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Article

WinClbclas, a Windows program for columbite-supergroup minerals

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Abstract

A Microsoft® Visual Basic software, *WinClbclas*, has been developed to calculate the chemical formulae of columbite-supergroup minerals based on data obtained from wet-chemical and electron-microprobe analyses and using the current nomenclature scheme adopted by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) for columbite-supergroup minerals. The program evaluates 36 IMA-approved species, three questionable in terms of their unit-cell parameters, four insufficiently studied questionable species and one ungrouped species, all according to the dominant valance and constituent status in five mineral groups including ixiolite (MO_2), wolframite ($M1M2O_4$), samarskite ($ABM2O_8$), columbite ($M1M2O_6$) and wodginite ($M1M2M3_2O_8$). Mineral compositions of the columbite supergroup are calculated on the basis of 24 oxygen atoms per formula unit. However, the formulae of the five ixiolite to wodginite groups can be estimated by the program on the basis of their cation and anion values in their typical mineral formulae (e.g. 4 cations and 8 oxygens for the wodginite group) with normalisation procedures. The Fe^{3+} and Fe^{2+} contents from microprobe-derived total FeO (wt.%) amounts are estimated by stoichiometric constraints. *WinClbclas* allows users to: (1) enter up to 47 input variables for mineral compositions; (2) type and load multiple columbite-supergroup mineral compositions in the data entry section; (3) edit and load the Microsoft® Excel files used in calculating, classifying, and naming the columbite-supergroup minerals, together with the total monovalent to hexavalent ion; and (4) store all the calculated parameters in the output of a Microsoft® Excel file for further data evaluation. 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: columbite supergroup; ixiolite group; wolframite group; samarskite group; columbite group; wodginite group; classification; software

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Introduction

Niobium-, tantalum- and wolfram-bearing minerals are considered strategic and critical materials because of their significance in several high-technology applications, for example the manufacturing of super-alloys for the aerospace industry, high-strength low-alloy steels for construction, low-temperature superconductor wires for medical equipment, and particle accelerators and nuclear fusion instruments (Sanchez-Segado *et al.*, 2017 and references therein). Tantalum (Ta), one of these strategic materials recovered from oxide minerals as a minor constituent, is commonly associated with pegmatite-related deposits, rare-element-enriched granites and peralkaline granite complexes. It can be an important resource in weathered crusts and placer deposits, where the Ta may be a co-product of tin, whereas most niobium (Nb) resources are observed in carbonatite complex-related deposits and peralkaline intrusions and coexists with rare-earth-element mineralisation (Melcher *et al.*, 2017; Simandl *et al.*, 2018).

The columbite-supergroup minerals have been established in five mineral groups including (questionable in italics): ixiolite [ixiolite-(Mn^{2+}), ixiolite-(Fe^{2+}), nioboixiolite-(Mn^{2+}), nioboixiolite-(□), scrutinyite, seifertite and srilankite]; wolframite [ferberite, hübnerite, huanzalaite, sanmartinite, heftetjernite, nioboheftetjernite, rossovskyite, riesite and dmitryvarlamovite]; samarskite [samarskite-(Y), ekebergite, shakhdaraite-(Y), *samarskite-(Yb)*, *ishikawaite* and *calciosamarskite*]; columbite [columbite-(Fe), columbite-(Mn), columbite-(Mg), tantalite-(Fe), tantalite-(Mn), tantalite-(Mg), fersmite, euxenite-(Y), tanteuxenite-(Y) and uranopolycrase]; and wodginite [wodginite, ferrowodginite, titanowodginite, ferrotitanowodginite, tantalowodginite, lithiowodginite and achalaite]. There are also four other questionable and insufficiently studied minerals [*qitianlingite*, *yttrocolumbite-(Y)*, *yttrotantalite-(Y)*, *yttrocrasite-(Y)*] and one ungrouped species [lithiotantite] in the general stoichiometry MO_2 – crystal structures based on the hexagonal close packing of anions, the six-fold coordination number of *M*-type cations and the presence of zig-zag chains of edge-sharing *M*-centred polyhedra (Chukanov *et al.*, 2023a). All the species in the columbite supergroup have the same topology of their atomic nets with different schemes of cation ordering and unit-cell dimensions (Udoratina *et al.*, 2024). There are quite a few mineral species that contain W, Mo, Nb, Ta, Sb, Ti, Sn, Si, Ge, Mn, Pb and Te as oxides with the stoichiometry MO_2, related structurally to columbite. Although these species show significant common characteristics, they differ from each other in many respects such as symmetry, cation ordering, unit-cell dimensions and coordination numbers of cations (Chukanov *et al.*, 2023a). In the current columbite supergroup nomenclature scheme, topologically similar minerals with different cation ordering (i.e. with similar unit-cell

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dimensions and the same end-member formulae) have been taken into account as different mineral species. For example, srilankite with *Pbcn*, $a = 4.71$, $b = 5.55$, $c = 5.02$ Å and riesite with *P2/b*, $a = 4.52$, $b = 5.50$, $c = 4.89$ Å, $\beta = 90.6°$, both TiO_2, are different minerals. Similarly, nioboixiolite-(Mn^{2+}) [$(Nb_{2/3}Mn^{2+}_{1/3})O_2 = Mn^{2+}Nb_2O_6$)] with *Pbcn*, $a = 4.756$, $b = 5.732$, $c = 5.134$ Å and columbite-(Mn) ($Mn^{2+}Nb_2O_6$) with *Pbcn*, $a = 14.32$, $b = 5.74$, $c = 5.11$ Å are also different species belonging to the ixiolite and columbite group, respectively (Udoratina *et al.*, 2024).

Many studies have shown that the investigation of paragenetic assemblages, together with the chemical composition of some accessory minerals (e.g. columbite–tantalite, tourmaline and gahnite) provides a useful knowledge about the magmatic evolution of the granitic pegmatite and pegmatite melts (Tindle and Breaks, 2000; Tindle *et al.*, 2002; López de Azarevich *et al.*, 2021). The root-name columbite within the columbite-group minerals is the oldest species among all of the mineral names and also important in numerous petrological and geochemical studies. For example, columbite crystals may show partial cation disorder depending on their chemical compositions as well as formation conditions. The compositional variations in columbite-group minerals (e.g. Nb–Ta and Fe–Mn pairs) are sensitive indicators of magmatic to subsolidus evolution of the parental rock. Hence, the columbite-group minerals are, actually, potential indicators in the evolutionary history of their parental rocks (Beurlen *et al.*, 2008; Novak *et al.*, 2018). Consequently, the columbite-group minerals are both economically and petrologically important in our understanding the regional and internal geochemical variations and specification of fractionation and crystallisation conditions of rare-element-enriched granitic pegmatites and fertile granite as well as for U–Pb age determination to obtain emplacement and rare-element mineralisation ages of granitic pegmatites due to their high U and low Pb common contents (Černý and Ercit, 1985; 1989; Černý *et al.*, 1986; Ercit *et al.*, 1995; Ercit, 1994; Tindle and Breaks, 2000; Novák *et al.*, 2018; Zhou *et al.*, 2021 and references therein; Ryznar *et al.*, 2023).

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; 2001a; 2003; 2007; 2013; Yavuz *et al.*, 2014; 2015; Yavuz and Yıldırım, 2020; Yavuz and Yavuz, 2023a, 2023b; 2024), none useful for columbite-supergroup minerals, according to the current IMA report, has yet appeared in the literature, except for a program specially focused on columbite-group minerals (Yavuz 2001b), possibly in part owing to the lack of classification scheme until the recent work by Chukanov *et al.* (2023a). Taking this situation into consideration, a computer program called *WinClbclas* 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 columbite-supergroup minerals on the basis of 24 O and 12 cations. However, options for different normalisation procedures [e.g. columbite group ($M1M2_2O_6$) to total cations = 3.00 atoms per formula unit (apfu)] can be applied to each group in the columbite supergroup from the pull-down menu of *Normalization* in the *Start-up Screen*. The calculation and classification procedures applied to columbite-supergroup minerals by *WinClbclas* are carried out based on the currently accepted IMA nomenclature scheme, but also take into account new species that post-date the IMA report. The program is capable of estimating the FeO and Fe_2O_3 (wt.%) contents from a microprobe-derived total FeO (wt.%) analysis using the stoichiometric constraints proposed by Droop (1987).

