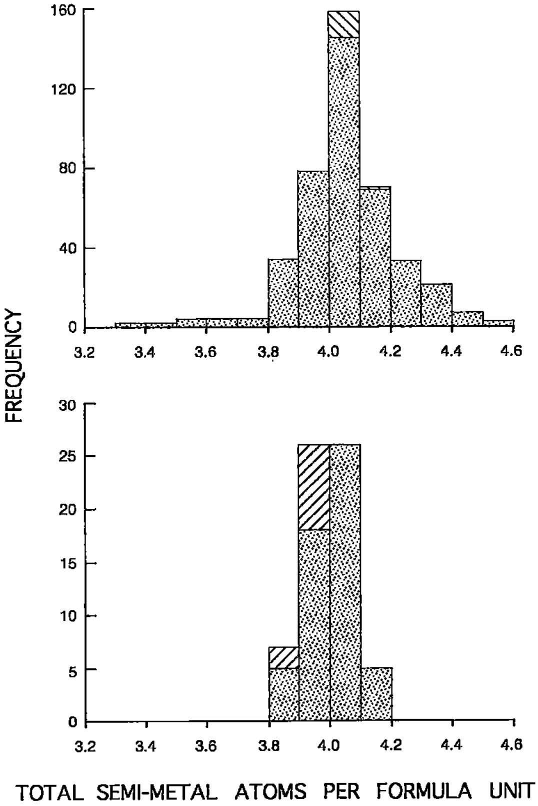

FIG. 10. Histograms of the occupancy of the *X* site by semimetal (As, Sb, Te and Bi) ions. The upper diagram represents all data on tellurian tetrahedrite$_{ss}$; the lower histogram shows compositions reported by Kase (1986; hatched pattern) and Trudu and Knittel (in press.; dotted pattern) for comparison.

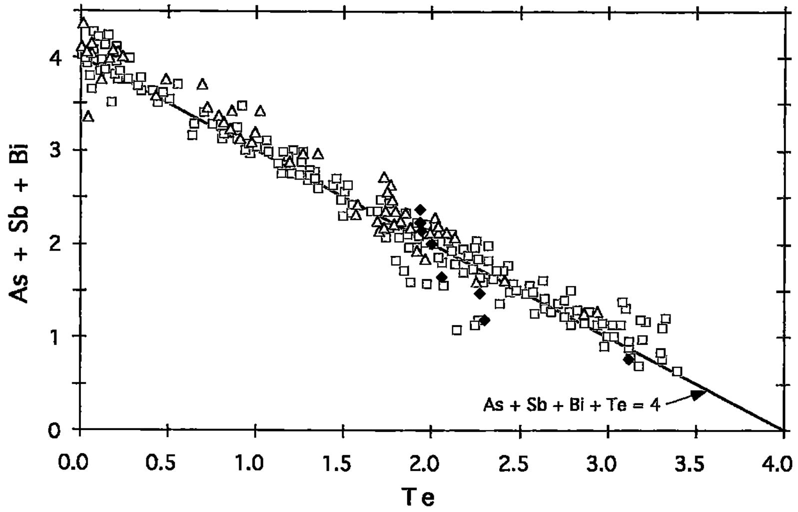

FIG. 11. Plot of Te content *versus* the sum of As, Sb, and Bi. The solid line in the diagram shows the trend of the ideal Te-for-(As + Sb + Bi) substitution. All values are in *apfu*, symbols as in Figure 5.

close to the detection limits that the reality of V incorporation in goldfieldite may be questioned. Besides, in an exploratory study of minor-element incorporation in synthetic tetrahedrite, Makovicky & Karup-Møller (1994) found that V does not enter this mineral. Reported contents of *cobalt* likewise are very low [Spiridonov *et al.* (1984) reported 0.03 wt.% Co in the same sample in which V occurs], but Makovicky & Karup-Møller (1994) were able to synthesize the Co end-member of tetrahedrite.

Concentrations of up to 0.17 wt.% *germanium* were reported by Spiridonov *et al.* (1984). Considering that Ge is invariably tetravalent (like Te), the most likely location for Ge is the *X* position, where it may substitute for As, Sb, Bi or Te. The only problem is that Ge tends to be 4- or 6-coordinated in sulfosalts, whereas the *X* site is a trigonal pyramid. This fact probably accounts for the very low Ge concentrations in goldfieldite.

Tin may be a relatively common trace constituent in the tellurian tetrahedrite$_{ss}$ from the Kochbulashk epithermal gold deposit in Uzbekistan: Kovalenker *et al.* (1980) reported up to 0.22 wt.% Sn, and Novgorodova *et al.* (1978), up to 2.95 wt.% Sn for tetrahedrite$_{ss}$ from this deposit. However, the data by Novgorodova *et al.* (1978) referred to tetrahedrite samples that contain only trace amounts (< 1 wt.%) of Te. Considering that Sn falls in the same column of the periodic table as Ge and tends to occur in nature in its tetravalent oxidation state (*e.g.*, in stannite, colusite, *etc.*), it is very likely that this element can best be accommodated within the *X* sites of the tellurian members of the tetrahedrite$_{ss}$, substituting for the semimetals like Ge.

