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WinTtrclas, A Windows program for tetrahedrite-group minerals

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ABSTRACT

A Microsoft® Visual Basic software, WinTtrclas, has been developed to calculate the chemical formulae of tetrahedrite-group minerals (TGM) based on data obtained from wet-chemical and electron-microprobe analyses. WinTtrclas evaluates currently 40 valid mineral species using the Commission on New Minerals, Nomenclature and Classification (CNMMN) of the International Mineralogical Association (IMA) nomenclature scheme for the TGM in the general formula $^{M(2)}A_6{}^{M(1)}(B_4C_2)_{\Sigma 6}{}^{X(3)}D_4{}^{S(1)}Y_{12}{}^{S(2)}Z$ within the tetrahedrite, tennantite, freibergite, arsenofreibergite, hakite, giraudite, rozhdestvenskayaite, goldfieldite, ústalečite and zvěstovite series as well as two unassigned species. Considering occurrence of vacancies at anion sites as well as at cation positions in some Te-bearing species, the program provides different estimation and normalization procedures such as the the Σ*Me*=32, 29, 27 and 16 atoms per formula unit (apfu), as well as Σ(As+Sb+Te+Bi)=4 apfu to estimate the chemical formulae of TGM species. Mineral formulae of the TGM are calculated based on the dominant cations at the *M*(1), *M*(2), *X*(3) and dominant anions at the S(1)+S(2) sites. WinTtrclas operates in four stages: (1) it estimates cation and anion contents provided by input chemical data; (2) it determines the dominant cation and anion at the *M*(1), *M*(2), *X*(3) and S(1)+S(2) sites; (3) it assigns the TGM to one of the ten series, based on the dominant cations and anions at these sites; and (4) it classifies the TGM species into an appropriate series. WinTtrclas allows users to: (1) enter up to 20 input variables for mineral-chemical analyses; (2) type and load multiple TGM compositions in the data entry section; (3) edit and load the Microsoft® Excel files used in calculating, classifying, and naming the TGM, and (4) store all the calculated parameters in the output of a Microsoft® Excel file for further data evaluations. The program is distributed as a self-extracting setup file, including the necessary support files used by the program, a help file, and representative sample data files.

Keywords: tetrahedrite; tennantite; freibergite; arsenofreibergite; hakite; giraudite; goldfieldite; rozhdestvenskayaite; ústalečite; zvěstovite; classification; software.

INTRODUCTION

The tetrahedrite-group minerals (TGM) are considered the most common and important sulfosalts occurring in a wide variety of geological settings, mostly in hydrothermal veins in porphyry epi- to mesothermal ore deposits, but also in regional metamorphic rocks, skarns, sedimentary exhalative (SEDEX) deposits, volcanogenic massive sulfide (VMS) deposits, Mississippi valley-type (MVT) deposits, black shales and orogenic and intrusion-related gold deposits as well as in active black smoker systems (Xiaochun, 2000; Sack et al., 2003; Kharbish et al., 2007; Keim et al., 2018; Nagornaya et al., 2021). Hence, the

TGM have been the subject of numerous studies and investigations from ancient up to modern times due to their scientific as well as economic importance as a source of copper and silver (Di Benedetto et al., 2002). Because of the members of TGM are sensitive tracers of chemical variations as well as redox state of hydrothermal fluids and host a large number of elements typical of hydrothermal environments, they provide an important information about the ore forming conditions in various types of ore deposits (Rezazadeh et al., 2021 and references therein). Due to the widespread isomorphism between tetrahedrite and tennantite, these minerals with their characteristics compositions, mineral associations and the sequence of their crystallization are of great importance to define the regularities in the evolution of the chemical composition of ore-generating solution systems (Shapovalova et al., 2019). The variations in chemical composition of tetrahedrite and tennantite are related to fluctuations in the physicochemical conditions such as changes in the acid-alkali environment depending on the temperature and sulfur fugacity in the ore-forming fluid, changes in the metal and semimetal migration conditions as well as fractionation of As, Sb, Cu and Ag between these minerals and fluid compositions (Lyubimtseva et al., 2020 and references therein).

Recently, the International Mineralogical Association-Commission on New Minerals, Nomenclature and Classification (IMA-CNMNC) has adopted a well-defined nomenclature for the TGM (Biagioni et al., 2020a) as well as defining species in the series, including those belonging to the tetrahedrite (e.g., Biagioni et al., 2020b; Mauro et al., 2021; Wang et al., 2023a; Sejkora et al., 2023, in press), tennantite (e.g., Biagioni et al., 2021, 2022 a,b; Voudouris et al., 2022; Wang et al., 2023b), freibergite and arsenofreibergite (e.g., Zakrzewski, 1989; Sejkora et al., 2022a; Shu et al., 2022; Mikuš et al., 2023), hakite and giraudite (e.g., Förster et al., 2002; Förster and Rhede, 2004; Škácha et al., 2016, 2017), goldfieldite (e.g., Knittel, 1989; Shimizu and Stanley, 1991; Makovicky and Karup-Møller, 2017; Biagioni et al., 2022c), rozhdestvenskayaite (e.g., Welch et al., 2018; Qu et al., 2024b), ústalečite (e.g., Sejkora et al., 2022b; Sejkora et al., 2024), zvěstovite (e.g., Sejkora et al., 2021) and unassigned pošepnýite (Škácha et al., 2020) and annivite-(Zn) species (Sejkora et al., 2024). Among these two unassigned tetrahedrite group minerals, annivite-(Zn) is a potential candidate for a new annivite series, probably with other species to be identified later and accepted by the IMA.

Minerals of the tetrahedrite-group, currently with a total of 40 isotypic species, show the widest chemical variability among sulfosalts due to their flexible crystal structure feature that enables to accommodate several cations of medium to small ionic radius and +1 to +4 charges (e.g., Ag^{+}, Cu^{+}, Cd^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}) with homo-and heterovalent substitutions. This situation causes the occurrence of different tetrahedrite-group species [e.g., tetrahedrite-(Zn), tetrahedrite-(Cu), tennantite-(Cd), tennantite-(Ni)] especially in hydrothermal ore deposits (Moëlo et al., 2008; Biagioni et al., 2020a; Sejkora et al., 2024). Considering the current IMA-accepted rules, the classification and nomenclature scheme of the TGM was recently proposed by Biagioni et al. (2020a). The general structural formula of TGM can be expressed as $^{M(2)}A_6{}^{M(1)}(B_4C_2)_{\Sigma 6}{}^{X(3)}D_4{}^{S(1)}Y_{12}{}^{S(2)}Z$, where A=$Cu^{+}$, Ag^{+} and □ (vacancy); B=Cu^{+}, and Ag^{+} ; C=Zn^{2+}, Fe^{2+}, Hg^{2+}, Cd^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+}, Cu^{+} , In^{3+} and Fe^{3+}; D=Sb^{3+}, As^{3+}, Bi^{3+}, and Te^{4+}; Y=S^{2-} and Se^{2-}; and Z=S^{2-}, Se^{2-} and □ (Biagioni et al., 2020a). Because of the occurrence of both mono- (Me^{+}) and divalent (Me^{2+}) cations at the *M*(1) site, with a 4:2 atomic ratio which is related to the valency-imposed double site-occupancy, various mineral species depending on the different combinations of B and C constituents are observed in the TGM (Biagioni et al., 2020a). However, one could say that pošepnýite is an exception to the rule of the 4:2 atomic ratio between B and C chemical constituents in the TGM. The TGM is divided into ten different series on the basis of the A, B, D, and Y constituents, including the tetrahedrite, tennantite, freibergite, arsenofreibergite, hakite, giraudite, rozhdestvenskayaite, goldfieldite, ústalečite and zvěstovite series. In the tetrahedrite-group, except for the goldfieldite and ústalečite series, mineral species is named using a hyphenated suffix between parentheses based on the dominant C constituent [e.g., argentotetrahedrite-(Fe) in the freibergite series]. Compared to the minerals within the tetrahedrite-group, members of the tetrahedrite and tennantite series are the most common species, whereas those with Se as the dominant Y and D chemical constituents, respectively, are rare or very rare occurrences (Sejkora et al., 2024).

Although various computer programs applicable to the calculation and classification of rock-forming silicate minerals have been developed over the past two decades (e.g., Yavuz, 1999, 2003, 2013; Yavuz et al., 2014, 2015; Yavuz and Yıldırım, 2020; Yavuz and Yavuz, 2023 a,b; 2024; Yavuz, in press), that useful for TGM, according to the current IMA report, has not yet appeared in the literature possibly in part owing to the lack of recent classification systematic by Biagioni et al. (2020a). Taking this situation into consideration, a computer program called WinTtrclas has been developed using the Microsoft® Visual Basic programming language. It can be used to calculate the chemical formulae from up to 200 analyses obtained from both wet-chemical and electron-microprobe techniques. The program estimates and classifies mineral analyses of the tetrahedrite-group on the basis of different estimation

and normalization procedures including the Σ*Me*=32, 29, 27 and 16 apfu as well as Σ(As+Sb+Te+Bi)=4 apfu from the pull-down menu of *Calculate Contents of Ions* in the *Start-up Screen* or *Data Entry Screen*. The calculation and classification procedures applied to TGM by WinTtrclas are carried out based on the currently accepted IMA nomenclature scheme by Biagioni et al. (2020a), but also takes into account new species that post-date the IMA report. WinTtrclas allows the user to display members of the tetrahedrite-group in several binary and ternary classification and compositional diagrams by using the Golden Software's Grapher program.