Columbite-supergroup minerals nomenclature

Using the available data on minerals with the stoichiometry MO_2 that are topologically related to columbite and constitute the columbite supergroup, Chukanov *et al.* (2023a) proposed a nomenclature and classification scheme for the columbite-supergroup minerals which has been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) for columbite-supergroup minerals (Miyawaki *et al.*, 2022). In this context, the 36 valid minerals of the columbite supergroup have been divided into five groups by Chukanov *et al.* (2023a, see Table 1) on the basis of the following criteria: (1) the general stoichiometry MO_2 is required; (2) the crystal structure based on the hexagonal close packing (*hcp*) of anions is considered; (3) only octahedral voids of *hcp* are occupied; and (4) the presence of zig-zag chains of edge-shared octahedra is taken into account. The mineral nomenclature procedure is carried out according to the dominant cation in each site(s) of the ixiolite (MO_2), wolframite ($M1M2O_4$), samarskite (ABM_2O_8), columbite ($M1M2_2O_6$) and wodginite ($M1M2M3_2O_8$) group.

According to Chukanov *et al.* (2023a), all minerals in the ixiolite group have the general formula $M1O_2$ (i.e. orthorhombic, *Pbcn*, $a = \mathbf{a_0}$, $b = \mathbf{b_0}$, $c = \mathbf{c_0}$ and $Z = 4$) with a disordered distribution of the cations occupied in a single *M*1 site. The chemical formula of ixiolite-group minerals, as an *aristotype* structure, is currently defined as $(Ta,Mn,Nb)O_2$ in which Mn is the main charge-balancing component, but also samples with Fe > Mn content in the *M*1 site [e.g. ixiolite-(Fe^{2+}), see Table 1]. The wolframite-group minerals with the wolframite-type structure ($M1M2O_4$, monoclinic, *P2/c*, $a = \mathbf{a_0}$, $b = \mathbf{b_0}$, $c = \mathbf{c_0}$, $\beta \approx 91°$ and $Z = 2$) is actually a derivative form of the ixiolite-type structure having a sequence of two kinds of structurally the same, but chemically different, octahedral layers of parallel zig-zag chains. In the wolframite-type structure, as cations with larger radius prefer to keep in the octahedral *M*1 site and the smaller ones occupy the *M*2 octahedron, species belonging to the wolframite group are double oxides with the general formula $M1^{2+}M2^{6+}O_4$ (*M*1 = Mg, Mn, Fe and Zn; *M*2 = W) or $M1^{3+}M2^{5+}O_4$ (*M*1 = Sc and Fe; *M*2 = Nb and Ta), except for riesite ($Ti^{4+}Ti^{4+}O_4$) that shows a slightly distorted variant of the wolframite structure (Chukanov *et al.*, 2023a). The samarskite-group minerals include three valid species [samarskite-(Y), ekebergite and shakhdaraite-(Y)] in monoclinic (*P2/c*, $a = \mathbf{2a_0}$, $b = \mathbf{b_0}$, $c = \mathbf{c_0}$, $\beta \approx 93°$ and $Z = 2$), cation-ordered double niobates and tantalates with the general formula $AM1M2_2O_8$ (*A* = Y and Th; *M*1 = Fe^{2+}, Fe^{3+} and Sc^{3+}; *M*2 = Nb and Ta). Compared to the other columbite-supergroup minerals, species belonging to the samarskite-group minerals contain a relatively large cation at the *A* site with 6 + 2-fold coordination owing to the slight irregularity of the *hcp*. This large cation insertion transforms parallel zig-zag chains into a rigid layer of edge-sharing AO_8 polyhedra with the preservation of the cation distribution between the 'octahedral' voids of *hcp* (Lima-de-Faria, 2012). Three insufficiently studied metamict minerals including 'samarskite-(Yb)', 'ishikawaite' and 'calciosamarskite' have been tentatively assigned to the samarskite group by Chukanov *et al.* (2023a) based on their stoichiometry and studies on the powder X-ray diffraction patterns of annealed samples. The

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Table 1. A list of the IMA-approved, currently questionable and insufficiently studied species in the columbite supergroup (from Chukanov *et al.*, 2023a).

Row	Species	Symbol	Formula	IMA status
Ixiolite group [MO_2 Orthorhombic *Pbcn*]				
1	Ixiolite-(Mn^{2+})	Ix-Mn	$(Ta_{2/3}Mn^{2+}_{1/3})O_2$	A
2	Ixiolite-(Fe^{2+})	Ix-Fe	$(Ta_{2/3}Fe^{2+}_{1/3})O_2$	A
3	†Nioboixiolite-(Mn^{2+})	Nbix-Mn	$(Nb_{2/3}Mn^{2+}_{1/3})O_2$	A
4	†Nioboixiolite-(□)	Nbix-□	$(Nb_{0.8}□_{0.2})^{4+}O_2$	A
5	Scrutinyite	Sny	α-PbO_2	A
6	Seifertite	Sft	SiO_2	A
7	Srilankite	Sri	TiO_2	A
Wolframite group [$M1M2O_4$ Monoclinic *P2/c*]				
8	Ferberite	Feb	$Fe^{2+}WO_4$	A
9	Hübnerite	Hbr	$Mn^{2+}WO_4$	A
10	Huanzalaite	Hza	$MgWO_4$	A
11	Sanmartinite	Sma	$ZnWO_4$	A
12	Heftetjernite	Hef	$ScTaO_4$	A
13	Nioboheftetjernite	Nhef	$ScNbO_4$	A
14	Rossovskyite	Rvy	$Fe^{3+}NbO_4$	A
15	Riesite	Rie	$TiTiO_4$	A
16	†Dmitryvarlamovite	Dmv	$Ti_2(Fe^{3+}Nb)O_8$	A
Samarskite group [ABM_2O_8 Monoclinic *P2/c*]				
17	Samarskite-(Y)	Smk-Y	$YFe^{3+}Nb_2O_8$	A
18	Ekebergite	Ekb	$ThFe^{2+}Nb_2O_8$	A
19	Shakhdaraite-(Y)	Skd-Y	$YScNb_2O_8$	A
20	'*Samarskite-(Yb)*'	Smk-Yb	$YbFe^{3+}Nb_2O_8$ (?)	A
21	'*Ishikawaite*'	Ikw	$U^{4+}Fe^{2+}Nb_2O_8$	A
22	'*Calciosamarskite*'	Csmk	$CaFe^{3+}Nb_2O_7(OH)$	A
Columbite group [$M1M2_2O_6$ Orthorhombic *Pbcn*]				
23	Columbite-(Fe)	Clb-Fe	$Fe^{2+}Nb_2O_6$	A
24	Columbite-(Mn)	Clb-Mn	$Mn^{2+}Nb_2O_6$	A
25	Columbite-(Mg)	Clb-Mg	$MgNb_2O_6$	A
26	Tantalite-(Fe)	Ttl-Fe	$Fe^{2+}Ta_2O_6$	A
27	Tantalite-(Mn)	Ttl-Mn	$Mn^{2+}Ta_2O_6$	A
28	Tantalite-(Mg)	Ttl-Mg	$MgTa_2O_6$	A
29	Fersmite	Fsm	$CaNb_2O_6$	A
30	Euxenite-(Y)	Eux-Y	$Y(NbTi)O_6$	A
31	Tanteuxenite-(Y)	Ttx-Y	$Y(TaTi)O_6$	A
32	Uranopolycrase	Uplc	UTi_2O_6	A
Wodginite group [$M1M2M3_2O_8$ Monoclinic *C2/c*]				
33	Wodginite	Wdg	$Mn^{2+}SnTa_2O_8$	A
34	Ferrowodginite	Fwdg	$Fe^{2+}SnTa_2O_8$	A
35	Titanowodginite	Twdg	$Mn^{2+}TiTa_2O_8$	A
36	Ferrotitanowodginite	Ftwdg	$Fe^{2+}TiTa_2O_8$	A
37	Tantalowodginite	Ttwdg	$(Mn_{0.5}□_{0.5})TaTa_2O_8$	A
38	Lithiowodginite	Lwdg	$LiTa_3O_8$	A
39	Achalaite	Ahl	$Fe^{2+}TiNb_2O_8$	A
Ungrouped species				
40	Lithiotantite	Ltan	$LiTa_3O_8$	A
Other questionable, insufficiently studied minerals				
41	'*Qitianlingite*'	Qit	$Fe^{2+}_2Nb_2W^{6+}O_{10}$ (?)	A, QMS
42	'*Yttrocolumbite-(Y)*'	Yclb-Y	$YNbO_4$ (?)	A, QMS
43	'*Yttrotantalite-(Y)*'	Yttl-Y	$YTaO_4$ (?)	A, QMS
44	'*Yttrocrasite-(Y)*'	Ycr-Y	$YTi_2O_5(OH)$ (?)	A, QMS

A = Approved by the IMA; QMS = Questionable mineral species; □ = Vacancy; † = new columbite-supergroup species approved by the IMA subsequent to the subcommittee report by Chukanov et al. (2023a): nioboixiolite-(Mn^{2+}) (Chukanov *et al.*, 2023b), nioboixiolite-(□) (Li *et al.*, 2023) and dmitryvarlamovite (Udoratina *et al.*, 2024). Insufficiently studied minerals are italicised.