Lead is another element that rarely occurs in goldfieldite (Kovalenker *et al.* 1980, Kovalenker & Rusinov 1986); its maximum concentration reaches 0.41 wt.%. In tetrahedrite$_{ss}$, however, values up to 12.3 wt.% have been recorded by Vavelidis & Melfos (1997) and Bishop *et al.* (1977). These studies show that plumbian tennantite is low in Fe and Zn; therefore, these authors infer that Pb substitutes for these divalent elements. In contrast, based upon data from tetrahedrite$_{ss}$ minerals with Pb concentrations of less than 2 wt.%, Basu *et al.* (1981) raised the possibility that Pb substitutes for the semimetals in the *X* site, because in some sulfides and sulfosalts, it can occur in 3-fold pyramidal coordination, which is the same as that of the *X* site. They still suggested that Pb should be divalent. Makovicky & Karup-Møller (1994) synthesized tetrahedrite with up to 0.4 Pb *apfu*, whereas attempts to synthesize Pb-rich tennantite failed (<0.1 Pb *apfu*). All tetrahedrite$_{ss}$ containing significant amounts of Pb (both synthetic and natural material) contain *ca.* 4 (As,Sb) *apfu*, hence we believe that Pb substitutes for Fe and Zn.

The preceding discussion leads us to propose the following chemical formulae:

1) for tellurian tetrahedrite and tennantite (Fig. 17 shows that tellurian Bi-bearing tetrahedrite does not occur in nature):

$$^{IV}[\mathrm{Cu}^{+}_{4+x}(\mathrm{Fe,Zn,Mn,Co,Cd,Hg,Pb})^{2+}_{2-x}]$$
$$^{III}[(\mathrm{Cu,Ag,Au})^{+}_{6}]^{IV}[(\mathrm{As,Sb,Bi})^{3+}_{4-x}(\mathrm{Te,Ge,Sn})^{4+}_{x}]$$
$$^{IV}[(\mathrm{S,Se})]_{12}{}^{VI}[(\mathrm{S,Se})]$$

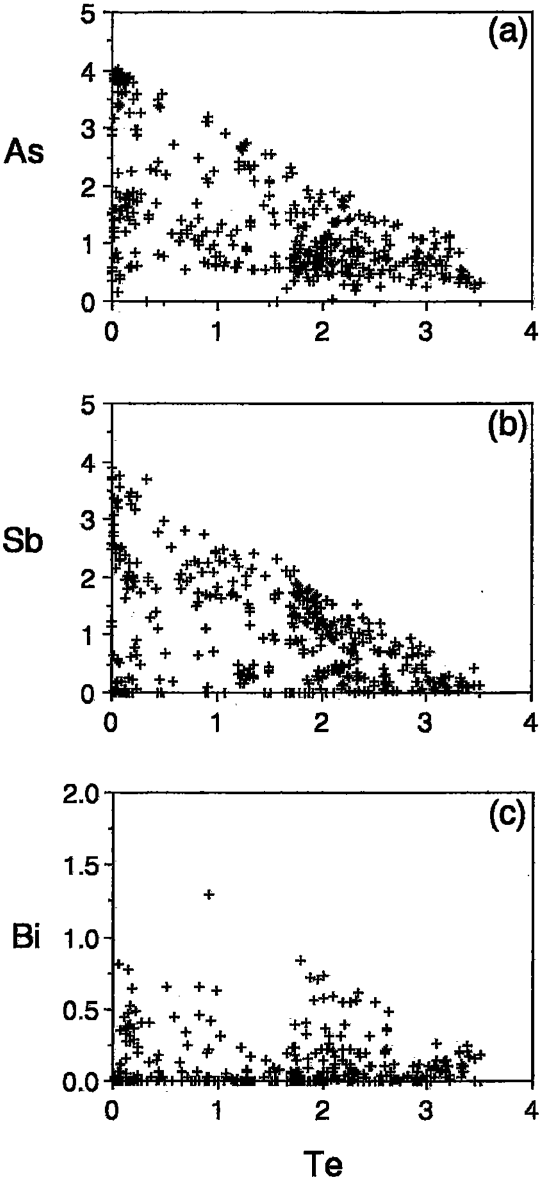

FIG. 12. Plots of Te content *versus* (a) As, (b) Sb and (c) Bi. All the values are in *apfu.*

where $0 \leq x \leq 2$, and

2) for goldfieldite, which according to Figure 17 can be pure, arsenoan or stiboan, the formula is:

$$^{IV}[Cu^{+}_{6}]^{III}[(Cu,Ag,Au)^{+}_{6-x}]^{IV}[(As,Sb,Bi)^{3+}_{2-x}(Te,Ge,Sn)^{4+}_{2+x}]^{IV}[(S,Se)_{12}]^{VI}[(S,Se)]$$

where $0 < x \leq 2$.