TETRAHEDRITE-GROUP MINERALS NOMENCLATURE

Using the available data on tetrahedrite isotypes with space group symmetry $I\bar{4}3m$, Biagioni et al. (2020a) proposed a nomenclature and classification scheme for the members of tetrahedrite- group which has been approved by the IMA-CNMNC. Since the publication of that report, 29 other new species belonging to the tetrahedrite-group have been approved by the IMA-CNMNC; that means the addition of approximately twice as many as new minerals in a few short years (see Table 1). The crystal structure of TGM which is characterized by three symmetry-independent cation positions and two anion ones currently includes 40 valid minerals divided into ten series with the structural formula $M(2)_6M(1)_6X(3)_4S(1)_{12}S(2)$ (Z=2). Members of the tetrahedrite-group are classified by Biagioni et al. (2020a) based on their crystal-chemical arguments in terms of the dominant ions at the M(1), M(2), X(3) and S(1)+S(2) sites in the general formula $^{M(2)}A_6{}^{M(1)}(B_4C_2)_{\Sigma 6}{}^{X(3)}D_4{}^{S(1)}Y_{12}{}^{S(2)}Z$, where the upper cases represent the following constituents:

A=Cu^+, Ag^+ and □ (vacancy); B=Cu^+, and Ag^+; C=Zn^{2+}, Fe^{2+}, Hg^{2+}, Cd^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+}, Cu^+ , In^{3+} and Fe^{3+}; D=Sb^{3+}, As^{3+}, Bi^{3+}, and Te^{4+}; Y=S^{2-}, and Se^{2-}; and Z=S^{2-}, Se^{2-} and □. According to Biagioni et al. (2020a), detailed investigations on the crystal chemistry of the TGM showed that no more than 2 apfu of divalent metals (e.g., Cu^{2+}, Cd^{2+}, Fe^{2+}, Hg^{2+}, Mn^{2+}, Ni^{2+} and Pb^{2+}) occur and the sum of the monovalent metals (Ag^++Cu^+) is usually about 10 apfu, with six of them hosted at the M(2) site and the rest of four at the M(1) site. Mineral formula calculated based on the total number of 13 anions (i.e., S^{2-}+Se^{2-}) apfu, yielding 26 negative charges. The excess of –4 charges is balanced by the accommodation of 2 Me^{2+}-cations distributed over the C constituent at the M(1) site as the sum of 10 monovalent cations (i.e., Ag^+ and Cu^+) at the M(1) and M(2) sites (A and B constituents) and the sum of 4 trivalent cations (i.e., Sb^{3+}, As^{3+}, Bi^{3+}) at the X(3) site (D constituent) gives +22 charges (Biagioni et al., 2020a). Mono- (Me^+) and divalent (Me^{2+}) cations at the M(1) site of the TGM show valency-imposed double-site occupancy. Consequently, sample with a different pair of B and C constituents at the M(1) site can be considered as a separate mineral species. On the other hand, since divalent metals (Me^{2+}) are also preferentially allocated at the M(1) site, the chemical data for the tetrahedrite isotypic series can be considered in classification of the TGM, in accord with the main requirement for a practical nomenclature system (Hatert and Burke, 2008). Finally, in agreement with Mills et al. (2009), the following nomenclature and classification scheme was proposed by Biagioni et al. (2020a) for the TGM:

(1) A mineral belonging to the tetrahedrite-group is a sulfosalt with a considerably collapsed sodalite-like framework, which is compatible with the general structural formula $^{M(2)}A_6{}^{M(1)}(B_4C_2)^{X(3)}D_4{}^{S(1)}Y_{12}{}^{S(2)}Z$.

(2) Each different combination of dominant constituents such as B, D and Y at the M(1), X(3) and S(1)+S(2) sites, respectively (i.e., $^{M(1)}$B, $^{X(3)}$D and $^{S(1)}$Y) deserves a distinct root-name as follow:

B=Cu^+, D=Sb^{3+}; Y=S^{2-}: tetrahedrite
B=Cu^+, D=As^{3+}, Y=S^{-2}: tennantite
B=Ag^+, D=Sb^{3+}, Y=S^{-2}: freibergite
B=Ag^+, D=As^{3+}, Y=S^{-2}: arsenofreibergite
B=Cu^+, D=Sb^{3+}, Y=Se^{2-}: hakite
B=Cu^+, D=As^{3+}, Y=Se^{2-}: giraudite
B=Ag^+, D=Sb^{3+}, Y=S^{2-}: rozhdestvenskayaite
B=Cu^+, D=Te^{4+}, Y=S^{2-}: goldfieldite
B=Ag^+, D=As^{3+}, Y=S^{2-}: zvěstovite
B=Cu^+, D=(Sb^{3+}/As^{3+})Te^{4+}, Y=Se^{2-}: ústalečite

(3) Each distinct mineral species belonging to the tetrahedrite-group must have a hyphenated suffix between parentheses, specifying the dominant $^{M(1)}$C constituent (also called as the charge compensating constituent). For example, hakite-(Hg) for $Cu_6(Cu_4Hg_2)Sb_4Se_{13}$.

(4) Considering the Cu^+/Ag^+ ratio, if two minerals have $^{M(1)}$B=Cu and the same dominant constituent at $^{X(3)}$D and $^{S(1)}$Y sites [e.g., tetrahedrite-(Fe) for $^{M(2)}Cu_6{}^{M(1)}(Cu_4Fe_2)^{X(3)}Sb_4{}^{S(1)+S(2)}Y_{12}Z$ and tetrahedrite-(Cu) for $^{M(2)}Cu_6{}^{M(1)}(Cu_4Cu_2)^{X(3)}Sb_4{}^{S(1)+S(2)}Y_{12}Z$], the same root-name (e.g., tetrahedrite) will be used for them. The adjectival prefix "argento" will be preferred to the root-name if $^{M(2)}$Ag> $^{M(2)}$Cu [e.g., argentotetrahedrite-(Cd) for $^{M(2)}Ag_6{}^{M(1)}(Cu_4Cd_2)^{X(3)}Sb_4{}^{S(1)+S(2)}Y_{12}Z$ and tetrahedrite-(Cd) for $^{M(2)}Cu_6{}^{M(1)}(Cu_4Cd_2)^{X(3)}Sb_4{}^{S(1)+S(2)}Y_{12}Z$]. No prefix will be used if $^{M(2)}$Cu>$^{M(2)}$Ag. On the other hand, minerals with $^{M(1)}$B=Ag deserve a different root-name [e.g., rozhdestvenskayaite-(Zn) for $^{M(2)}Ag_6{}^{M(1)}(Ag_4Zn_2)^{X(3)}Sb_4{}^{S(1)+S(2)}Y_{12}Z$].

(5) The chemical composition of TGM was indicated by an end-member formula using the criteria proposed by Hawthorne (2002).

(6) Members of the tetrahedrite-group were currently

Table 1. A list of the 40 IMA-approved species in the tetrahedrite group (revised from Biagioni et al. 2020a) classified by the WinTtrclas program.

	Tetrahedrite series					
Row	Mineral	Symbol	$^{M(2)}$A	$^{M(1)}$B$^{M(1)}$C	$^{X(3)}$D	$^{S(1)}$Y $^{S(2)}$Z
1	Tetrahedrite-(Cd)§	Ttr-Cd	Cu_6	Cu_4 Cd_2	Sb_4	S_{13}
2	Tetrahedrite-(Cu)§	Ttr-Cu	Cu_6	Cu_4 Cu_2	Sb_4	S_{13}
3	Tetrahedrite-(Fe)	Ttr-Fe	Cu_6	Cu_4 Fe_2	Sb_4	S_{13}
4	Tetrahedrite-(Hg)§	Ttr-Hg	Cu_6	Cu_4 Hg_2	Sb_4	S_{13}
5	Tetrahedrite-(Mn)§	Ttr-Mn	Cu_6	Cu_4 Mn_2	Sb_4	S_{13}
6	Tetrahedrite-(Ni)§	Ttr-Ni	Cu_6	Cu_4 Ni_2	Sb_4	S_{13}
7	Tetrahedrite-(Zn)	Ttr-Zn	Cu_6	Cu_4 Zn_2	Sb_4	S_{13}
	Tennantite series					
8	Tennantite-(Cd)§	Tnt-Cd	Cu_6	Cu_4 Cd_2	As_4	S_{13}
9	Tennantite-(Cu)§	Tnt-Cu	Cu_6	Cu_4 Cu_2	As_4	S_{13}
10	Tennantite-(Fe)	Tnt-Fe	Cu_6	Cu_4 Fe_2	As_4	S_{13}
11	Tennantite-(Hg)§	Tnt-Hg	Cu_6	Cu_4 Hg_2	As_4	S_{13}
12	Tennantite-(In)§	Tnt-In	Cu_6	Cu_4 In_2	As_4	S_{13}
13	Tennantite-(Mn)§	Tnt-Mn	Cu_6	Cu_4 Mn_2	As_4	S_{13}
14	Tennantite-(Ni)§	Tnt-Ni	Cu_6	Cu_4 Ni_2	As_4	S_{13}
15	Tennantite-(Zn)	Tnt-Zn	Cu_6	Cu_4 Zn_2	As_4	S_{13}
	Freibergite series					
16	Argentotetrahedrite-(Cd)§	Attr-Cd	Ag_6	Cu_4 Cd_2	Sb_4	S_{13}
17	Argentotetrahedrite-(Fe)	Attr-Fe	Ag_6	Cu_4 Fe_2	Sb_4	S_{13}
18	Argentotetrahedrite-(Hg)§	Attr-Hg	Ag_6	Cu_4 Hg_2	Sb_4	S_{13}
19	Argentotetrahedrite-(Zn)§	Attr-Zn	Ag_6	Cu_4 Zn_2	Sb_4	S_{13}
20	Kenoargentotetrahedrite-(Fe)	Kattr-Fe	Ag_6	Cu_4 Fe_2	Sb_4	$S_{12}\square$
21	Kenoargentotetrahedrite-(Zn)§	Kattr-Zn	Ag_6	Cu_4 Zn_2	Sb_4	$S_{12}\square$
	Arsenofreibergite series					
22	Argentotennantite-(Zn)	Atnt-Zn	Ag_6	Cu_4 Zn_2	As_4	S_{13}
23	Argentotennantite-(Fe)§	Atnt-Fe	Ag_6	Cu_4 Fe_2	As_4	S_{13}
24	Kenoargentotennantite-(Fe)§	Katnt-Fe	Ag_6	Cu_4 Fe_2	As_4	$S_{12}\square$
	Hakite series					
25	Hakite-(Cd)§	Hak-Cd	Cu_6	Cu_4 Cd_2	Sb_4	Se_{13}
26	Hakite-(Fe)§	Hak-Fe	Cu_6	Cu_4 Fe_2	Sb_4	Se_{13}
27	Hakite-(Hg)	Hak-Hg	Cu_6	Cu_4 Hg_2	Sb_4	Se_{13}
28	Hakite-(Zn)§	Hak-Zn	Cu_6	Cu_4 Zn_2	Sb_4	Se_{13}
	Giraudite series					
29	Giraudite-(Zn)	Gir-Zn	Cu_6	Cu_4 Zn_2	As_4	Se_{13}
	Rozhdestvenskayaite series					
30	Rozhdestvenskayaite-(Zn)	Roz-Zn	Ag_6	Ag_4 Zn_2	Sb_4	S_{13}
31	Kenorozhdestvenskayaite-(Fe)§	Kroz-Fe	Ag_6	Ag_4 Fe_2	Sb_4	$S_{12}\square$
	Goldfieldite series					
32	Goldfieldite	Gf	$(Cu_4\square_2)$	Cu_6	Te_4	S_{13}
33	Stibiogoldfieldite§	Sbgf	Cu_6	Cu_6	(Sb_2Te_2)	S_{13}