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

Row	Explanations	Column Numbers
1	Major oxides from the wolframite, samarskite, columbite and wodginite (WSCW)-group mineral compositions (wt.%)	1–49
2	Blank	50
3	Total rare earth oxide (REO) from the WSCW-group mineral compositions (wt.%)	51
4	Blank	52
5	Recalculated cations from the WSCW-group mineral compositions (apfu)	53–98
6	Blank	99
7	Recalculated F and OH contents from WSCW-group mineral compositions (apfu)	100–101
8	Blank	102
9	Some useful cation ratio values [e.g. Mn/(Mn+Fe), Ta/(Ta+Nb), Ti/(Ti+Ta+Nb)] from the WSCW-group mineral compositions	103–105
10	Blank	106
11	Total mono- to hexavalent cations (i.e. M^+, M^{2+}, M^{3+}, M^{4+}, M^{5+}, M^{6+}) from the WSCW-group mineral compositions (apfu)	107–112
12	Blank	113
13	Group name and species from the WSCW-group mineral compositions	114–115
14	Blank	116
15	Major oxides from the ixiolite-group mineral compositions (wt.%)	117–153
16	Blank	154
17	Recalculated cations from the ixiolite-group mineral compositions (apfu)	155–187
18	Blank	188
19	Recalculated F and OH contents from ixiolite-group mineral compositions (apfu)	189–190
20	Blank	191
21	Some useful cation ratio values [e.g. Mn/(Mn+Fe), Ta/(Ta+Nb), Ti/(Ti+Ta+Nb)] from the ixiolite-group mineral data	192–194
22	Blank	195
23	Total mono- to hexavalent cations (i.e. M^+, M^{2+}, M^{3+}, M^{4+}, M^{5+}, M^{6+}) from the ixiolite-group mineral compositions (apfu)	196–201
24	Blank	202
25	Species of ixiolite-group mineral	203–204
26	Blank	205

Notes: (apfu) = Atoms per formula unit; M^+ = Total monovalent cations, M^{2+} = Total divalent cations, M^{3+} = Total trivalent cations, M^{4+} = Total tetravalent cations, M^{5+} = Total pentavalent cations, M^{6+} = Total hexavalent cations.

columbite-group minerals consist of ten species including double oxides with the general formula $M1^{2+}M2^{5+}_2O_6$ (orthorhombic, *Pbcn*, $a = \mathbf{3a_0}$, $b = \mathbf{b_0}$, $c = \mathbf{c_0}$ and $Z = 4$; $M1$ = Mg, Ca, Mn and Fe; $M2$ = Nb and Ta). In the crystal structure of columbite-group minerals, $M1O_6$ octahedra share edges to form infinite zig-zag chains along the c axis with similar chains at the $M2O_6$ octahedra resulting in alternating [100] 'layers' with a single 'layer' occurring of chains of $M1O_6$ octahedra and double 'layers' including chains of $M2O_6$ octahedra (Chukanov *et al.*, 2023a). The wodginite-group minerals comprise monoclinic species (*C2/c*; $a = \mathbf{2a_0}$, $b = \mathbf{2b_0}$, $c = \mathbf{c_0}$, $\beta \approx 91°$ and $Z = 4$) with the general formula $M1M2M3_2O_8$ where the dominant cations at the M sites are: $M1$ = Mn^{2+}, Fe^{2+} and Li; $M2$ = Ti, Sn^{4+} and Ta; $M3$ = Ta (Chukanov *et al.*, 2023a). According to Ercit *et al.* (1992), the structure of wodginite-group minerals are characterised by a different degree of ordering of cations among the M sites with alternating (100) 'layers' including chains of edge-sharing MO_6 octahedra running along the c axis. Consequently, in the wodginite-group minerals, the 'layers' of the first type include chains of $M3O_6$ octahedra, whereas the 'layers' of the second type contain chains of alternating $M1O_6$ and $M2O_6$ octahedra (Chukanov *et al.*, 2023a).

In the current columbite-supergroup minerals nomenclature scheme, lithiotantite ($LiTa_3O_8$) which is chemically and

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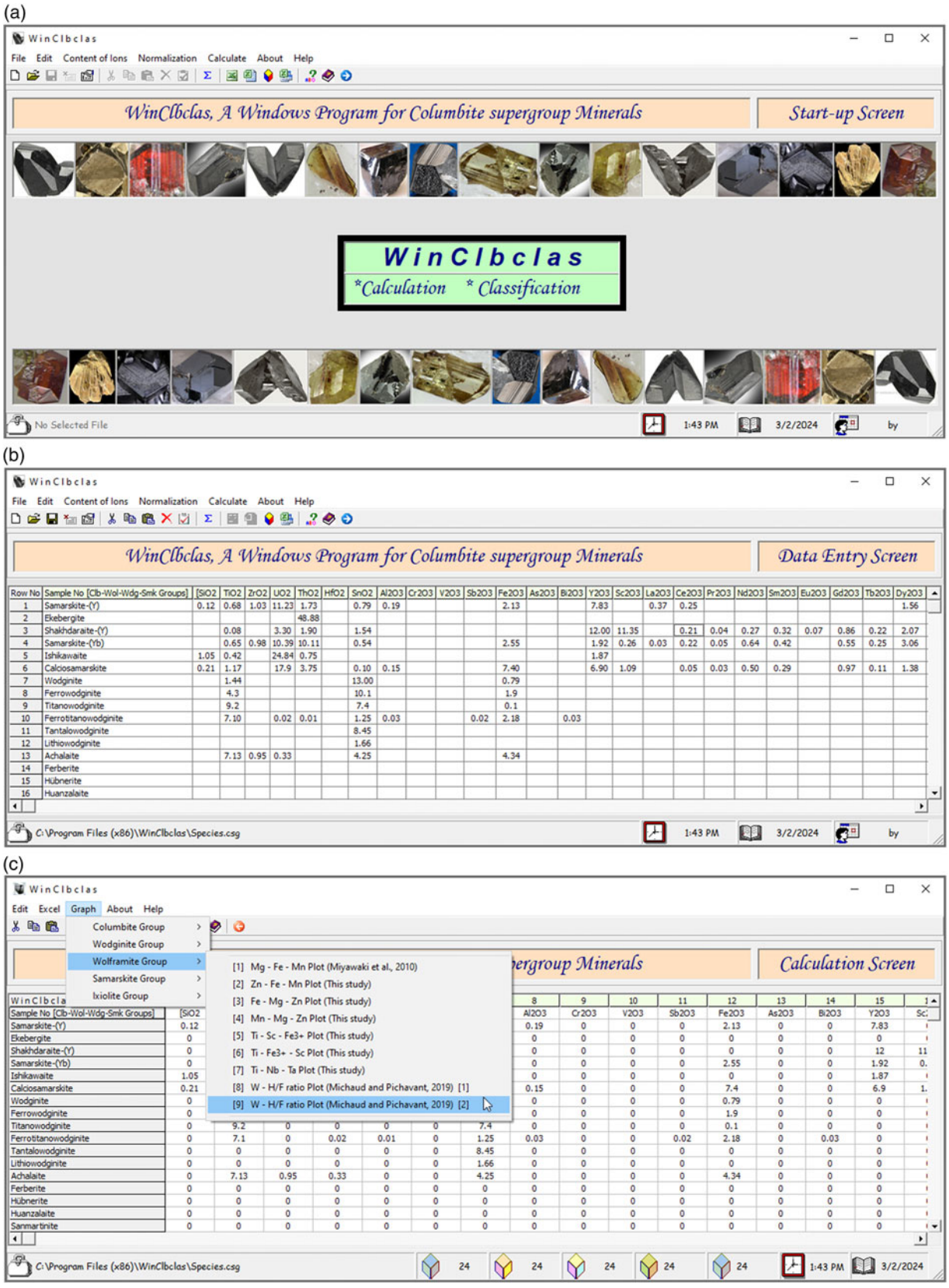

Figure 1. (a) A screenshot of the *WinClbclas* Start-up window with various pull-down menus and equivalent shortcuts. (b) A screenshot of the *WinClbclas Data Entry* window with a total of 47 analytes (wt.%). (c) A screenshot of the *WinClbclas Calculation Screen* with plot options from the pull-down menu of the *Graph*.