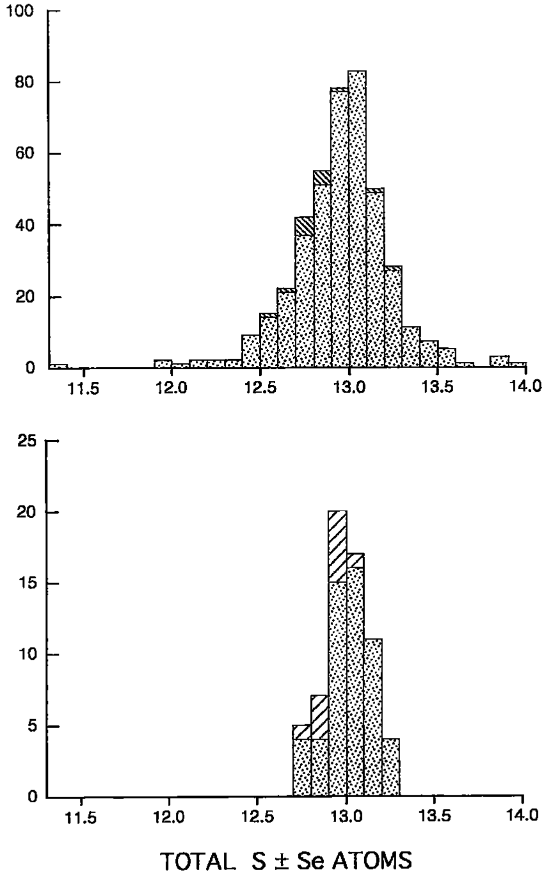

FIG. 13. Histograms of the occupancy of the *Y* and *Z* sites by (S ± Se) in tellurian tetrahedrite$_{ss}$. All values are in *apfu.* The upper diagram represents all available data on tellurian tetrahedrite$_{ss}$; the lower histogram shows analytical results of Trudu & Knittel (in press; dotted pattern) and Kase (1986; hatched pattern) for comparison.

NOMENCLATURE

No official system of nomenclature exists to define tetrahedrite$_{ss}$ minerals according to their Te content. Two definitions of goldfieldite exist: Kato & Sakurai (1970a) and Spiridonov (1984) suggested to name the tetrahedrite$_{ss}$ goldfieldite where Te is the most abundant semimetal, whereas Dmitriyeva *et al.* (1987) suggested that the mineral be named goldfieldite only where Te is greater than the sum of the other three semimetals. The former definition conforms with the rules on the nomenclature of the tetrahedrite$_{ss}$ minerals set by the IMA (Spiridonov 1984).

Kovalenker *et al.* (1990) proposed an equilateral triangular projection with Te (goldfieldite), Sb ± Bi

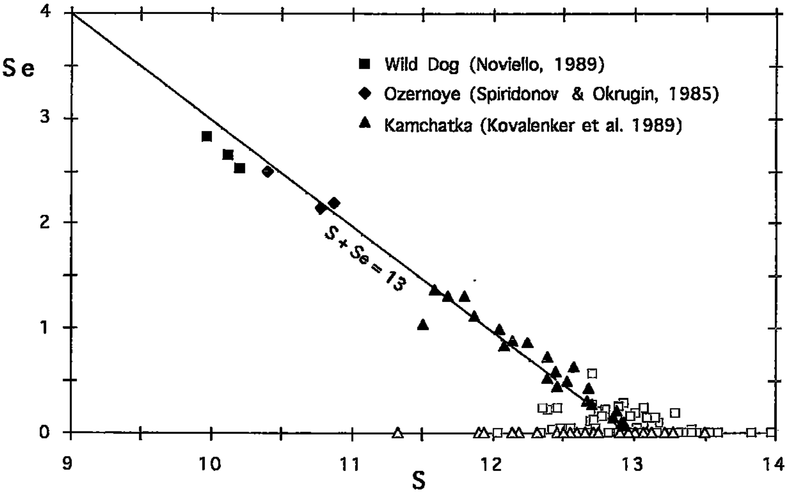

FIG. 14. Plot of S content *versus* Se (*apfu*) illustrating the substitution between these elements. The line in the diagram corresponds to a total of 13 (S + Se) *apfu*. Symbols as in Figure 5, except for those for Se-rich compositions, which are identified in the figure.

(tetrahedrite) and As (tennantite) at the vertices. They divided it into six fields: Sb-goldfieldite, As-goldfieldite, Te-tetrahedrite, Te-tennantite, As-tetrahedrite and Sb-tennantite. We believe that this nomenclature for the tetrahedrite$_{ss}$ is inadequate for the following reasons: 1) it implies that the Sb substitutes for Bi only, an interpretation that is not always correct (see below). 2) Some misnaming is likely to take place near the vertices, where nearly pure end-members will have the prefix of the second most abundant element, which is present in insignificant concentrations. 3) The terms used by Kovalenker *et al.* (1990) to name the different fields do not conform the IMA recommendations (Nickel & Mandarino 1987): the use of a hyphenated chemical symbol preceding the name of a mineral is incorrect and is to be avoided.