Symbols from Warr (2021). (§) = New tetrahedrite group species approved by the IMA later than the subcommittee report by Biagoni et al. (2020a).

Table 1. ... Continued

Row	Mineral	Symbol	$^{M(2)}$A	$^{M(1)}$B$^{M(1)}$C	$^{X(3)}$D	$^{S(1)}$Y $^{S(2)}$Z
34	Arsenogoldfieldite§	Asgf	Cu_6	Cu_6	(As_2Te_2)	S_{13}
	Ústalečite series					
35	Stibioústalečite§	Súč	Cu_6	Cu_6	(Sb_2Te_2)	Se_{13}
36	Arsenoústalečite§	Aúč	Cu_6	Cu_6	(As_2Te_2)	Se_{13}
	Zvěstovite series					
37	Zvěstovite-(Fe)§	Zvě-Fe	Ag_6	Ag_4Fe_2	As_4	S_{13}
38	Zvěstovite-(Zn)§	Zvě-Zn	Ag_6	Ag_4Zn_2	As_4	S_{13}
	Unassigned species					
39	Pošepnýite§	Pšý	$(Cu^{+}_{3+x}\square_{3-x})_{\Sigma 6}$	$(Hg^{2+}_{4-x}Cu^{+}_{2+x})_{\Sigma 6}$	Sb_4	$(Se_{12.5}\square_{0.5})_{\Sigma 13}$
40	Annivite-(Zn)§	Anv-Zn	Cu_6	Cu_4Zn_2	Bi_4	S_{13}

Symbols from Warr (2021). (§) = New tetrahedrite group species approved by the IMA later than the subcommittee report by Biagioni et al. (2020a).

divided into ten series, on the basis of the combination of $^{M(2)}$A, $^{M(1)}$B, $^{X(3)}$D, and $^{S(1)}$Y constituents. Due to the some uncertainties in the end-member composition of TGM (e.g., poor attention at the dominant charge compensating cation), unsuffixed names such as "tetrahedrite", "tennantite" or "hakite" were considered as series names. Similarly, freibergite was also expressed as a series name to show different Ag-rich members of the tetrahedrite-group. Consequently, the proposed series are as follow:

Tetrahedrite series: A=Cu, B=Cu, D=Sb, Y=S
Tennantite series: A=Cu, B=Cu, D=As, Y=S
Freibergite series: A=Ag, B=Cu, D=Sb, Y=S
Arsenofreibergite series: A=Ag, B=Cu, D=As, Y=S
Hakite series: A=Cu, B=Cu, D=Sb, Y=Se
Giraudite series: A=Cu, B=Cu, D=As, Y=Se
Rozhdestvenskayaite series: A=Ag, B=Ag, D=Sb, Y=S
Goldfieldite series: A=Cu, B=Cu, D=Te, Y=S
Ústalečite series: A=Cu, B=Cu, D=(SbAs)Te, Y=Se
Zvěstovite series: A=Ag, B=Ag, D=As, Y=S

(7) In the freibergite, arsenofreibergite, rozhdestvenskayaite, and zvěstovite series, Ag constitutes the dominant cation at the *M*(2) site being as trigonally coordinated or as discrete $(Ag_6)^{4+}$ clusters, which is characterized by Ag-Ag bonds coupled with vacancy at the S(2) site. Depending on the vacancies at the S(2) site, the prefix "keno" (i.e., empty from the Greek word "keno") is proposed on the root-name to define the exact relation between the S(2) vacant site and the $(Ag_6)^{4+}$ cluster in the cited series [e.g., kenoargentotetrahedrite-(Fe) for $^{M(2)}Ag_6{}^{M(1)}(Cu_4Fe_2)^{X(3)}Sb_4{}^{S(1)}S_{12}{}^{S(2)}\square$].

The current sulfur determination by routine EPMA technique seems to be in general inadequate to reliably determine the number of vacancies at the S(2) site and also the presence of $(Ag_6)^{4+}$ clusters. Hence, specific structural information on the *M*(2) and S(2) sites may be required to distinguish some of mineral species as in the case of members of the anion-omission homeotype series $Ag_6(Cu_4Me_2)Sb_4S_{13-x}$, with end-member compositions of x=0 [e.g., argentotetrahedrite-(*Me*) for $Ag_6(Cu_4Me_2)Sb_4S_{13}$] and x=1 [e.g., kenoargentotetrahedrite-(*Me*) for $Ag_6(Cu_4Me_2)Sb_4S_{12}$] (Biagioni et al., 2020a). Within this scope, for example, the following boundaries between members of the tetrahedrite-group were established by Biagioni et al. (2020a): (1) 3<Ag<8 apfu, 0.5<$^{S(2)}$S<1.0= argentotetrahedrite; (2) 3<Ag<8 apfu, 0.0<$^{S(2)}$S<0.5= kenoargentotetrahedrite; (3) 8<Ag<10 apfu, 0.5<$^{S(2}$S<1.0=rozhdestvenskayaite. Considering the TGM series in terms of Te apfu content, the following boundaries were proposed (Biagioni et al., 2020a; Sejkora et al., 2022b, 2024): (1) Tetrahedrite/tennantite, with 0<Te apfu<1; (2) New name, with 1<Te apfu<3. (3) Goldfieldite, with 3<Te apfu<4. However, for 3<Te apfu<4, the dominant trivalent constituent (e.g., Sb^{3+}, As^{3+}) is considered to define a different name (e.g., stibioústalečite, arsenoústalečite and potential "ústalečite"; (4) Hakite/giraudite, with 0<Te apfu<1. Recently, following the Hazen et al. (2022) approach about the lumping and splitting of minerals for a series of 57 unique paragenetic modes to classify them in a termed evolutionary scheme, Johnson (2024) proposed a scheme for the TGM with a splitting speculation including 12 separate series, each with eight unique species for a total of 96 possible tetrahedrites.

PROGRAM DESCRIPTION

WinTtrclas is a user-friendly, compiled program package (≈11 Mb) developed for personal computers running on the Microsoft® Windows operating system.

The program first calculates the cation and anion values apfu for analyses made on TGM (wet-chemical or electron-microprobe techniques) and then uses these to classify the mineral into the 40 IMA-approved species within the tetrahedrite, tennantite, freibergite, arsenofreibergite, hakite, giraudite, rozhdestvenskayaite, goldfieldite, ústalečite and zvěstovite series as well as two unassigned species (see Table 1). A list of the calculation steps in the *Calculation Screen* and in the output of a Microsoft Excel file developed by the program is given in Table 2.

Upon successful installation of WinTtrclas, the start-up screen, with various pull-down menus and equivalent shortcuts, appears on the screen (Figure 1a). The program allows the user to input data from wet-chemical or electron-microprobe analyses by clicking the *New* icon on the toolbar, then selecting the *New File* from the pull-down menu of the *File* option or pressing the *Ctrl + N* keys (Figure 1b). Up to 20 chemical constituents (in wt%) are used by WinTtrclas, in the following order:

Sample No, Cu, Ag, Cd, Fe, Mn, Zn, Co, Ni, Pb, Hg, Tl, In, Sb, Bi, As, Sn, Te, Ge, Se, and S.

Data from a TGM analysis can also be input into a blank Excel file following the above order, saving it with the extension of ".xls" or ".xlsx", after which it can then be loaded into the *Data Entry Screen* of the program by clicking the *Open Excel File* option from the pull-down menu of *File*. By selecting the *Edit Excel File* option from the pull-down menu of *File*, data can be inserted into a blank Excel file (i.e., MyTetrahedrite), saved using a different file name (with the extension of ".xls" or ".xlsx"), and then loaded into the *Data Entry Screen* of the program by clicking the *Open Excel File* option from the pull-down menu of *File*. Additional information about the data entry or similar topics can be accessed by pressing the F1 function key to display the WinTtrclas.chm file on the screen. The current version of WinTtrclas includes a total of 46 binary and ternary classification and

Table 2. Description of column numbers in the *Calculation Screen* window of WinTtrclas program and an output Excel file.