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topologically identical to lithiowodginite ($LiTa_3O_8$) has been regarded as the ungrouped species. Similarly, 'qitianlingite' [$Fe^{2+}_2Nb_2W^{6+}O_{10}$], 'yttrocolumbite-(Y)' [$YNbO_4$ (?)], 'yttrotantalite-(Y)' [$YTaO_4$ (?)] and 'yttrocrasite-(Y)' [$YTi_2O_5(OH)$ (?)] are not currently included in the columbite supergroup due to lack of reliable data on their chemical composition and crystal structure.

Program description

WinClbclas is a user-friendly, compiled program package (≈14 Mb) developed for personal computers running on the Microsoft® Windows operating system. The program first calculates the cation values (in apfu) from analyses made on columbite-supergroup minerals (wet-chemical or electron-microprobe techniques) and then uses these to classify the mineral into the 36 IMA-approved species that belong to five groups including ixiolite, wolframite, samarskite, columbite and wodginite, as well as those of eight species that are currently questionable and insufficiently studied (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 *WinClbclas*, the start-up screen, with various pull-down menus and equivalent shortcuts, appears on the screen (Fig. 1a). The program allows the user to input wet-chemical or electron-microprobe wolframite-, samarskite-, columbite-, wodginite- as well as ixiolite-group analytical data, both together or as a separate form, by clicking the *New* icon on the tool bar, by selecting the *New File* from the pull-down menu of *File* option, or pressing the *Ctrl* + *N* keys (Fig. 1b). In the *New File*, *Data Entry Screen* and *Calculation Screen*; these parameters are highlighted by the soft green (i.e. data entry for wolframite, samarskite, columbite and wodginite) and pink colours (i.e. data entry for ixiolite). Up to 47 chemical analytes (in wt.%) are used by *WinClbclas* for calculation and classification of the columbite-supergroup minerals using in the following orders:

Sample No [wolframite, samarskite, columbite and wodginite group], SiO_2, TiO_2, ZrO_2, UO_2, ThO_2, HfO_2, SnO_2, Al_2O_3, Cr_2O_3, V_2O_3, Sb_2O_3, Fe_2O_3, As_2O_3, Bi_2O_3, Y_2O_3, Sc_2O_3, La_2O_3, Ce_2O_3, Pr_2O_3, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, Nb_2O_5, Ta_2O_5, P_2O_5, WO_3, FeO, MnO, PbO, ZnO, MgO, CaO, SrO, BaO, Na_2O, K_2O, Li_2O, F and H_2O (in wt.%).

Sample No [ixiolite group], SiO_2, TiO_2, ZrO_2, UO_2, ThO_2, HfO_2, SnO_2, Al_2O_3, Cr_2O_3, V_2O_3, Sb_2O_3, Fe_2O_3, As_2O_3, Bi_2O_3, Y_2O_3, Sc_2O_3, TotalREE_2O_3, Nb_2O_5, Ta_2O_5, P_2O_5, WO_3, FeO, MnO, PbO, ZnO, MgO, CaO, SrO, BaO, Na_2O, K_2O, Li_2O, F and H_2O (in wt.%).

Data from analysis of a columbite-supergroup mineral 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. MyColumbite), 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 WinClbclas.chm file on the screen. The current version of *WinClbclas* includes a total of 26 binary

Table 3. Chemical compositions of selected ixiolite-group minerals with calculations and classifications by *WinClbclas*.

Row		S1	S2	S3	S4	S5	S6
1	SiO_2	0.00	0.12	0.00	0.00	97.90	0.00
2	TiO_2	2.68	0.38	7.66	56.30	0.00	0.00
3	ZrO_2	0.20	0.60	1.74	43.97	0.00	0.00
4	UO_2	0.00	0.00	1.44	0.00	0.00	0.00
5	ThO_2	0.00	0.00	0.26	0.00	0.00	0.00
6	SnO_2	11.38	12.27	1.01	0.00	0.00	0.00
7	Al_2O_3	0.00	0.16	0.00	0.00	1.60	0.00
8	Sb_2O_2	0.02	0.00	0.00	0.00	0.00	0.00
9	Fe_2O_3	0.00	0.00	0.20	0.00	0.00	0.00
10	As_2O_3	0.04	0.00	0.00	0.00	0.00	0.00
11	Bi_2O_3	0.00	0.00	0.00	0.00	0.00	0.00
12	Y_2O_3	0.00	0.00	1.34	0.00	0.00	0.00
13	Sc_2O_3	0.16	0.00	1.80	0.00	0.00	0.00
14	Nb_2O_5	6.12	10.50	42.80	0.00	0.00	0.00
15	Ta_2O_5	63.79	61.47	26.77	0.00	0.00	0.00
16	WO_3	1.87	0.30	0.00	0.00	0.00	0.00
17	FeO	2.98	8.08	0.00	0.00	0.00	0.00
18	MnO	9.19	5.40	14.94	0.00	0.00	0.00
19	PbO	0.00	0.00	0.00	0.00	0.00	98.20
20	MgO	0.01	0.00	0.00	0.00	0.00	0.00
21	CaO	0.00	0.11	0.00	0.00	0.00	0.00
22	Na_2O	0.00	0.00	0.00	0.00	0.50	0.00
23	H_2O	0.00	0.16	0.00	0.00	0.00	1.80
24	Σ (wt.%)	98.44	99.55	99.96	100.27	100.00	100.00
31	Si	0.000	0.037	0.000	0.000	11.800	0.000
32	Ti	0.640	0.089	1.416	7.967	0.000	0.000
33	Zr	0.031	0.091	0.208	4.033	0.000	0.000
34	U	0.000	0.000	0.079	0.000	0.000	0.000
35	Th	0.000	0.000	0.015	0.000	0.000	0.000
36	Sn	1.441	1.529	0.099	0.000	0.000	0.000
37	Al	0.000	0.059	0.000	0.000	0.227	0.000
38	Sb^{3+}	0.003	0.000	0.000	0.000	0.000	0.000
39	Fe^{3+}	0.000	0.000	0.037	0.000	0.000	0.000
40	As^{3+}	0.008	0.000	0.000	0.000	0.000	0.000
41	Bi	0.000	0.000	0.000	0.000	0.000	0.000
42	Y	0.000	0.000	0.175	0.000	0.000	0.000
43	Sc	0.044	0.000	0.385	0.000	0.000	0.000
44	Nb	0.878	1.483	4.755	0.000	0.000	0.000
45	Ta	5.508	5.224	1.789	0.000	0.000	0.000
46	W	0.154	0.024	0.000	0.000	0.000	0.000
47	Fe^{2+}	0.791	2.112	0.000	0.000	0.000	0.000
48	Mn^{2+}	2.471	1.429	3.110	0.000	0.000	0.000
49	Pb	0.000	0.000	0.000	0.000	0.000	24.000
50	Mg	0.005	0.000	0.000	0.000	0.000	0.000
51	Ca	0.000	0.037	0.000	0.000	0.000	0.000
52	Na	0.000	0.000	0.000	0.000	0.117	0.000
54	Σ (apfu)	11.974	12.115	12.068	12.000	12.144	24.000
55	Mn/(Mn +Fe)	0.76	0.40	1.00	0.00	0.00	0.00
56	Ta/(Ta +Nb)	0.86	0.78	0.27	0.00	0.00	0.00
57	Ti/(Ti+Ta +Nb)	0.09	0.01	0.18	1.00	0.00	0.00
63	Σ M^{1+}	0.00	0.00	0.00	0.00	0.12	0.00
64	Σ M^{2+}	6.53	7.16	6.22	0.00	0.00	48.00
65	Σ M^{3+}	0.16	0.18	1.79	0.00	0.68	0.00
66	Σ M^{4+}	8.45	6.99	7.27	48.00	47.20	0.00
67	Σ M^{5+}	31.93	33.53	32.72	0.00	0.00	0.00
68	Σ M^{6+}	0.92	0.15	0.00	0.00	0.00	0.00
69	Group	IxG	IxG	IxG	IxG	IxG	IxG
70	Species	Ix-Mn	Ix-Fe	Nbix-Mn	Sri	Sft	Sny

Notes: (apfu) = Atoms per formula unit. Sample sources: S1, S2, S4, S5 and S6 = *Handbook of Mineralogy* (Anthony *et al*., 2001–2005); S3 = Chukanov *et al*. (2023b). The formulae were recalculated to content of ions on the basis of 24 O and 12 cations (apfu); M^{1+} = Total monovalent cations, M^{2+} =Total divalent cations, M^{3+} = Total trivalent cations, M^{4+} = Total tetravalent cations, M^{5+} = Total pentavalent cations, M^{6+} = T otal hexavalent cations; IxG = ixiolite group; Ix-Mn = ixiolite-(Mn^{2+}), Ix-Fe = ixiolite-(Fe^{2+}), Nbix-Mn = nioboixiolite-(Mn^{2+}), Sri = srilankite, Sft = seifertite and Sny = scrutinyite.