Therefore, we suggest a new chemical nomenclature grid for tetrahedrite$_{ss}$, in which the *M* sites are predominantly occupied by Cu, and S is the main anion. Ideally, as there is probably complete solid-solution amongst As, Sb, Te and Bi in the tetrahedrite$_{ss}$, a tetrahedron with each end-member occupying a vertex constitutes the most appropriate representation (see center of Fig. 15). We neglect other elements, such as Ge and Sn, which may be accommodated in the *X* site, because they occur in insignificant amounts only in goldfieldite. The values used for this plot must be in *apfu* and normalized to 100%. However, as three-dimensional representations are very difficult to portray on a sheet of paper, it is more convenient to use the four faces of the tetrahedron individually. If only three of the four elements are present, then the selection of the appropriate triangle is obvious. If all four elements occur in the mineral, then an approximation has to be made: it is proposed that the triangle containing the three most abundant elements be used. Geometrically, this form of approximation is performed by extending the line connecting the vertex of least abundant element to the point inside the tetrahedron representing the composition of the mineral until this line intersects the face of the tetrahedron. Numerically, this procedure is followed by recasting the quantities of the three most abundant semimetals to 100%. This geometric approximation has the advantage of retaining the proportions amongst the three most abundant semimetals as they occur in the original structural formula. Considering that in tetrahedrite$_{ss}$, the least abundant semimetal, where present, occurs in very low concentrations, the error introduced by this procedure is negligible.

The four triangles of the "exploded" tetrahedron representing the tetrahedrite$_{ss}$ are shown in Figure 15. Regarding the nomenclature of the different fields in the triangles, we have followed these criteria:

1) the tetrahedrite$_{ss}$ mineral is named after the most abundant semimetal present, as is usually done.

2) The same principle is applied to distinguish between a pure end-member (*i.e.*, it must have a ratio greater than 3:1 between the two most abundant semimetals) and one that has substantial amounts of another element. In the latter case, the appropriate adjectival modifier has been used, as outlined by Nickel & Mandarino (1987).

3) The lack of an approved name for the Bi-bearing end-member of the tetrahedrite$_{ss}$ creates some problems in nomenclature. In the Soviet literature, the term "annivite", eponymous after the Annivier Valley in Switzerland, is commonly used for this mineral. However, this name is not officially recognized by the IMA

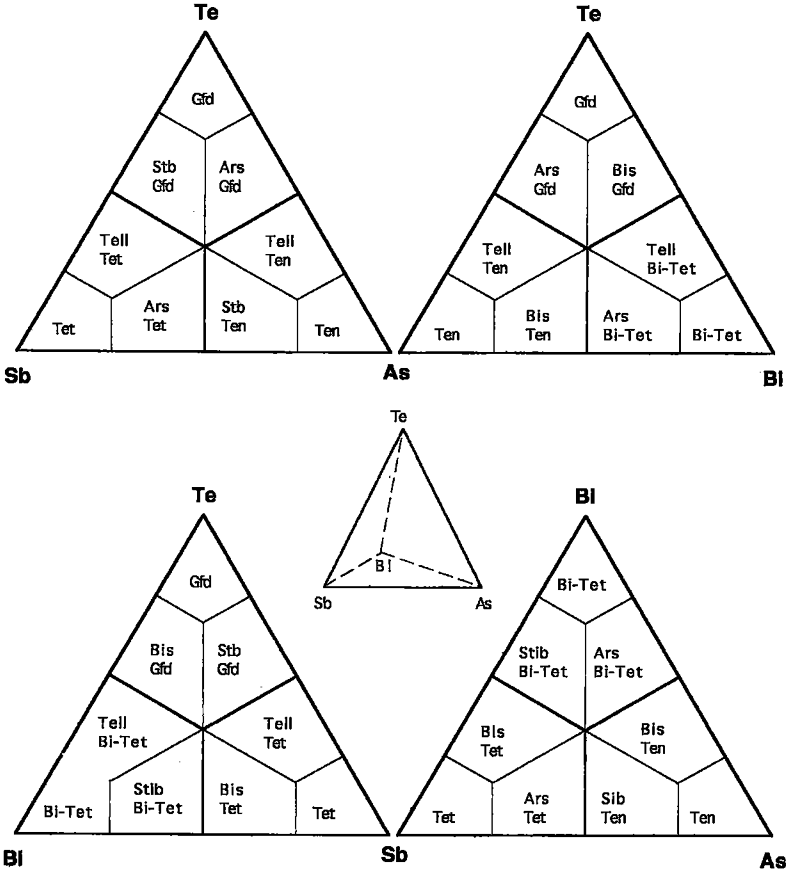

FIG. 15. New nomenclature grid for minerals of the tetrahedrite$_{ss}$ group in which the *M* sites are predominantly occupied by Cu. The triangles correspond to the faces of the tetrahedron shown in the center of the figure. Abbreviations: Gfd: goldfieldite, Ten: tennantite, Tet: tetrahedrite, Bi-Tet: Bi-bearing tetrahedrite, Ars: arsenoan, Bis: bismuthoan, Stb: stiboan, and Tell: tellurian.