Row	Explanations	Column Numbers
1	Content of the tetrahedrite-group mineral analyses (wt%)	1-21
2	Blank	50
3	Recalculated cation and anion (apfu)	23-43
4	Blank	44
5	Recalculated cation (apfu) at the *M*(2) site [i.e., $^{M(2)}$A]	45-47
6	Blank	48
7	Recalculated cation (apfu) at the *M*(1) site [i.e., $^{M(1)}$B]	49-51
8	Blank	52
9	Recalculated cation (apfu) at the *M*(1) site [i.e., $^{M(1)}$C]	53-64
10	Blank	65
11	Recalculated cation (apfu) at the *X*(3) site [i.e., $^{X(3)}$D]	66-72
12	Blank	73
13	Recalculated anion (apfu) at the S(1)+S(2) sites [i.e., $^{S(1)}$Y$^{S(2)}$Z]	74-77
14	Blank	78
15	Dominant cation at the *M*(2) site [i.e., $^{M(2)}$A]	79
16	Dominant cation at the *M*(1) site [i.e., $^{M(1)}$B]	80
17	Dominant cation at the *M*(1) site [i.e., $^{M(1)}$C]	81
18	Dominant cation at the *X*(3) site [i.e., $^{X(3)}$D]	82
19	Dominant anion at the S(1) site [i.e., $^{S(1)}$Y]	83
20	Blank	84
21	Series names defined by the program	85
22	Species defined by the program	86
23	Blank	87

(apfu) = Atoms per formula unit.

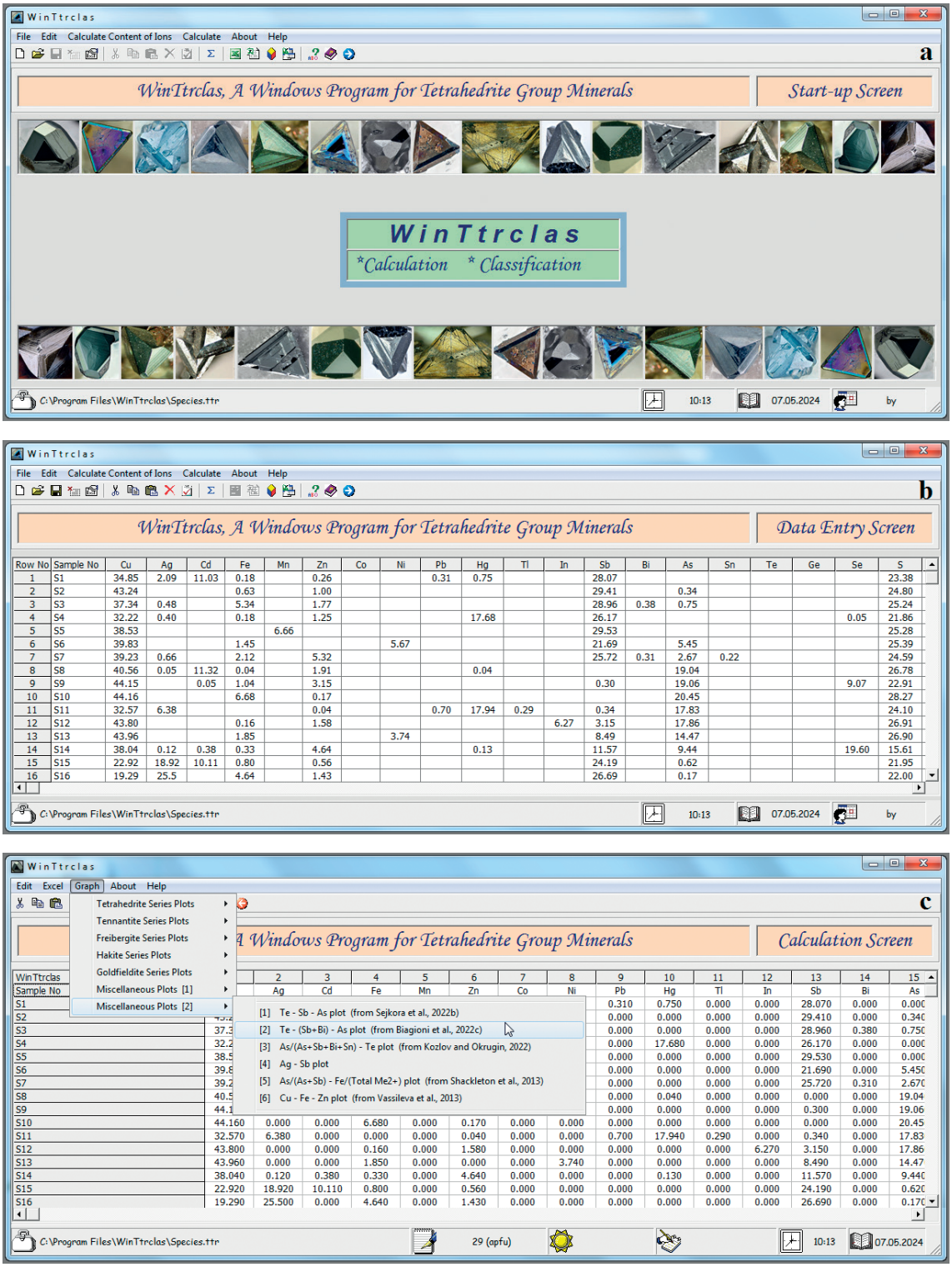


Figure 1. a) A screenshot of the WinTtrclas *Start-up* window with various pull-down menus and equivalent shortcuts. b) A screenshot of the WinTtrclas *Data Entry* window with a total of 20 constituents (wt%). c) A screenshot of the WinTtrclas *Calculation Screen* with plot options from the pull-down menu of the *Graph*.

compositional plots. Data on any of these plots can be displayed using the program Grapher (Golden, 2024) by selecting the diagram type from the pull-down menu of *Graph* in the *Calculation Screen* of the program (Figure 1c).

WORKED EXAMPLES

Using the selected data set from literature as well as "Species.ttr" file in the installation document (i.e., WinTtrclas setup file), examples showing how WinTtrclas can be used in the determination of chemical formulae and TGM classification are presented. The previously typed or loaded analyses are processed by clicking the *Calculate* icon (i.e., ∑) in the *Data Entry Screen* of the program, after which all input and estimation parameters are displayed in columns 1-86 (see Table 2) of the *Calculation Screen*. Pressing the Ctrl + F keys or clicking the *Open File to Calculate* option from the *Calculate* menu also executes processing of a selected data file with the extension of ".ttr" that refers to the tetrahedrite-group. By clicking the *Send results to Excel file* icon in the *Calculation Screen*, all calculations can be stored in an Excel file (Output. xlsx) and then displayed by clicking the *Open and edit Excel file* icon.

To take a decision in recalculation procedure for the chemical formula is an important issue for understanding the crystal chemistry of TGM. As discussed in previous papers (e.g., Trudu and Knittel, 1998; Welch et al., 2018; Sejkora et al., 2021), different approaches were proposed to recalculate the chemical formulae of TGM. (1) Normalization on the basis ΣS (+Se)=13 apfu. Application of this approach to the TGM is observed especially in the older literature. It is believed that the sulfur content of the TGM determined by EPMA technique can be highly variable, with a clear crystallographic evidence of vacancies at the S(2) site (i.e., $^{S(2)}$Z). The miscalculation of formula unit is not a realistic approach by using ΣS=13 apfu for kenoargentotetrahedrite-(Fe) as well as kenorozhdestvenskayaite-(Fe) in which they contain Σ12 S apfu at the S(1) site (i.e., $^{S(1)}$Y). Hence, recalculation procedure on the basis of Σ13 anions apfu may cause clearly unsatisfactory results as it assumes a fixed (S+ Se) content (Welch et al., 2018; Sejkora et al., 2021). (2) Normalization on the basis of Σ*Me*=16 apfu. Although vacancies exist at the *M*(2), *M*(1) and *X*(3) sites for goldfieldite, ústalečite or pošepnýite, this recalculation procedure takes into consideration that no vacancies occur there. However, Welch et al. (2018) suggested that a much more reliable basis for formula recalculation is to use this normalization as cations fully occupied the *M*(1), *M*(2) and *X*(3) sites. In conclusion, this normalization can be used in some situations, but it should be ignored for Te-rich members of the tetrahedrite-group series such as goldfieldite and ústalečite (Makovicky and Karup-Møller, 2017; Škácha et al., 2020; Sejkora et al., 2022b, 2024). (3) Normalization on the basis of Σ(As+Sb+Bi+Te)=4 apfu. Previous studies (e.g., Johnson et al., 1986) showed that this approach does not cause significant variations in the ideal number of D atoms at the *X*(3) site. (4) Normalization on the basis of Σ*Me*=29 apfu for the general formula of TGM. According to Sejkora et al. (2021), this recalculation approach may give rise to mask some S deficit [e.g., kenoargentotetrahedrite- (Fe)] or vacancies at the *M*(2) and *M*(1) sites. On the other hand, Trudu and Knittel (1998) preferred to calculate the structural formula of goldfieldite and other Te-bearing minerals of the tetrahedrite solid-solution group using the method based on the total number of atoms due to the advantage of spreading the analytical error over all the elements sought. Thus, taking into account the occurrence of vacancies for Te>2 apfu, they suggested that (1) for Te/(Te+As+Sb+Bi)≤0.5, the calculation should be carried out based on Σ*Me* = 29 apfu, as no vacancies occur in the crystal structure and (2) for Te/(Te+As+Sb+Bi)>0.5, the formulae are to be calculated on the basis of 29 - 4*[Te/(Te+As+Sb+Bi)-0.5] apfu. Considering these criteria, they also proposed a new chemical nomenclature grid for tetrahedrite solid-solution group, in which the *M* sites are predominantly occupied by Cu, and S is the main anion.