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Table 4. Compositions of selected wolframite- and samarskite-group minerals with calculations and classifications by *WinClbclas*.

Row		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
1	SiO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.00	0.00
2	TiO_2	0.00	0.00	0.00	0.00	1.61	5.94	7.69	99.25	37.72	0.68	0.00	0.08
3	ZrO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.03	0.00	0.00
4	UO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	11.23	0.00	3.30
5	ThO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.73	48.88	1.90
6	SnO_2	0.00	0.00	0.00	0.00	6.93	1.45	0.00	0.00	0.00	0.79	0.00	1.54
7	Al_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.00	0.00
8	Cr_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.00	0.00	0.00
9	V_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.89	0.00	0.00	0.00
10	Fe_2O_3	0.00	0.00	0.00	0.00	0.00	12.14	14.66	0.00	19.26	2.13	0.00	0.00
11	Y_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.83	0.00	12.00
12	Sc_2O_3	0.00	0.00	0.00	0.00	15.59	11.34	0.00	0.00	0.00	0.00	0.00	11.35
13	La_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.37	0.00	0.00
14	Ce_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.25	0.00	0.21
15	Pr_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04
16	Nd_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.27
17	Sm_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.32
18	Eu_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07
19	Gd_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.86
20	Tb_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22
21	Dy_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.56	0.00	2.07
22	Ho_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.29
23	Er_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	13.37	0.00	1.33
24	Tm_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.35
25	Yb_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.80
26	Lu_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.32
27	Nb_2O_5	0.00	0.00	0.00	0.00	14.25	32.23	26.59	0.00	40.08	32.02	43.88	50.70
28	Ta_2O_5	0.00	0.00	0.00	0.00	53.58	29.93	37.51	0.00	0.00	11.18	0.00	4.42
29	WO_3	75.21	76.57	84.81	72.62	0.00	3.38	5.61	0.00	0.00	1.41	0.00	0.79
30	FeO	24.37	0.00	1.39	7.24	2.07	0.00	5.92	0.42	1.51	11.15	11.94	0.01
31	MnO	0.19	23.43	1.78	1.73	3.02	2.49	1.68	0.00	0.11	0.69	0.00	1.38
32	PbO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.00	0.24
33	ZnO	0.00	0.00	0.00	18.18	0.00	0.00	0.00	0.00	0.00	0.17	0.00	0.00
34	MgO	0.00	0.00	12.49	0.00	0.00	0.06	0.00	0.00	0.00	0.41	0.00	0.00
35	CaO	0.00	0.00	0.02	1.48	0.00	0.00	0.00	0.03	0.00	0.51	0.00	1.01
36	Na_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.00	0.00
37	K_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.21	0.00	0.00
38	H_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.22	0.00	0.00
39	Σ (wt.%)	99.77	100.00	100.49	101.25	97.05	98.96	99.66	99.70	99.85	100.68	104.70	97.87
40	Si	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.035	0.000	0.000
41	Ti	0.000	0.000	0.000	0.000	0.341	1.070	1.471	11.969	5.382	0.150	0.000	0.015
42	Zr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.148	0.000	0.000
43	U	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.735	0.000	0.184
44	Th	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.116	3.262	0.108
45	Sn	0.000	0.000	0.000	0.000	0.779	0.138	0.000	0.000	0.000	0.093	0.000	0.154
46	Al	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.066	0.000	0.000
47	Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.042	0.000	0.000	0.000
48	V	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.135	0.000	0.000	0.000
49	Fe^{3+}	0.630	0.000	0.000	1.840	0.322	2.188	2.805	0.056	2.749	0.471	0.039	0.000
50	Y	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.226	0.000	1.601
51	Sc	0.000	0.000	0.000	0.000	3.829	2.366	0.000	0.000	0.000	0.000	0.000	2.480
52	La	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.040	0.000	0.000
53	Ce	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.027	0.000	0.019
54	Pr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.004
55	Nd	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.024
56	Sm	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.028
57	Eu	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.006
58	Gd	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.071
59	Tb	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.018
60	Dy	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.148	0.000	0.167
61	Ho	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.023
62	Er	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.235	0.000	0.105
63	Tm	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.027
64	Yb	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.214
65	Lu	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.024
66	Nb	0.000	0.000	0.000	0.000	1.816	3.489	3.056	0.000	3.436	4.258	5.818	5.747
67	Ta	0.000	0.000	0.000	0.000	4.107	1.949	2.593	0.000	0.000	0.894	0.000	0.301
68	W	5.920	6.000	6.046	5.718	0.000	0.210	0.370	0.000	0.000	0.107	0.000	0.051
69	Fe^{2+}	5.561	0.000	0.320	0.000	0.166	0.000	1.259	0.000	0.239	2.743	2.890	0.002
70	Mn	0.049	6.000	0.415	0.445	0.721	0.505	0.362	0.000	0.018	0.172	0.000	0.293

(*Continued*)

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Table 4. (*Continued.*)

Row		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
71	Pb	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.012	0.000	0.016
72	Zn	0.000	0.000	0.000	4.078	0.000	0.000	0.000	0.000	0.000	0.037	0.000	0.000
73	Mg	0.000	0.000	5.122	0.000	0.000	0.021	0.000	0.000	0.000	0.180	0.000	0.000
74	Ca	0.000	0.000	0.006	0.482	0.000	0.000	0.000	0.005	0.000	0.161	0.000	0.271
75	Na	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.160	0.000	0.000
76	K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.079	0.000	0.000
77	Σ (apfu)	12.159	12.000	11.908	12.563	12.081	11.937	11.914	12.031	12.001	13.292	12.010	11.957
78	Mn/(Mn+Fe)	0.01	1.00	0.56	1.00	0.81	1.00	0.22	0.00	0.07	0.06	0.00	0.99
79	Ta/(Ta+Nb)	0.00	0.00	0.00	0.00	0.69	0.36	0.46	0.00	0.00	0.17	0.00	0.05
80	Ti/(Ti+Ta+Nb)	0.00	0.00	0.00	0.00	0.05	0.16	0.21	1.00	0.61	0.03	0.00	0.00
81	Σ M^{1+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.24	0.00	0.00
82	Σ M^{2+}	11.22	12.00	11.73	10.01	1.77	1.05	3.24	0.01	0.51	6.61	5.78	1.16
83	Σ M^{3+}	1.89	0.00	0.00	5.52	12.45	13.66	8.42	0.17	8.78	9.64	0.12	14.43
84	Σ M^{4+}	0.00	0.00	0.00	0.00	4.48	4.83	5.88	47.88	21.53	5.11	13.05	1.84
85	Σ M^{5+}	0.00	0.00	0.00	0.00	29.62	27.19	28.25	0.00	17.18	25.76	29.09	30.24
86	Σ M^{6+}	35.52	36.00	36.28	34.31	0.00	1.26	2.22	0.00	0.00	0.64	0.00	0.31
87	Group	WfG	WfG	WfG	WfG	WfG	WfG	WfG	WfG	WfG	SmkG	SmkG	SmkG
88	Species	Fer	Hbr	Hza	Sma	Hef	Nhef	Rvy	Rie	Dvm	Smk-Y	Ekb	Skd-Y

Note: (apfu) =Atoms per formula unit. Sample sources: S1, S2, S3, S4, S5, S7, S8 and S10 = *Handbook of Mineralogy* (Anthony *et al*., 2001–2005); S6 = Lykova *et al*. (2021); S9 = Udoratina *et al*. (2024); S11 = https://www.mineralienatlas.de; S12 = Pautov *et al*. (2022). The formulae were recalculated to content of ions on the basis of 24 O and 12 cations (apfu); M^{1+} = Total monovalent cations, M^{2+} =Total divalent cations, M^{3+} = Total trivalent cations, M^{4+} =Total tetravalent cations, M^{5+} = Total pentavalent cations, M^{6+} =Total hexavalent cations; WfG = wolframite group; SmkG = samarskite group; Fer = ferberite, Hbr = hübnerite, Hza = huanzalaite, Sma = sanmartinite, Hef = heftetjernite, Nhef = nioboheftetjernite, Rvy = rossovskyite, Rie = riesite, Dvm = dmitryvarlamovite, Smk-Y = samarskite-(Y), Ekb = ekebergite and Skd-Y = shakhdaraite-(Y).