(E.H. Nickel, pers. commun. 1991), because a natural mineral close to $Cu_{10}(Fe, Zn)_2Bi_4S_{13}$ has not been found; one of the highest Bi contents in a tetrahedrite$_{ss}$ mineral is 1.60 *apfu* reported by Lur'ye and coworkers (Jambor & Vanko 1990). Therefore, the name of "Bi-bearing tetrahedrite" has been chosen, bearing in mind that the name "tetrahedrite" does not imply that Bi substitutes exclusively for Sb. The proposed chemical nomenclature aims at emphasizing the chemistry of tetrahedrite$_{ss}$ minerals. It conforms to the recommendation of the IMA for ternary solid-solutions (Nickel 1992) in the sense that in each triangle the three main areas subdivided by the 50% rule keep the name of the end-member. The further subdivisions are informal.

The structural formulae of all the samples in the database have been calculated following the criteria previously outlined; the results, which exclude synthetic goldfieldite, are plotted in Figure 16 according to the nomenclature of Figure 15. Most of the compositions fall within the Te–Sb–As triangle; only a few plot in the Te–As–Bi triangle; in only four is Te the least abundant semimetal. Only about 10% of the compositions fall within the goldfieldite field, the majority being either arsenoan or stiboan, but not bismuthoan. The remaining compositions show an approximately even distribution in all the other fields (tellurian tetrahedrite and tennantite, arsenoan tetrahedrite and stiboan tennantite); only a few cluster in the fields of the pure tetrahedrite and tennantite.

DISCUSSION

From a crystallochemical point of view, two aspects deserve further clarification: (a) the substitutions involving atoms with relatively large differences in radii (*e.g.*, Cd for Fe and Zn), and (b) the absence of
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goldfieldite with a Te content greater than 3.5 *apfu* in nature. Although goldfieldite and tellurian tetrahedrite$_{ss}$ are ore minerals, they have never been reported to occur in quantities of economic significance within orebodies, unlike tetrahedrite, tennantite and freibergite. Sakharova *et al.* (1984) regarded goldfieldite as "typomorphic of gold–telluride deposits localized within volcanic regions". Knittel (1989) suggested that As-rich goldfieldite is more common in "polymetallic Cu mineralization", whereas the Sb-rich variety seems to be prevalent in "base-metal-poor precious metal deposits". We will reassess these hypotheses on the basis of our database.

Substitutions of relatively large atoms in tellurian tetrahedrite$_{ss}$ minerals

One of Goldschmidt's rules (Faure 1991) on substitutions in minerals states that the radii of the two atoms involved in the substitution should not differ by more than 15%. In tellurian members of tetrahedrite$_{ss}$, there are a few cases that do not follow this rule: they involve Cd and Hg for the *M*1 site, Ag for *M*2, and As for *X*. Considering that tetrahedrite$_{ss}$ minerals have a structure that is sufficiently "flexible" to allow distortions, the replacement of smaller atoms (*e.g.*, Cu, Fe and Zn) by larger ones (Cd and Hg) can be accommodated through rotation of tetrahedra around their 4-fold axes (N.E. Johnson, pers. commun., 1992). This is very likely the case for goldfieldite, in which the Cd and Hg concentrations are extremely low.

The substitution of Ag for Cu in tetrahedrite$_{ss}$ has puzzled scientists for a long time, as with more than 4 Ag *apfu* the cell size decreases, rather than increases, as suggested by the larger size of Ag. Charnock *et al.* (1988) attributed this to Ag – Sb interaction as deduced from EXAFS spectroscopic results. In goldfieldite, however, the maximum observed Ag content barely exceeds 1 *apfu*; thus it outside the high-Ag region, and it is likely that the Ag-for-Cu substitution is accommodated through distortion. The Te-for-As substitution is reflected by a change in the cell dimension, as previously shown.

Absence of end-member goldfieldite in nature

There appear to be no crystallographic reasons to explain why end-member goldfieldite does not form in nature. Hydrothermal synthesis of goldfieldite was carried out by Kalbskopf (1974): his runs lasted 25 hours at 230°C under vapor-saturated conditions and produced goldfieldite (88 wt.%), digenite (8 wt.%) and native Te (4 wt.%). Kalbskopf (1974) inferred that 180°C should be considered as the lower limit of stability of goldfieldite, and favorable pH conditions are neutral to mildly alkaline. Kovalenker & Rusinov (1986) suggested that the formation of goldfieldite requires oxidizing conditions and high activity of sulfur. Dry