The validity of program output has been tested with representative TGM analyses selected from the literature (see references in Tables 3, 4 and 5). If any of estimation and normalization approach was not selected from the pull-down menu of *Calculate Contents of Ions* in the *Start-up Screen* or *Data Entry Screen*, WinTtrclas calculates the chemical formula for a given TGM analysis on the basis of Σ*Me*=29 apfu as default. However, different normalization recalculation procedures [e.g., Σ*Me*=32 apfu, Σ*Me*=27 apfu, Σ*Me*=16 apfu and Σ(As+Sb+Bi+Te)=4 apfu] can be applied to the TGM analyses by clicking the options from the pull-down menu of *Calculate Contents of Ions* in the *Start-up Screen* or *Data Entry Screen*. At this stage of the program execution, the users should consider the restrictions in terms of occurrence of vacancies at anion sites as well as cation positions in some Te-bearing species during the evaluation process of TGM analyses. All input and estimation parameters are presented in the *Calculation Screen* and Excel output file for selected mineral analyses from the literature. WinTtrclas calculates the TGM analyses (e.g., see rows 17-32 in Table 3) and allocates the recalculated ions at the $^{M(2)}$A (see rows 33-35 in Table 3), $^{M(1)}$B (see rows 36-38 in Table 3), $^{M(1)}$C (see rows 39-47 in Table 3), $^{X(3)}$D (see rows 48-52 in Table 3) and $^{S(1)}$Y+$^{S(2)}$Z sites (see rows 53-56 in Table 3). The determination of dominant constituents by the program

Table 3. The chemical compositions of selected tetrahedrite and tennantite series minerals with calculations and classifications by WinTtrclas.

Row		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
1	Cu	34.850	43.240	37.340	32.220	39.830	39.230	40.560	44.150	44.160	32.570	43.960	38.040
2	Ag	2.090	0.000	0.480	0.400	0.000	0.660	0.050	0.000	0.000	6.380	0.000	0.120
3	Cd	11.030	0.000	0.000	0.000	0.000	0.000	11.320	0.050	0.000	0.000	0.000	0.380
4	Fe	0.180	0.630	5.340	0.180	1.450	2.120	0.040	1.040	6.680	0.000	1.850	0.330
5	Zn	0.260	1.000	1.770	1.250	0.000	5.320	1.910	3.150	0.170	0.040	0.000	4.640
6	Ni	0.000	0.000	0.000	0.000	5.670	0.000	0.000	0.000	0.000	0.000	3.740	0.000
7	Pb	0.310	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.700	0.000	0.000
8	Hg	0.750	0.000	0.000	17.680	0.000	0.000	0.040	0.000	0.000	17.940	0.000	0.130
9	Tl	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.290	0.000	0.000
10	Sb	28.070	29.410	28.960	26.170	21.690	25.720	0.000	0.300	0.000	0.340	8.490	11.570
11	Bi	0.000	0.000	0.380	0.000	0.000	0.310	0.000	0.000	0.000	0.000	0.000	0.000
12	As	0.000	0.340	0.750	0.000	5.450	2.670	19.040	19.060	20.450	17.830	14.470	9.440
13	Sn	0.000	0.000	0.000	0.000	0.000	0.220	0.000	0.000	0.000	0.000	0.000	0.000
14	Se	0.000	0.000	0.000	0.050	0.000	0.000	0.000	9.070	0.000	0.000	0.000	19.600
15	S	23.380	24.800	25.240	21.860	25.390	24.590	26.780	22.910	28.270	24.100	26.900	15.610
16	Total (wt%)	100.920	99.420	100.260	99.810	99.480	100.840	99.740	99.730	99.730	100.190	99.410	99.860
17	Cu	9.709	11.429	9.729	9.683	10.143	10.173	9.958	10.901	10.221	8.960	10.612	10.607
18	Ag	0.343	0.000	0.074	0.071	0.000	0.101	0.007	0.000	0.000	1.034	0.000	0.020
19	Cd	1.737	0.000	0.000	0.000	0.000	0.000	1.571	0.007	0.000	0.000	0.000	0.060
20	Fe	0.057	0.189	1.583	0.062	0.420	0.626	0.011	0.292	1.759	0.000	0.508	0.105
21	Zn	0.070	0.257	0.448	0.365	0.000	1.341	0.456	0.756	0.038	0.011	0.000	1.257
22	Ni	0.000	0.000	0.000	0.000	1.563	0.000	0.000	0.000	0.000	0.000	0.978	0.000
23	Pb	0.026	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.059	0.000	0.000
24	Hg	0.066	0.000	0.000	1.683	0.000	0.000	0.003	0.000	0.000	1.563	0.000	0.011
25	Tl	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.025	0.000	0.000
26	Sb	4.081	4.057	3.938	4.105	2.883	3.481	0.000	0.039	0.000	0.049	1.070	1.684
27	Bi	0.000	0.000	0.030	0.000	0.000	0.024	0.000	0.000	0.000	0.000	0.000	0.000
28	As	0.000	0.076	0.166	0.000	1.177	0.587	3.965	3.992	4.015	4.160	2.963	2.232
29	Sn	0.000	0.000	0.000	0.000	0.000	0.031	0.000	0.000	0.000	0.000	0.000	0.000
30	Se	0.000	0.000	0.000	0.012	0.000	0.000	0.000	1.802	0.000	0.000	0.000	4.398
31	S	12.909	12.991	13.032	13.019	12.814	12.637	13.029	11.211	12.967	13.139	12.870	8.626
32	Total (apfu)	29.000	29.000	29.000	29.000	29.000	29.000	29.000	29.000	29.000	29.000	29.000	29.000
33	Cu	5.657	6.000	5.926	5.929	6.000	5.899	5.993	6.000	6.000	4.966	6.000	5.980
34	Ag	0.343	0.000	0.074	0.071	0.000	0.101	0.007	0.000	0.000	1.034	0.000	0.020
35	Total A (apfu)	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
36	Cu	4.000	4.000	3.802	3.754	4.000	4.000	3.965	4.000	4.000	3.994	4.000	4.000
37	Ag	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
38	Total B (apfu)	4.000	4.000	3.802	3.754	4.000	4.000	3.965	4.000	4.000	3.994	4.000	4.000
39	Cu	0.052	1.429	0.000	0.000	0.143	0.274	0.000	0.901	0.221	0.000	0.612	0.626
40	Cd	1.737	0.000	0.000	0.000	0.000	0.000	1.571	0.007	0.000	0.000	0.000	0.060
41	Fe	0.057	0.189	1.583	0.062	0.420	0.626	0.011	0.292	1.759	0.000	0.508	0.105
42	Zn	0.070	0.257	0.448	0.365	0.000	1.341	0.456	0.756	0.038	0.011	0.000	1.257

Table 3. ... Continued

Row		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
43	Ni	0.000	0.000	0.000	0.000	1.563	0.000	0.000	0.000	0.000	0.000	0.978	0.000
44	Pb	0.026	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.059	0.000	0.000
45	Hg	0.066	0.000	0.000	1.683	0.000	0.000	0.003	0.000	0.000	1.563	0.000	0.011
46	Tl	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.025	0.000	0.000
47	Total C) (apfu)	2.010	1.876	2.031	2.110	2.126	2.240	2.041	1.957	2.018	1.658	2.098	2.060
48	Sb	4.081	4.057	3.938	4.105	2.883	3.481	0.000	0.039	0.000	0.049	1.070	1.684
49	Bi	0.000	0.000	0.030	0.000	0.000	0.024	0.000	0.000	0.000	0.000	0.000	0.000
50	As	0.000	0.076	0.166	0.000	1.177	0.587	3.965	3.992	4.015	4.160	2.963	2.232
51	Sn	0.000	0.000	0.000	0.000	0.000	0.031	0.000	0.000	0.000	0.000	0.000	0.000
52	Total D (apfu)	4.081	4.133	4.134	4.105	4.060	4.123	3.965	4.030	4.015	4.209	4.032	3.916
53	Se	0.000	0.000	0.000	0.012	0.000	0.000	0.000	1.802	0.000	0.000	0.000	4.398
54	S	12.909	12.991	13.032	13.019	12.814	12.637	13.029	11.211	12.967	13.139	12.870	8.626
55	Vacancy	0.091	0.009	0.000	0.000	0.186	0.363	0.000	0.000	0.033	0.000	0.130	0.000
56	Total (Y+Z) (apfu)	13.000	13.000	13.032	13.032	13.000	13.000	13.029	13.013	13.000	13.139	13.000	13.024
57	Dominant A	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu
58	Dominant B	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu
59	Dominant C	Cd	Cu	Fe	Hg	Ni	Zn	Cd	Cu	Fe	Hg	Ni	Zn
60	Dominant D	Sb	Sb	Sb	Sb	Sb	Sb	As	As	As	As	As	As
61	Dominant Y	S	S	S	S	S	S	S	S	S	S	S	S
62	Series	TtrS	TtrS	TtrS	TtrS	TtrS	TtrS	TntS	TntS	TntS	TntS	TntS	TntS
63	Species	Ttr-Cd	Ttr-Cu	Ttr-Fe	Ttr-Hg	Ttr-Ni	Ttr-Zn	Tnt-Cd	Tnt-Cu	Tnt-Fe	Tnt-Hg	Tnt-Ni	Tnt-Zn

(apfu*)*=Atoms per formula unit; Samples of S1 (from Sejkora et al., 2023), S2 (from Sejkora et al., in press), S3 (from Mauro et al., 2021), S4 (from Biagioni et al., 2020b), S5 (from Wang et al., 2023a), S6 (from Lyubimtseva et al., 2021), S7 (from Biagioni et al., 2022b), S8 and S12 (from Förster and Rhede, 2004), S9 (from Lyubimtseva et al., 2020), S10 (from Biagioni et al., 2021), S11 (from Wang et al., 2023b); The formulae were recalculated to content of ions on the basis of 29 (apfu); TtrS=Tetrahedrite series; TntS=Tennantite series; Ttr-Cd=Tetrahedrite-(Cd), Ttr-Cu=Tetrahedrite-(Cu), Ttr-Fe=Tetrahedrite-(Fe), Ttr-Hg=Tetrahedrite-(Hg), Ttr-Ni=Tetrahedrite-(Ni), Ttr-Zn=Tetrahedrite-(Zn); Tnt-Cd=Tennantite-(Cd), Tnt-Cu=Tennantite-(Cu), Tnt-Fe=Tennantite-(Fe), Tnt-Hg=Tennantite-(Hg), Tnt-Ni=Tennantite-(Ni), Tnt-Zn=Tennantite-(Zn),

at each site with a series and a specific species according to the current tetrahedrite-group nomenclature scheme are given in the *Calculation Screen* window. It is also presented in the Excel output file for selected mineral analyses from the literature (e.g., see rows 57-63 in Table 3 for the tetrahedrite-tennantite series). The number of ions is calculated on the basis of 29 apfu in Tables 3-5.