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

Worked examples

Using the selected data set from literature (see references in Tables 3, 4, and 5), examples showing how *WinClbclas* can be used in the determination of chemical formulae and columbite-supergroup minerals classification are presented. The previously typed or loaded analyses are processed by clicking the *Calculate* icon (i.e. Σ) in the *Data Entry Section* of the program, after which all input and estimation parameters are displayed in columns 1–204 (see Table 2) of the *Calculation Screen* (i.e. 1–116 for wolframite, samarskite, columbite and wodginite groups highlighted by the soft green colour; 117–204 for the ixiolite group, highlighted by the soft pink colour). 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 '.csg' that refers to the columbite supergroup. 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.

The validity of program output has been tested with representative columbite-supergroup minerals data selected from the literature (see references in Tables 3, 4, and 5). The program calculates Fe^{3+} and Fe^{2+} (apfu) from electron-microprobe-derived FeO (wt.%) content using the stoichiometric constraints according to the Droop (1987) method (see sample number S1 in Table 4). *WinClbclas* calculates the compositional formula for a given columbite-supergroup mineral analytical data on the basis of 24 O and 12 cations (apfu). Alternatively, by clicking the one of options, for example, *Columbite group minerals* [*M1M2(2)O6*] *on the basis of 6 O and 3 cations (apfu)* from the pull-down menu of *Content of Ions* in the *Start-up Screen* the program calculates columbite-group minerals according to the selected criteria. Similarly, by clicking one of the options [e.g. *Normalize wodginite group minerals* [*M1M2M3(2)O8*] *to total cations = 4.00 (apfu)*] from the pull-down menu of *Normalization* in the *Start-up Screen* the program normalises the total cation content according to the selected criteria. The program provides the users with some useful ratios, such as Mn/(Mn+Fe), Ta/(Ta+Nb) and Ti/(Ti+Ta+Nb) in the *Calculation Screen* (see rows 78–80 in Table 4). Classification of a given analysis into its proper group is carried out on the basis of the dominant cation at the site(s). *WinClbclas* lists total monovalent (i.e. M^{+}) to hexavalent (i.e. M^{6+}) ions, resulting in the same valence state as a single constituent, together with the cations on the type of valence state (i.e. M^{+}) in the *Calculation Screen* and an Excel output file (e.g. see rows 53–58 in Table 5).

In a case where a chemical composition corresponds to a hitherto unknown species within the columbite supergroup (i.e. a new species), *WinClbclas* warns the user with a 'Not classified' statement in column number 115 of the *Calculation Screen*. For example, a columbite-supergroup mineral with the following analytical data (see Table 2 in Alekseev, 2023; wt.%): TiO_2 1.68, SnO_2 4.35, Nb_2O_5 17.98, Ta_2O_5 38.97, WO_3 18.39, FeO 8.85, MnO 8.33, Li_2O 0.21, total 98.76 is defined as 'wolframowodginite' that yields the empirical formula $(Mn_{2.0659}Fe^{2+}_{1.251}Li_{0.247})_{\Sigma 3.563}(Fe^{3+}_{0.916}Sn_{0.508}Ti_{0.37})_{\Sigma 1.794}(Ta_{3.102}Nb_{2.379}W_{1.395})_{\Sigma 6.876}O_8$. As can be seen from the empirical formula, calculated content of ions on the basis of 24 O and 12 cations (apfu), means the dominant ions at the *M*1, *M*2 and *M*3 sites correspond to Mn, Fe^{3+} and Ta, respectively. As no species corresponding to this composition exists in the current classification scheme (i.e. *M*1 = Mn, *M*2 = Fe^{3+} and *M*3 = Ta), the program designates it as 'Not classified' rather than applying the name of one of known species given in Table 1.

WinClbclas provides options to display various binary and ternary classification and compositional diagrams in the *Calculation Screen* by using the Grapher program. Some of these plots with selected columbite-supergroup mineral data

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Table 5. Compositions of selected columbite- and wodginite-group minerals with calculations and classifications by WinClbclas.

Row		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
1	SiO_2	0.00	0.00	0.46	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	TiO_2	0.75	1.28	4.61	1.17	0.00	0.91	16.39	27.36	1.44	4.30	9.20	7.10	0.00	7.13
3	ZrO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.95
4	UO_2	0.00	0.00	0.00	0.08	0.00	0.00	0.67	39.08	0.00	0.00	0.00	0.02	0.00	0.33
5	ThO_2	0.00	0.00	0.00	0.00	0.00	0.00	4.95	4.14	0.00	0.00	0.00	0.01	0.00	0.00
6	SnO_2	0.02	0.04	0.00	0.60	0.00	0.00	0.12	0.00	13.00	10.10	7.40	1.25	8.45	4.25
7	Al_2O_3	0.00	0.00	1.12	0.00	0.00	0.00	0.13	0.00	0.00	0.00	0.00	0.03	0.00	0.00
8	Sb_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
9	Fe_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	1.32	0.00	0.79	1.90	0.10	2.18	0.00	4.34
10	Bi_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00
11	Y_2O_3	0.00	0.00	0.00	0.00	0.00	0.76	18.22	7.78	0.00	0.00	0.00	0.00	0.00	0.00
12	Ce_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	4.34	0.00	0.00	0.00	0.00	0.00	0.00	0.00
13	Nd_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.37	0.00	0.00	0.00	0.00	0.00	0.00
14	Nb_2O_5	54.62	37.25	70.59	23.75	1.39	79.50	41.43	11.27	3.96	14.80	11.10	6.52	3.48	29.05
15	Ta_2O_5	25.89	42.84	10.45	56.98	84.47	0.00	3.84	5.98	68.64	56.30	59.90	70.68	80.72	38.22
16	WO_3	0.39	0.28	0.86	0.000	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.02	0.00	2.65
17	FeO	10.36	8.08	2.21	10.93	0.33	0.000	0.77	0.00	0.00	9.30	3.10	10.27	0.21	7.91
18	MnO	8.37	9.20	0.00	6.090	13.81	0.000	0.59	0.48	10.74	2.80	9.00	1.05	6.15	4.67
19	PbO	0.00	0.00	0.00	0.000	0.00	0.000	0.37	0.00	0.00	0.00	0.00	0.05	0.00	0.00
20	MgO	0.00	0.00	9.00	0.000	0.00	0.000	0.13	0.00	0.00	0.00	0.00	0.01	0.00	0.00
21	CaO	0.00	0.00	0.00	0.000	0.00	15.82	4.86	0.22	0.00	0.00	0.00	0.01	0.00	0.04
22	Na_2O	0.00	0.00	0.00	0.000	0.00	0.070	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
23	Li_2O	0.00	0.00	0.00	0.000	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	0.51	0.00
24	H_2O	0.00	0.00	0.00	0.000	0.00	0.000	1.90	0.00	0.00	0.00	0.00	0.00	0.00	0.00
25	Σ (wt.%)	100.40	98.97	99.30	99.60	100.00	97.08	100.14	96.68	98.57	99.50	99.80	99.25	99.52	99.54
26	Si	0.000	0.000	0.098	0.000	0.000	0.000	0.016	0.000	0.000	0.000	0.000	0.000	0.000	0.000
27	Ti	0.140	0.261	0.739	0.257	0.000	0.151	2.895	5.860	0.324	0.949	1.993	1.619	0.000	1.406
28	Zr	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.121
29	U	0.000	0.000	0.000	0.005	0.000	0.000	0.035	2.476	0.000	0.000	0.000	0.001	0.000	0.019
30	Th	0.000	0.000	0.000	0.000	0.000	0.000	0.264	0.268	0.000	0.000	0.000	0.001	0.000	0.000
31	Sn	0.002	0.004	0.000	0.070	0.000	0.000	0.011	0.000	1.549	1.181	0.850	0.151	1.124	0.444
32	Al	0.000	0.000	0.281	0.000	0.000	0.000	0.036	0.000	0.000	0.000	0.000	0.011	0.000	0.000
33	Sb	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000
34	Fe^{3+}	0.000	0.065	0.000	0.681	0.093	0.000	0.233	0.000	0.178	0.419	0.022	0.497	0.000	0.856
35	Bi	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000
36	Y	0.000	0.000	0.000	0.000	0.000	0.089	2.277	1.179	0.000	0.000	0.000	0.000	0.000	0.000
37	Ce	0.000	0.000	0.000	0.000	0.000	0.000	0.373	0.000	0.000	0.000	0.000	0.000	0.000	0.000
38	Nd	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.038	0.000	0.000	0.000	0.000	0.000	0.000
39	Nb	6.139	4.627	6.799	3.137	0.213	7.920	4.398	1.451	0.535	1.963	1.445	0.893	0.525	3.442
40	Ta	1.750	3.159	0.605	4.527	7.768	0.000	0.245	0.463	5.580	4.491	4.691	5.826	7.321	2.724
41	W	0.025	0.020	0.047	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.180
42	Fe^{2+}	2.154	1.768	0.394	1.989	0.000	0.000	0.151	0.000	1.978	2.281	0.747	2.603	0.059	1.734
43	Mn	1.763	2.113	0.000	1.507	3.956	0.000	0.117	0.116	2.720	0.696	2.195	0.270	1.737	1.037
44	Pb	0.000	0.000	0.000	0.000	0.000	0.000	0.023	0.000	0.000	0.000	0.000	0.004	0.000	0.000
45	Mg	0.000	0.000	2.858	0.000	0.000	0.000	0.046	0.000	0.000	0.000	0.000	0.005	0.000	0.000
46	Ca	0.000	0.000	0.000	0.000	0.000	3.735	1.223	0.067	0.000	0.000	0.000	0.003	0.000	0.011
47	Na	0.000	0.000	0.000	0.000	0.000	0.030	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
48	Li	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.684	0.000
49	Σ (apfu)	11.973	12.016	11.822	12.173	12.029	11.925	12.349	11.917	12.864	11.980	11.942	11.890	11.450	11.973
50	Mn/(Mn+Fe)	0.45	0.54	0.00	0.43	1.00	0.00	0.44	1.00	0.58	0.23	0.75	0.09	0.97	0.37
51	Ta/(Ta+Nb)	0.22	0.41	0.08	0.59	0.97	0.00	0.05	0.24	0.91	0.70	0.76	0.87	0.93	0.44
52	Ti/(Ti+Ta+Nb)	0.02	0.03	0.09	0.03	0.00	0.02	0.38	0.75	0.05	0.13	0.25	0.19	0.00	0.19
53	ΣM^{1+}	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.68	0.00
54	ΣM^{2+}	7.83	7.76	6.50	6.99	7.91	7.47	3.12	0.37	9.40	5.95	5.88	5.77	3.59	5.56
55	ΣM^{3+}	0.00	0.20	0.84	2.04	0.28	0.27	8.76	3.65	0.53	1.26	0.07	1.54	0.00	2.57
56	ΣM^{4+}	0.57	1.06	3.35	1.33	0.00	0.60	12.90	34.42	7.49	8.52	11.37	7.09	4.50	7.96
57	ΣM^{5+}	39.45	38.93	37.02	38.32	39.91	39.60	23.22	9.57	30.58	32.27	30.68	33.60	39.23	30.83
58	ΣM^{6+}	0.15	0.12	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	1.08
59	Group	ClbG	ClbG	ClbG	ClbG	ClbG	ClbG	ClbG	ClbG	WdgG	WdgG	WdgG	WdgG	WdgG	WdgG
60	Species	Clb-Fe	Clb-Mn	Clb-Mg	Ttl-Fe	Ttl-Mn	Fsm	Eux-Y	Uplc	Wdg	Fwdg	Twdg	Ftwdg	Ttwdg	Ahl