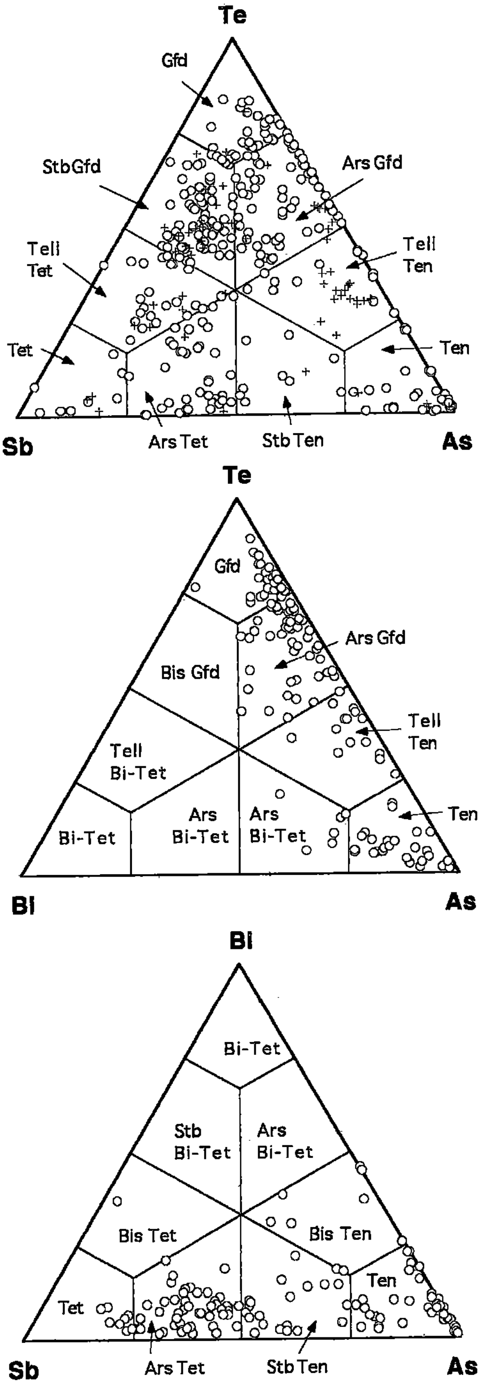

FIG. 16. Classification of 361 samples of natural goldfieldite (electron-microprobe data). In the Te–Sb–As plot, the crosses indicate compositions for which Bi was not sought, whereas the circles refer to compositions with values for Bi. The abbreviations of the fields are as the same as in Figure 15.

synthesis within the system Cu–Te–S was undertaken by S. Karup-Møller (unpubl.) to determine phase relationships at 350°, 450°, 550°, 675°, 800° and 900°C. Only runs at 350° and 450°C produced goldfieldite: at the former temperature, it coexists with digenite, covellite, native Te, phase A ($Cu_{30}Te_{23}S_{47}$) and a liquid of composition $Te_{13}S_{87}$, whereas at 450°C, goldfieldite is in equilibrium with digenite, covellite and a liquid of composition $Cu_{10.0}Te_{80.5}S_{8.5}$. These experiments indicate that pure goldfieldite is stable at certain conditions and could precipitate under natural conditions given the optimum composition of hydrothermal fluid. However, natural hydrothermal fluids from which tellurian tetrahedrite$_{ss}$ precipitate probably always contain at least minor amounts of As, Sb and Bi, hence these elements are incorporated to some extent in the solid solution.

Ore deposits hosting goldfieldite

Our review shows that tellurian tetrahedrite$_{ss}$ is most commonly found in epithermal gold deposits. Although we have only scant information on the mineralogy and alteration of the majority of these deposits, it appears that high-sulfidation epithermal gold deposits are the most common host of this sulfosalt. This is not surprising, as high base-metal contents and the presence of sulfosalts (*e.g.*, enargite – luzonite) are two of the characteristics of high-sulfidation systems (White & Hedenquist 1990).

Five occurrences of goldfieldite in porphyry environments are reported. At Tirad, in the Philippines, goldfieldite is associated with deep-seated advanced argillic alteration (Trudu & Knittel, in press), which cross-cuts the main porphyry-style mineralization and shows strong similarities to the high-sulfidation Lepanto Cu–Au–As deposit, where Gonzalez (1956) reported the occurrence of tellurian phases. At the Marian gold deposit, also in the Philippines, goldfieldite belongs to an assemblage of minerals typical of low-sulfidation epithermal systems that precipitated in polymetallic veins at the periphery of porphyry-Cu mineralization (Knittel 1989).

At Butte, Montana, Springer (1969) reported the occurrence of goldfieldite in association with colusite, but he did not give precise indications regarding the timing of precipitation of these minerals. There is only very limited reference to the timing of the deposition of colusite at Butte: Thompson (1973) reported it in the "horsetail zone", which is characterized by predominantly sericitic and minor advanced argillic alterations (Meyer *et al.* 1968), indicating that colusite and the associated goldfieldite precipitated toward the end of the geochemical evolution of the porphyry-style mineralization at Butte. In the Goldfield area, Nevada, orebodies form irregular sheets and pipes within systems of silicified veins hosted by extensively acid-sulfate (alunite – quartz) altered rhyodacite, and it has been speculated that a porphyry-type system may lie at depth nearby, although probably not directly beneath Goldfield (Wallace 1979).