In a case where a chemical composition corresponds to a hitherto unknown species within the tetrahedrite-group (i.e., a new species), WinTtrclas warns the user with a "Not classified" statement in column numbers 85 and 86 of the *Calculation Screen* for series and species, respectively. For example, a TGM with the following analytical data [Förster et al., 2002; wt%; (i.e., "mercurian giraudite")]: Cu 27.34, Ag 0.31, Hg 15.32, Zn 0.17, As 6.90, Sb 9.68, S 2.43, Se 37.73, total 99.88 yields the empirical formula, on the basis of $\sum Me$=29 apfu content of normalization procedure, as $(Cu_{5.933}Ag_{0.067})_{\sum 6.000}Cu_{4.000}(Hg_{1.790}Cu_{0.151}Zn_{0.061})_{\sum 2.002}(As_{2.159}Sb_{1.863})_{\sum 4.022}(Se_{11.200}S_{1.776}\square_{0.024})_{\sum 13.000}$, where □= vacancy. As can be seen from the empirical formula, the dominant ions at the A, B, C, D and Y constituents correspond to a Cu, Cu, Hg, As and Se, respectively. Since no species corresponding to this composition currently exists in the current classification scheme (i.e., A=Cu, B=Cu, C=Hg, D=As, Y=Se), the program designates it as "Not classified" rather than applying the name of one of known species given in Table 1. All input and calculated parameters from an *Output* tab of an Excel file (i.e., Output.xlsx) are transposed automatically by the *Transpose* tab of the program. This procedure provides the user with the ability to prepare a quick table for presentation as well as publication by using the *Copy-Paste* options. The program provides options to display 46 binary and ternary classification and compositional diagrams in the *Calculation Screen* by using the Grapher

Table 4. The chemical compositions of selected freibergite, arsenofreibergite and hakite series minerals with calculations and classifications by WinTtrclas.

Row		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
1	Cu	22.920	19.290	23.970	14.190	21.750	15.600	14.970	27.250	28.520	24.960	27.970
2	Ag	18.920	25.500	19.780	31.780	22.510	33.540	38.130	0.760	0.960	1.510	0.940
3	Cd	10.110	0.000	0.150	0.020	1.620	0.100	0.000	6.140	0.000	0.240	1.110
4	Fe	0.800	4.640	0.730	5.230	2.160	1.130	6.580	0.040	2.150	0.150	0.030
5	Zn	0.560	1.430	6.200	1.100	4.280	5.440	0.000	1.690	1.400	0.430	3.830
6	Pb	0.000	0.000	0.000	0.000	0.000	0.180	0.000	0.030	0.000	0.000	0.000
7	Hg	0.000	0.000	0.060	0.000	0.000	0.000	0.000	0.640	2.140	13.660	3.690
8	Tl	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.020	0.000
9	Sb	24.190	26.690	26.330	25.840	24.970	12.590	0.000	21.020	18.700	19.170	20.680
10	As	0.620	0.170	0.710	0.140	1.150	8.800	17.650	0.620	1.930	0.810	0.850
11	Te	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
12	Se	0.000	0.000	0.000	0.000	0.000	0.000	0.000	41.360	43.940	37.260	38.040
13	S	21.950	22.000	22.850	20.730	21.290	22.660	22.670	0.840	0.220	1.480	2.560
14	Total (wt%)	100.070	99.720	100.780	99.030	99.730	100.040	100.000	100.390	99.960	99.790	99.700
15	Cu	6.790	5.670	6.801	4.349	6.388	4.480	4.142	9.938	10.241	9.707	9.980
16	Ag	3.302	4.416	3.306	5.737	3.895	5.674	6.215	0.163	0.203	0.346	0.198
17	Cd	1.693	0.000	0.024	0.003	0.269	0.016	0.000	1.266	0.000	0.053	0.224
18	Fe	0.270	1.552	0.236	1.824	0.722	0.369	2.072	0.017	0.878	0.066	0.012
19	Zn	0.161	0.409	1.710	0.328	1.222	1.518	0.000	0.599	0.489	0.163	1.328
20	Pb	0.000	0.000	0.000	0.000	0.000	0.016	0.000	0.003	0.000	0.000	0.000
21	Hg	0.000	0.000	0.005	0.000	0.000	0.000	0.000	0.074	0.243	1.683	0.417
22	Tl	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000
23	Sb	3.740	4.095	3.899	4.133	3.827	1.887	0.000	4.001	3.504	3.891	3.851
24	As	0.156	0.042	0.171	0.036	0.286	2.143	4.142	0.192	0.588	0.267	0.257
25	Te	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.019	0.000
26	Se	0.000	0.000	0.000	0.000	0.000	0.000	0.000	12.140	12.697	11.662	10.923
27	S	12.887	12.816	12.848	12.590	12.391	12.896	12.430	0.607	0.157	1.141	1.810
28	Total (apfu)	29.000	29.000	29.000	29.000	29.000	29.000	29.000	29.000	29.000	29.000	29.000
29	Cu	2.698	1.584	2.694	0.263	2.105	0.326	0.000	5.837	5.797	5.654	5.802
30	Ag	3.302	4.416	3.306	5.737	3.895	5.674	6.215	0.163	0.203	0.346	0.198
31	Total A (apfu)	6.000	6.000	6.000	6.000	6.000	6.000	6.215	6.000	6.000	6.000	6.000
32	Cu	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
33	Ag	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
34	Total B (apfu)	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
35	Cu	0.092	0.086	0.107	0.086	0.282	0.154	0.142	0.102	0.444	0.053	0.177
36	Cd	1.693	0.000	0.024	0.003	0.269	0.016	0.000	1.266	0.000	0.053	0.224
37	Fe	0.270	1.552	0.236	1.824	0.722	0.369	2.072	0.017	0.878	0.066	0.012
38	Zn	0.161	0.409	1.710	0.328	1.222	1.518	0.000	0.599	0.489	0.163	1.328
39	Pb	0.000	0.000	0.000	0.000	0.000	0.016	0.000	0.003	0.000	0.000	0.000
40	Hg	0.000	0.000	0.005	0.000	0.000	0.000	0.000	0.074	0.243	1.683	0.417
41	Tl	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000
42	Total C (apfu)	2.217	2.047	2.082	2.241	2.495	2.074	2.213	2.060	2.054	2.020	2.159

Table 4. ... Continued

Row		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
43	Sb	3.740	4.095	3.899	4.133	3.827	1.887	0.000	4.001	3.504	3.891	3.851
44	As	0.156	0.042	0.171	0.036	0.286	2.143	4.142	0.192	0.588	0.267	0.257
45	Sn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
46	Te	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.019	0.000
47	Total D (apfu)	3.896	4.137	4.070	4.169	4.114	4.030	4.142	4.193	4.092	4.177	4.108
48	Se	0.000	0.000	0.000	0.000	0.000	0.000	0.000	12.140	12.697	11.662	10.923
49	S	12.887	12.816	12.848	12.590	12.391	12.896	12.430	0.607	0.157	1.141	1.810
50	Vacancy	0.113	0.184	0.152	0.410	0.609	0.104	0.570	0.253	0.146	0.197	0.267
51	Total (Y+Z) (apfu)	13.000	13.000	13.000	13.000	13.000	13.000	13.000	13.000	13.000	13.000	13.000
52	Dominant A	Ag	Ag	Ag	Ag	Ag	Ag	Ag	Cu	Cu	Cu	Cu
53	Dominant B	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu
54	Dominant C	Cd	Fe	Zn	Fe	Zn	Zn	Fe	Cd	Fe	Hg	Zn
55	Dominant D	Sb	Sb	Sb	Sb	Sb	As	As	Sb	Sb	Sb	Sb
56	Dominant Y	S	S	S	S	S	S	S	Se	Se	Se	Se
57	Series	FrbS	FrbS	FrbS	FrbS	FrbS	AsfrbS	AsfrbS	HakS	HakS	HakS	HakS
58	Species	Attr-Cd	Attr-Fe	Attr-Zn	Kattr-Fe	Kattr-Zn	Atnt-Zn	Katnt-Fe	Hak-Cd	Hak-Fe	Hak-Hg	Hak-Zn

(apfu)=Atoms per formula unit; Samples of S1 (from Mikuš et al., 2023), S2 (from Anthony et al., 2001-2005), S3 (from Sejkora et al., 2022a), S4 (from Shu et al., 2022), S5 (from Qu et al., 2024a), S6 and S7 (from Zakrzewski, 2021), S8 and S11 (from Škácha et al., 2016), S9 and S10 (from Škácha et al., 2017); The formulae were recalculated to content of ions on the basis of 29 (apfu); FrbS=Freibergite series; AsfrbS=Arsenofreibergite series; HakS=Hakite series; Attr-Cd=Argentotetrahedrite-(Cd), Attr-Fe=Argentotetrahedrite-(Fe), Attr-Zn=Argentotetrahedrite-(Zn), Kattr-Fe=Kenoargentotetrahedrite-(Fe), Kattr-Zn=Kenoargentotetrahedrite-(Zn), Atnt-Zn=Argentotennantite-(Zn), Katnt-Fe=Kenoargentotennantite-(Fe), Hak-Cd=Hakite-(Cd), Hak-Fe=Hakite-(Fe), Hak-Hg=Hakite-(Hg), Hak-Zn=Hakite-(Zn).

program (Golden, 2024). Some of these plots obtained from the pull-down menu of *Graph* in the *Calculation Screen* are given in Figure 2.