Note: (apfu) = Atoms per formula unit. Sample sources: S1, S2 = Wenger *et al.* (1991); S3 = https://www.mineralienatlas.de; S4 = Dias and Chavez (2015); S5 = Zwaan *et al.* (2016); S6 = Simandl *et al.* (2018); S7 = *Handbook of Mineralogy* (Anthony *et al.*, 2001–2005); S8 = Aurisicchio *et al.* (1993); S9 = Udoratina *et al.* (2024); S10 = *Handbook of Mineralogy* (Anthony *et al.*, 2001–2005); S11 = https://www.mineralienatlas.de; S12 = Galliski *et al.* (1999); S13 = Hanson *et al.* (2018); S14 = Galliski *et al.* (2016). The formulae were recalculated to content of ions on the basis of 24 O and 12 cations (apfu); M^{1+} = Total monovalent cations, M^{2+} = Total divalent cations, M^{3+} = Total trivalent cations, M^{4+} = Total tetravalent cations, M^{5+} = Total pentavalent cations, M^{6+} = Total hexavalent cations; ClbG = columbite group; WdgG = wodginite group; Clb-Fe = columbite-(Fe), Clb-Mn = columbite-(Mn), Clb-Mg = columbite-(Mg), Ttl-Fe = tantalite-(Fe), Ttl-Mn = tantalite-(Mn), Fsm = fersmite, Eux-Y = euxenite-(Y), Uplc = uranopolycrase, Wdg = wodginite, Fwdg = ferrowodginite, Twdg = titanowodginite, Ftwdg = ferrotitanowodginite, Ttwdg = tantalowodginite and Ahl = Achalaite.

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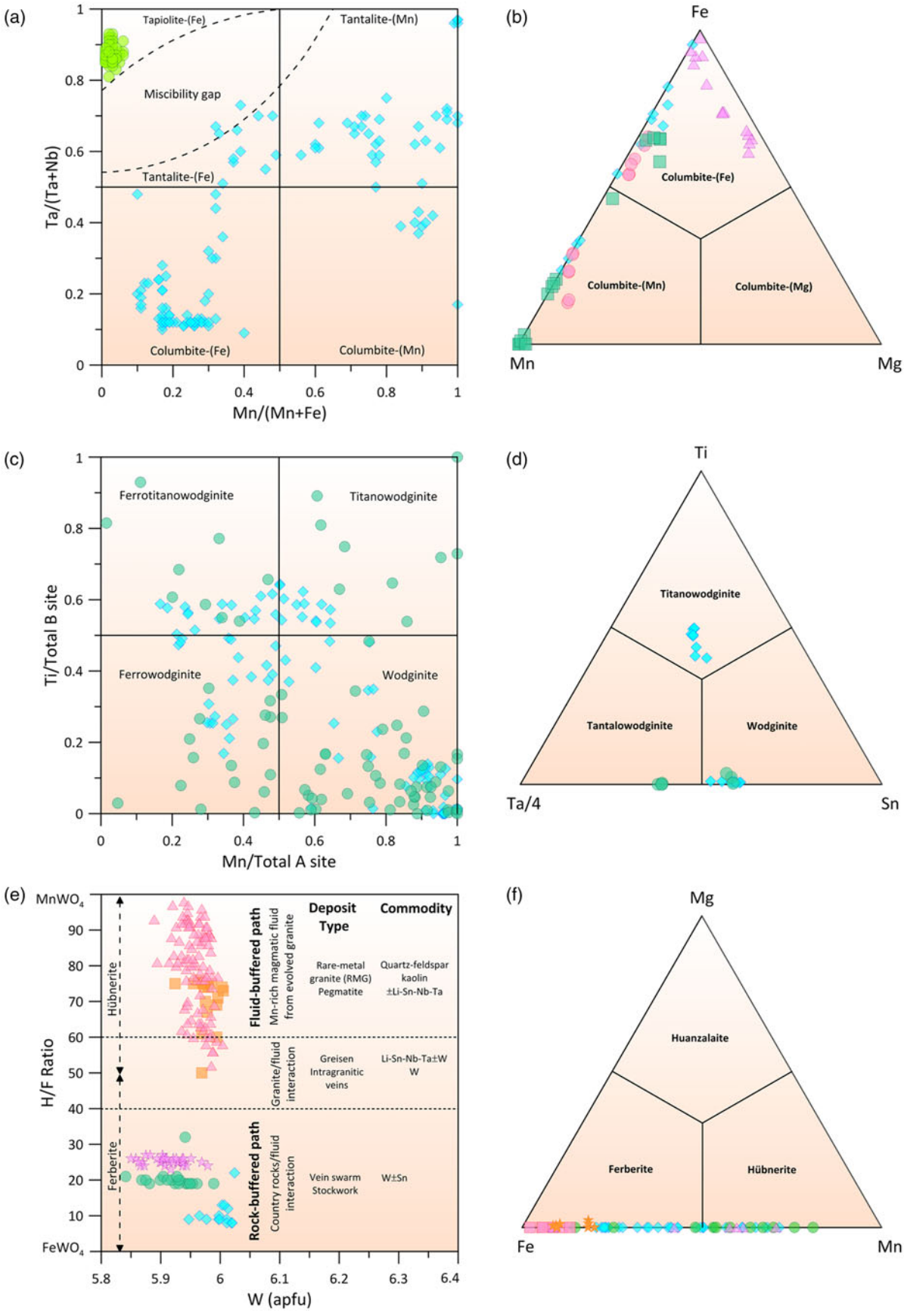

Figure 2.