Finally, at the Murgul copper deposit in Turkey (Willgallis *et al.* 1990), bismuthoan tennantite with up to 0.87 wt.% Te has been analyzed, but no data on its paragenetic position were provided. Schneider *et al.* (1988) showed that "fahlore" is related to the latest stage of alteration, which is siliceous in character; although they infer a volcanogenic origin for the Murgul deposit, most of their observations appear to be indicative of a porphyry-Cu style mineralization.

The occurrence of goldfieldite in the Besshi-type deposits in Japan (Kase 1986) suggests that this mineral also is associated with volcanogenic massive sulfide (VMS) mineralization. Kase (1986) reported that lower-amphibolite-grade metamorphism affected the Sazare and Ikadazu deposits, and that tennantite and tellurian tennantite, together with chalcopyrite, bornite and sphalerite, occur in the interstices of granular pyrite. The description does not provide enough detail to infer whether the tellurian minerals of the tetrahedrite$_{ss}$ formed prior or during metamorphism. The Bittibulashk deposit, in Russia, where tellurian tennantite occurs (Loginov *et al.* 1983), likewise appears to be a VMS deposit.

We conclude that goldfieldite and other tellurian members of tetrahedrite$_{ss}$ occur in both high- and low-sulfidation epithermal Au mineralization, but also can form during the last stages of porphyry-style mineralization and in VMS deposits. Our review also shows that As and Sb enrichment in goldfieldite is not related to specific styles of mineralization, as Knittel (1989) suspected. Triangular Te – Sb – As and tetrahedral Te – Sb – As – Bi plots (Fig. 17) show that goldfieldite from the Tirad deposit in the Philippines (Trudu & Knittel, in press) and the Megradzor deposit in Armenia are enriched in As. In contrast, at the Goldfield deposit, Nevada (Knittel & Johnson, in prep.), the Au deposits of the Kamchatka Peninsula, Russia (Kovalenker *et al.* 1989) and the Au deposits from the Kuraminski Range in Uzbekistan (Novgorodova *et al.* 1978), the tellurian members of the tetrahedrite$_{ss}$ are enriched in Sb. All these deposits display characteristics typical of epithermal-style mineralization.

Another interesting aspect of the data displayed in Figure 17 is that in each deposit, the ratio of the two most abundant trivalent semimetals is approximately constant, whereas the Te content is variable. This may reflect constant As/Sb and variable Te contents in the hydrothermal fluids from which the tellurian tetrahedrite precipitated, but may also reflect a variable ability of tetrahedrite$_{ss}$ to accommodate Te, depending on the physicochemical conditions. Thermodynamic data regarding the As–Sb–Te exchange are not available. In their study of the thermodynamic properties of tetrahedrite and tennantite, Sack & Loucks (1985) stated that "tetrahedrites–tennantites with intermediate Sb/(As + Sb) ratios have greater As/Sb ratio than the