SUMMARY AND AVAILABILITY OF THE PROGRAM

As a principal source of Ag and to a lesser extend Cu to the mining industry, members of the tetrahedrite-group, with a simplified general formula $A_6(B,C)_6X_4Y_{12}Z$ (i.e., A=Cu^+, Ag^+ in triangular coordination; B = Cu^+, Ag^+ in tetrahedral coordination; C=Me^{2+} such as Fe^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Hg^{2+}, Cd^{2+}, Cu^{2+} in tetrahedral coordination as well as monovalent (e.g., Cu^+) and trivalent (e.g., In^{3+}) cations; X=Sb^{3+}, As^{3+}, Bi^{3+}, Te^{4+}, $\pm Sn^{4+}$ in trigonal pyramidal coordination; Y=S^{2-} or Se^{2-} in tetrahedral coordination and Z=S^{2-} or Se^{2-} in a special octahedral coordination), are an important ore component in various epi-mesotermal precious metal deposits, base-metals sulfide veins as well as SEDEX and VMS deposits in a wide range of tectonic setting worldwide (Sack et al., 2003; Moëlo et al. 2008). However, since TGMs incorporate heavy metals and toxic elements (e.g., Hg, Cd, Ni, Cu, As, Bi, Sb) into their crystal structure and, in common with other sulfides, they prone to alteration process when they exposed to the oxidizing conditions at the Earth surface, a better understanding of their weathering behaviours as well as details of their weathering processes depending on mobilization should also be considered as an important issue to determine the environmental risks both local and global metal fluxes in stream waters and oceans (Keim et al., 2018; D'Orazio et al., 2024). It has recently determined that the TGM show also high-thermoelectric performance in contribution as exceptionally efficient thermoelectric materials for waste heat recovery applications (Sack et al., 2022).

WinTtrclas is a user-friendly program which is specially developed for personal computers running on the Windows operating system to estimate and classify the TGM compositions obtained from both electron-microprobe and wet chemical analyses. The program calculates multiple analyses, up to 200, for each program execution. WinTtrclas evaluates the TGM analyses into ten series such as tetrahedrite, tennantite, freibergite, arsenofreibergite, hakite, giraudite, rozhdestvenskayaite, goldfieldite, ústalečite and zvěstovite series with two unassigned species based on the current IMA-approved nomenclature scheme and then classifies the total 40 species according to the dominant ions at the *M*(1), *M*(2),

Table 5. The chemical compositions of selected giraudite, rozhdestvenskayaite, goldfieldite, ústalečite and zvěstovite series minerals with calculations and classifications by WinTtrclas.

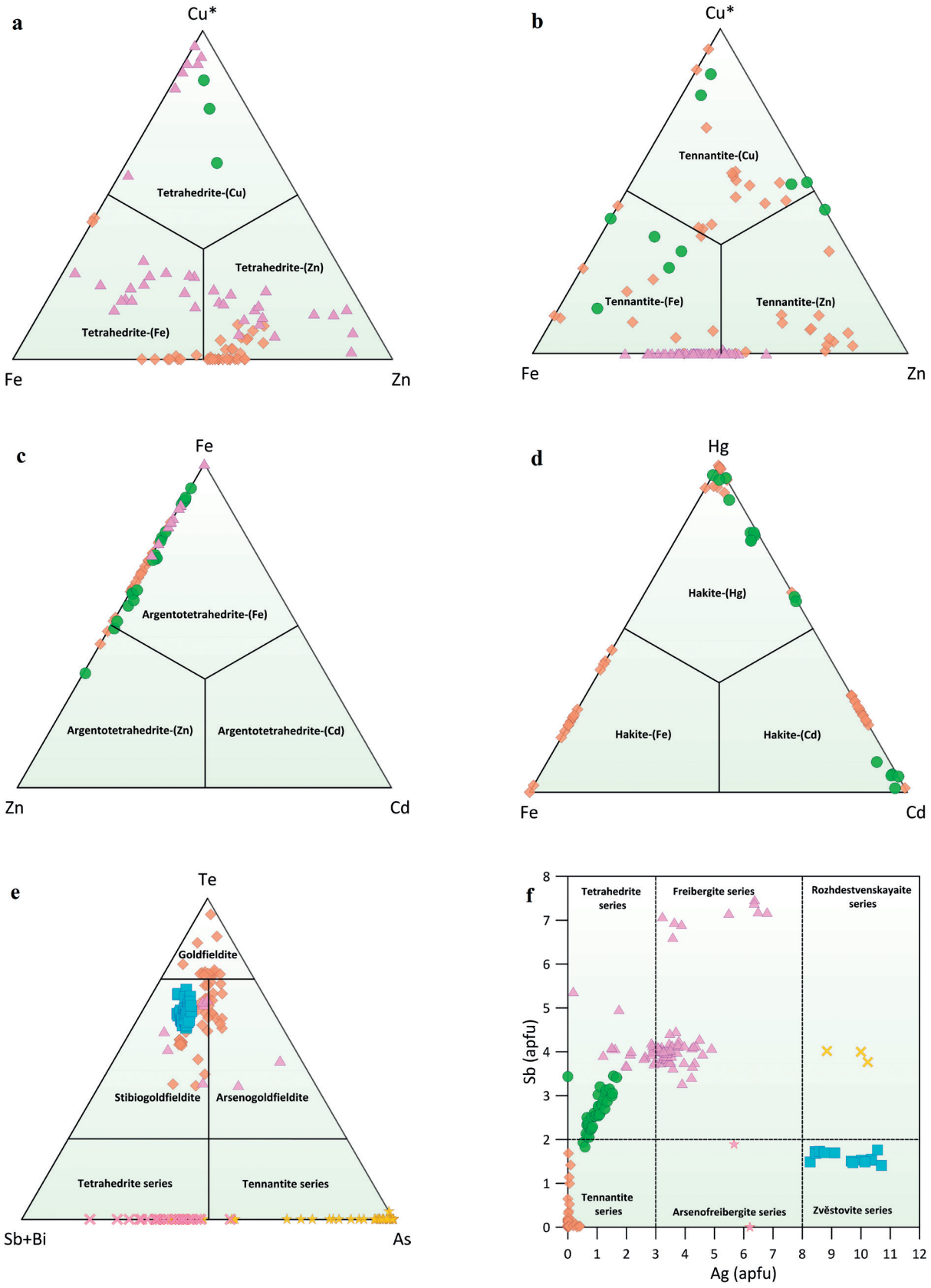
Row		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
1	Cu	30.060	0.140	3.870	43.380	45.620	45.030	35.550	34.340	1.540	14.950
2	Ag	3.890	51.300	45.870	0.000	0.500	0.260	0.870	0.890	53.730	1.210
3	Cd	0.000	0.900	0.000	0.000	0.000	0.000	0.000	0.000	0.170	0.120
4	Fe	0.190	0.230	5.180	0.000	0.670	0.020	0.060	0.000	0.250	0.030
5	Mn	0.000	0.000	0.000	0.000	0.170	0.000	0.000	0.000	0.000	0.000
6	Zn	3.370	5.000	2.360	0.000	0.140	0.130	0.060	0.190	5.430	0.080
7	Pb	0.000	0.000	0.000	0.000	0.000	0.050	0.000	0.000	0.000	0.000
8	Hg	0.570	0.000	0.000	0.000	0.000	0.000	0.090	2.030	0.000	27.740
9	Tl	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.030
10	Sb	10.660	21.300	23.520	0.230	6.240	8.020	5.040	9.360	9.250	19.060
11	Bi	0.000	0.000	0.000	0.000	0.220	2.770	0.000	0.000	0.000	0.000
12	As	7.610	1.200	0.040	5.300	7.020	2.800	5.000	4.140	8.700	0.370
13	Sn	0.000	0.000	0.000	0.000	0.000	0.020	0.000	0.000	0.000	0.000
14	Te	0.000	0.000	0.000	25.740	13.380	15.150	10.500	6.710	0.000	0.000
15	Se	41.090	0.000	0.000	0.000	0.050	0.520	38.700	39.620	0.000	34.510
16	S	2.730	18.930	18.800	25.560	25.320	24.500	3.540	2.850	20.510	1.660
17	Total (wt%)	100.170	99.000	99.640	100.210	99.330	99.270	99.410	100.130	99.580	99.760
18	Cu	10.075	0.047	1.266	11.286	11.690	11.950	11.921	11.721	0.487	6.573
19	Ag	0.768	10.234	8.840	0.000	0.075	0.041	0.172	0.179	10.010	0.313
20	Cd	0.000	0.172	0.000	0.000	0.000	0.000	0.000	0.000	0.030	0.030
21	Fe	0.072	0.089	1.928	0.000	0.195	0.006	0.023	0.000	0.090	0.015
22	Mn	0.000	0.000	0.000	0.000	0.050	0.000	0.000	0.000	0.000	0.000
23	Zn	1.098	1.646	0.750	0.000	0.035	0.034	0.020	0.063	1.669	0.034
24	Pb	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000
25	Hg	0.061	0.000	0.000	0.000	0.000	0.000	0.010	0.220	0.000	3.863
26	Tl	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.004
27	Sb	1.865	3.764	4.016	0.031	0.835	1.111	0.882	1.667	1.527	4.373
28	Bi	0.000	0.000	0.000	0.000	0.017	0.224	0.000	0.000	0.000	0.000
30	As	2.163	0.345	0.011	1.170	1.526	0.630	1.422	1.199	2.334	0.138
31	Sn	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.000
32	Te	0.000	0.000	0.000	3.335	1.708	2.002	1.754	1.141	0.000	0.000
33	Se	11.084	0.000	0.000	0.000	0.010	0.111	10.444	10.883	0.000	12.210
34	S	1.813	12.704	12.188	13.178	12.858	12.885	2.353	1.928	12.854	1.446
35	Total (apfu)	29.000	29.000	29.000	29.000	29.000	29.000	29.000	29.000	29.000	29.000
36	Cu	5.232	0.047	1.266	6.000	5.925	5.959	5.828	5.821	0.487	5.687
37	Ag	0.768	5.953	4.734	0.000	0.075	0.041	0.172	0.179	5.513	0.313
38	Total A (apfu)	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
39	Cu	4.000	0.000	0.000	4.000	4.000	4.000	4.000	4.000	0.000	0.886
40	Ag	0.000	4.281	4.106	0.000	0.000	0.000	0.000	0.000	4.497	0.000
41	Total B (apfu)	4.000	4.281	4.106	4.000	4.000	4.000	4.000	4.000	4.497	0.886
42	Cu	0.844	0.000	0.000	1.286	1.766	1.991	2.093	1.900	0.000	0.000
43	Cd	0.000	0.172	0.000	0.000	0.000	0.000	0.000	0.000	0.030	0.030