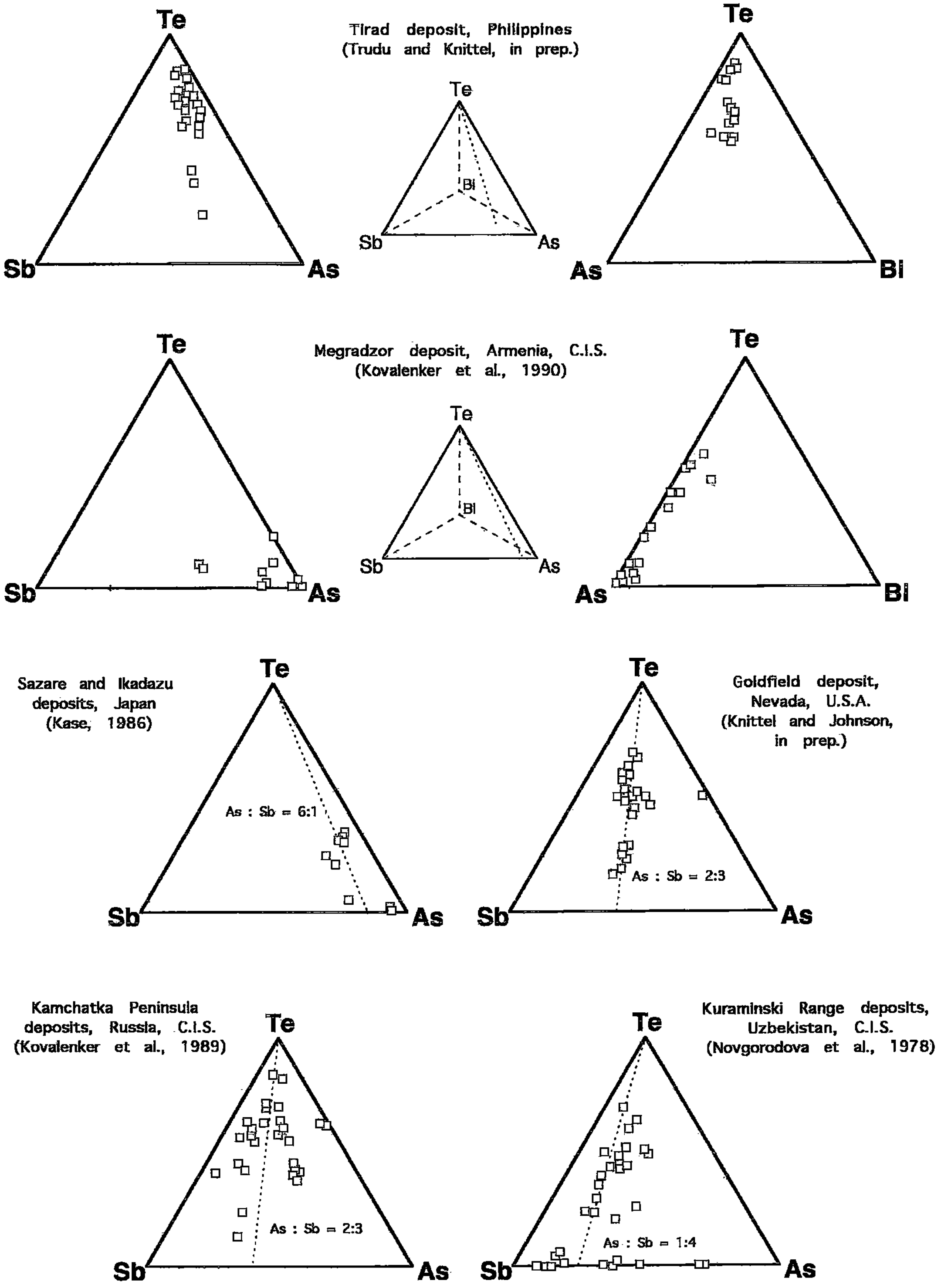

FIG. 17. Triangular plots of tellurian tetrahedrite$_{ss}$ minerals from selected ore deposits. The dashed lines represent the best fit to the data of each plot.

hydrothermal solutions from which they precipitated". Therefore, the ratios amongst semimetals in tetrahedrite$_{ss}$ minerals are not directly indicative of the composition of the fluid from which they precipitated. In several ore deposits in which tetrahedrite–tennantite is the only As- and Sb-bearing phase, its Sb content increases with the evolution of the hydrothermal fluid (Sack & Loucks 1985).

CONCLUSIONS

In the present study, we show that goldfieldite and other tellurian phases of the tetrahedrite$_{ss}$ seem to be relatively rare in comparison to other species of the same group, such as tetrahedrite, tennantite and freibergite. This may be due to the fact that Te is rarely enriched in nature. Furthermore, Te has not been routinely sought during electron-microprobe studies of sulfosalts.

Incorporation of Te into tetrahedrite$_{ss}$ leads to coupled substitutions to maintain an overall charge-balance. These substitutions, initially proposed by Kase (1986) and confirmed by data obtained by Trudu & Knittel (1991) and Shimizu & Stanley (1991), can be summarized as follows:

For replacement of up to two atoms of trivalent semimetal by tetravalent Te, divalent Fe and Zn are replaced by monovalent Cu. Higher Te contents are compensated by a reduced number of Cu atoms. Interestingly, Cu – M^{2+} substitution in goldfieldite takes place in the *M*1 site, whereas the vacancies occur in the *M*2 position.

Where substitutions involving elements of different valence take place, then the charge balance in the mineral can be maintained in two ways, either through a coupled substitution or through a vacancy in the structure. In renierite, which according to Bernstein *et al.* (1989) has the formula $Cu_{10}(Zn_{1-x}Cu_x)(Ge_{2-x}As_x)Fe_4S_{16}$ where $0 \leq x \leq 1$, only the coupled substitution occurs: as trivalent As replaces tetravalent Ge, monovalent Cu takes the place of divalent Zn. An example of the second mechanism is shown by colusite (S. Merlino, pers. commun., 1992): the charge balance in the solid solution between the Sn-rich ($Cu_{26}V_2Sn_2As_4S_{32}$) and Sn-poor varieties ($Cu_{24}V_2As_6S_{32}$) is maintained through vacancies in one of the Cu sites (note that As is pentavalent in this mineral) with a reduction of Cu atoms from 26 to 24. As shown throughout this paper, goldfieldite seems to be unusual in that both mechanisms of maintaining charge balance occur, as Te progressively substitutes for As, Sb and Bi.

We hope that this work will make geoscientists more aware that Te (and also Bi and Se) may be significant components in minerals of the tetrahedrite$_{ss}$ series. With more analytical data, we will be able to re-assess whether a specific signature in mineral composition is typical of a certain style of mineralization. Petersen & McMillan (1992) have shown an application of the compositional data of the tetrahedrite$_{ss}$ minerals to mineral exploration and mine development; however, they have not extended their work to the tellurian members of this series.

We have experimental work in progress on the tetrahedrite$_{ss}$ with variable Te content in order to measure the coordination of Te through EXAFS spectroscopy and the variation in cell size as a function of crystal chemistry. We hope that one day the work on the thermodynamic properties of tetrahedrite and tennantite will be extended to goldfieldite as well, so that we can gain a better understanding of the conditions under which it precipitates in ore environments.

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