Table 5. ...Continued

Row		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
44	Fe	0.072	0.089	1.928	0.000	0.195	0.006	0.023	0.000	0.090	0.015
45	Mn	0.000	0.000	0.000	0.000	0.050	0.000	0.000	0.000	0.000	0.000
46	Zn	1.098	1.646	0.750	0.000	0.035	0.034	0.020	0.063	1.669	0.034
47	Pb	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000
48	Hg	0.061	0.000	0.000	0.000	0.000	0.000	0.010	0.220	0.000	3.863
49	Tl	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.004
50	Total C (apfu)	2.074	1.907	2.679	1.286	2.046	2.034	2.145	2.182	1.789	3.947
51	Sb	1.865	3.764	4.016	0.031	0.835	1.111	0.882	1.667	1.527	4.373
52	Bi	0.000	0.000	0.000	0.000	0.017	0.224	0.000	0.000	0.000	0.000
53	As	2.163	0.345	0.011	1.170	1.526	0.630	1.422	1.199	2.334	0.138
54	Sn	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.000
55	Te	0.000	0.000	0.000	3.335	1.708	2.002	1.754	1.141	0.000	0.000
56	Total D (apfu)	4.028	4.109	4.027	4.536	4.085	3.970	4.058	4.006	3.860	4.511
57	Se	11.084	0.000	0.000	0.000	0.010	0.111	10.444	10.883	0.000	12.210
59	S	1.813	12.704	12.188	13.178	12.858	12.885	2.353	1.928	12.854	1.446
59	Vacancy	0.103	0.296	0.812	0.000	0.131	0.004	0.203	0.189	0.146	0.000
60	Total (Y+Z) (apfu)	13.000	13.000	13.000	13.178	13.000	13.000	13.000	13.000	13.000	13.656
61	Dominant A	Cu	Ag	Ag	$(Cu_4\square_2)$	Cu	Cu	Cu	Cu	Ag	$(Cu_{3+x}\square_{3-x})$
62	Dominant B	Cu	Ag	Ag	Cu	Cu	Cu	Cu	Cu	Ag	Hg_{4-x}
63	Dominant C	Zn	Zn	Fe	Cu	Cu	Cu	Cu	Cu	Zn	Cu_{2+x}
64	Dominant D	As	Sb	Sb	Te	(As_2Te_2)	(Sb_2Te_2)	(As_2Te_2)	(Sb_2Te_2)	As	Sb
65	Dominant Y	Se	S	S	S	S	S	Se	Se	S	$(Se_{12.5}\square_{0.5})$
66	Series	GirS	RozS	RozS	GfS	GfS	GfS	ÚslS	ÚslS	ZvěS	Unassigned
67	Species	Gir-Zn	Roz-Zn	Kroz-Fe	Gf	Asgf	Sbgf	Aúč	Súč	Zvě-Zn	Pšý

(apfu)=Atoms per formula unit; Samples of S1, S2 and S4 (from Anthony et al., 2001-2005), S3 (from Qu et al., 2024b), S5 (from Shimizu and Stanley, 1991), S6 (from Biagioni et al., 2022c), S7 (from Sejkora et al., 2024), S8 (from=Sejkora et al., 2022b), S9 (from Sejkora et al., 2021), S10 (from Škácha et al., 2020); The formulae were recalculated to content of ions on the basis of 29 (apfu); GirS=Giraudite series; AsfrbS=Arsenofreibergite series; RozS=Rozhdestvenskayaite series; GfS=Goldfieldite series; ÚslS=Ústalečite series; ZvěS=Zvěstovite series; Gir-Zn=Giraudite-(Zn), Roz-Zn=Rozhdestvenskayaite-(Zn), Kroz-Fe=Kenorozhdestvenskayaite-(Fe), Aúč=Arsenoústalečite, Súč=Stibioústalečite, Zvě-Zn =Zvěstovite-(Zn), Pšý=Pošepnýite.

Figure 2 - Selected plots of the TGM classification and compositional diagrams from the pull-down menu of *Graph* in the *Calculation Screen* of WinTtrclas program using the selected mineral analyses from the literature. a - Compositions of the tetrahedrite series in Cu* - Fe - Zn ternary diagram; filled diamonds from Hu et al., 2018; filled circles from Sejkora et al., in press; filled triangles from Arlt and Diamond, 1998). b - Compositional plot of the tennantite series in Cu* - Fe - Zn ternary diagram; filled diamonds from Förster and Rhede, 2004; filled circles from Repstock et al., 2015; filled triangles from Lyubimtseva et al., 2020). c - Compositional plot of the freibergite series in Fe - Zn - Cd ternary diagram (filled diamonds from Gallego Hernández and Akasaka, 2007; filled circles from Swinkels et al., 2021; filled triangles from Torró et al., 2019). d - Compositional plot of the hakite series in Hg - Fe - Cd ternary diagram (filled diamonds from Škácha et al., 2017; filled circles from Škácha et al., 2016). e - Compositional plot of the goldfieldite, tetrahedrite and tennantite series in Te - (Sb+Bi) - As ternary diagram (from Biagioni et al., 2022c; filled diamonds from Kozlov and Okrugin 2022; filled triangles from Shimizu and Stanley, 1991; filled squares from Biagioni et al., 2022c; filled stars from Förster and Rhede, 2004; filled cross from Hu et al., 2018). f - Compositional plot of the tetrahedrite, tennantite, freibergite, arsenofreibergite, rozhdestvenskayaite and zvěstovite series in Ag versus Sb apfu binary classification diagram (filled diamonds from Förster and Rhede, 2004; filled circles from Hu et al., 2018; filled triangles from Gallego Hernández and Akasaka, 2010; filled squares from Sejkora et al., 2021; filled stars from Zakrzewski, 1989; filled cross from Anthony et al., 2001-2005; Welch et al., 2018; Qu et al., 2024b). Cu*= "Cu-excess" or Cu content apfu at the $^{M(1)}$C chemical constituent.


a
Cu*
Tetrahedrite-(Cu)
Tetrahedrite-(Zn)
Tetrahedrite-(Fe)
Fe
Zn
b
Cu*
Tennantite-(Cu)
Tennantite-(Fe)
Tennantite-(Zn)
Fe
Zn
c
Fe
Argentotetrahedrite-(Fe)
Argentotetrahedrite-(Zn)
Argentotetrahedrite-(Cd)
Zn
Cd
d
Hg
Hakite-(Hg)
Hakite-(Fe)
Hakite-(Cd)
Fe
Cd
e
Te
Goldfieldite
Stibiogoldfieldite
Arsenogoldfieldite
Tetrahedrite series
Tennantite series
Sb+Bi
As
f
Tetrahedrite series
Freibergite series
Rozhdestvenskayaite series
Tennantite series
Arsenofreibergite series
Zvěstovite series
Sb (apfu)
Ag (apfu)
0
1
2
3
4
5
6
7
8
9
10
11
12

X(3) and S(1) sites. The program generates two main windows. The first window (*i.e.*, *Start-up/Data Entry Screen*), with several pull-down menus and equivalent shortcuts, enables one to edit a given TGM analysis, based on (wt%) in 20 columns. By clicking the *Calculate* icon (i.e., ∑) in the *Data Entry Screen*, all input and estimated parameters by WinTtrclas are displayed in the second window (i.e., *Calculation Screen*). The program reports the output in a tabulated form with a numbered column number from 1 to 87 in the *Calculation Screen* window as well as in an Output Excel file. These columns include tetrahedrite-group compositions (wt%), recalculated cation and anion values apfu, contents of ions allocated at the sites apfu, dominant components, series and species names. The results in the *Calculation Screen* can be exported to a Microsoft® Excel file (i.e., Output.xlsx), by clicking the *Send Results to Excel File (Output.xlsx)* icon or selecting the *Send Results to Excel File (Output.xlsx)* option from the pull-down menu of *Excel*. This file is then opened by Excel by clicking the *Open and Edit Excel File (Output.xlsx)* icon or selecting the *Open Excel File (Output.xlsx)* option from the pull-down menu of *Excel*. WinTtrclas is a compiled program that consists of a self-extracting setup file containing all the necessary support files (*i.e.*, dll and ocx) for the 32-bit system. By clicking the setup file, the program and its associated files (*i.e.*, support files, help file, data files with the extension of ".ttr", ".xls", ".xlsx" and plot files with the extension of ".grf" are installed into the personal computer (*i.e.*, the directory of C:\Program Files\WinTtrclas or C:\Program Files (x86)\WinTtrclas) with the Windows XP and later operating systems. An installation of the program into a personal computer with the 64-bit operating system may require the msflexgrd adjustment. The self-extracting setup file is approximately 11 Mb and can be obtained from the journal's server as a Supplementary Material.

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