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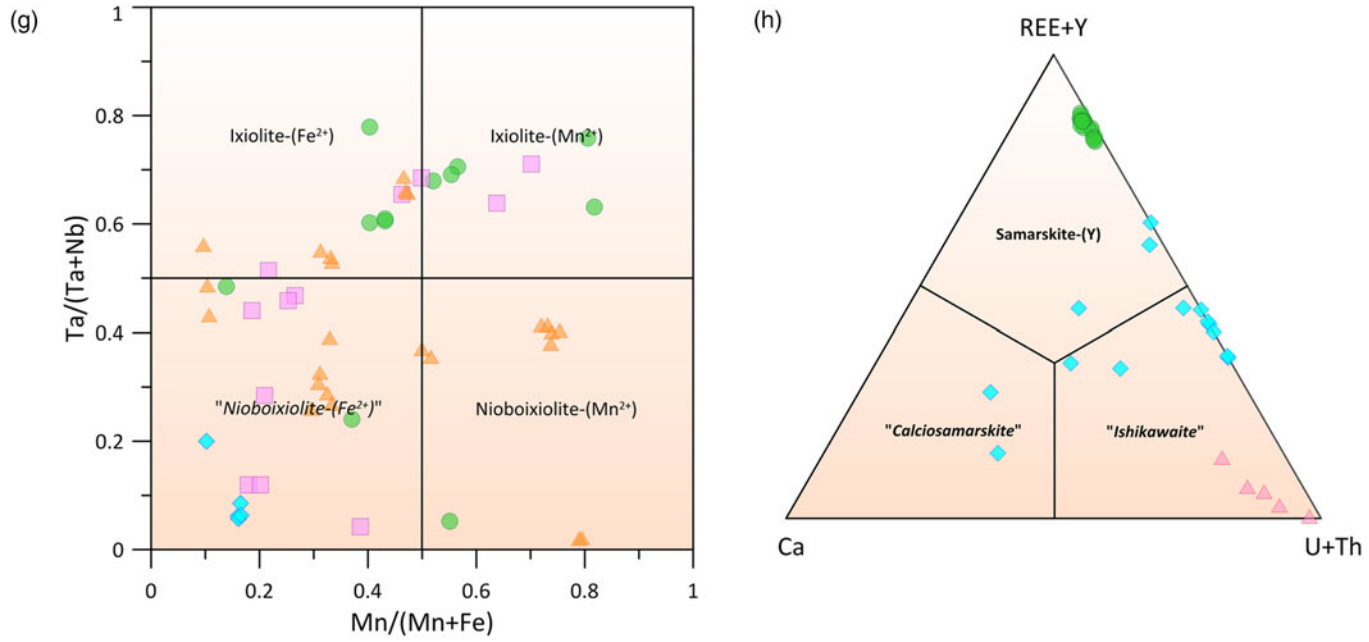

Figure 2. (*Continued*) Selected plots of the columbite-supergroup minerals classification and compositional diagrams from the pull-down menu of *Graph* in the *Calculation Screen* of the *WinClbclas* program using the selected mineral analyses from the literature. (a) Compositions of the columbite-group minerals in the columbite–tantalite quadrilateral (from Černý and Ercit, 1985; 1989; samples from Tindle and Breaks, 2000) with the empirically derived tantalite–tapiolite miscibility gap (from Černý *et al.*, 1992). (b) Compositional plot of the columbite-group minerals in a ternary Fe–Mn–Mg diagram (filled diamonds from Sosa *et al.*, 2002; filled circles from Baumgartner *et al.*, 2006; filled squares from Aurisicchio *et al.*, 2002; filled triangles from Mackay and Simandl, 2015). (c) Compositional plot of the wodginite-group minerals in a Mn/Total A site versus Ti/Total B site diagram (revised from Tindle *et al.*, 1998; filled diamonds from Tindle and Breaks, 2000; filled circles from Alekseev, 2023). (d) Compositional plot of the wodginite-group minerals in a ternary Ti-Ta/4-Sn diagram (filled diamonds from Tindle and Breaks, 2000; filled circles from Hanson *et al.*, 2018). (e) Environments and mechanisms of W deposition in W versus H/F ratio diagram (from Michaud and Pichavant, 2019; samples from Monnier *et al.*, 2019). (f) Compositional plot of the wolframite-group minerals in a ternary Mg–Fe–Mn diagram (from Miyawaki *et al.*, 2010; filled diamonds from Moore and Howie, 1978; filled circles from Michaud and Pichavant, 2019; filled squares from d'Aquin Tumukunde and Piestrzynski, 2018; filled triangles from Llorens and Moro, 2012; filled stars from Novák *et al.*, 2008). (g) Compositional plot of the ixiolite-group minerals (IGM) in a Mn/(Mn+Fe) versus Ta/(Ta+Nb) diagram (filled diamonds from René, 2019; filled circles from Bergstøl and Juve, 1988; filled squares from Wise *et al.*, 1998; filled triangles from Tindle and Breaks, 2000). (h) Compositional plot of the samarskite-group minerals in a ternary (REE+Y)–Ca–(U+Th) diagram (from Černý and Ercit, 1989; filled diamond from Pieczka *et al.*, 2014; filled circles from Guastoni *et al.*, 2019; filled triangles from Raslan, 2008).

from the literature are given in Fig. 2. The columbite-group minerals with widespread niobium and tantalum phases in geochemically highly evolved rocks such as leucogranites and granitic pegmatites show compositional variations, especially in Nb–Ta and Fe–Mn pairs. During primary magmatic crystallisation, these pairs, which are sensitive indicators of magmatic to subsolidus evolution of the parental rock, usually show a progressive increase in terms of the Ta/(Ta+Nb) and Mn/(Mn+Fe) ratios with a characteristic evolutionary trend in the columbite–tantalite quadrilateral diagram (Černý and Ercit 1985; Černý *et al.*, 1986; Tindle and Breaks, 2000; Novák *et al.*, 2018). In a classical columbite–tantalite quadrilateral plot (see Fig. 2a), there exists an empirically derived tantalite–tapiolite miscibility gap restricted by the two, upward and downward, concave curves. The program classifies a sample that plots between these curves as 'miscibility gap' instead of naming it tantalite-(Fe) or tantalite-(Mn). Similarly, a sample that plots above the upwards concave curve is classified as tapiolite-(Fe) by the *WinClbclas* program.

Differentiation of highly evolved peraluminous crustal magmas may cause a high Mn/Fe ratio in the fluid that controls the deposition of hübnerite. Hence, in understanding the wolfram deposition environments in perigranitic ore-forming systems, Michaud and Pichavant (2019) proposed the H/F ratio [i.e. hübnerite/ferberite = 100*Mn/(Mn+Fe)] as an indicator of contrasted wolframite deposition mechanisms, as well as environments in perigranitic wolfram ore-forming systems, in three distinctive domains: (1) for a H/F ratio > 60, wolframite precipitates from a Mn-rich magmatic fluid evolving under a fluid-buffered path; (2) for a H/F ratio between 40 and 60, wolframite precipitates from a fluid buffered by granite/fluid interactions; and (3) for a H/F ratio < 40, wolframite precipitates from a fluid carrying a significant non-magmatic signature derived from country rocks. In this context, for example, by clicking option nine belonging to the Wolframite Group from the pull-down menu of *Graph* in the *Calculation Screen* (see Fig. 1c), the W versus H/F Ratio plot with selected data file in the *Data Entry Screen* is displayed on screen through the Grapher software (Fig. 2e). 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.

Conclusions

WinClbclas is a user-friendly program developed specially for personal computers running on the Windows operating system to estimate and classify columbite-supergroup minerals using data obtained from both electron-microprobe and wet-chemical analyses. The program processes multiple analytical data (up to 200) for each program execution. The current version of

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WinClbclas classifies a total of 44 species for a given analysis into one of five groups – ixiolite, wolframite, samarskite, columbite and wodginite, as well as other questionable and ungrouped species, using the current IMA-approved nomenclature scheme (Chukanov *et al.*, 2023a). 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 analysis, based on chemistry (wt.%). By clicking the *Calculate* icon (i.e. Σ) in the *Data Entry Screen*, all input and estimated parameters by *WinClbclas* 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 204 (1–115 for wolframite, samarskite, columbite and wodginite groups; 117–204 for the ixiolite group) in the *Calculation Screen* window as well as in an Output Excel file. 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*. *WinClbclas* 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 '.csg', '.xls', '.xlsx', and plot files with the extension '.grf') are installed into the personal computer (i.e. the directory of C:\Program Files\WinClbclas or C:\Program Files (x86)\WinClbclas) with Windows XP and subsequent operating systems. An installation of the program into a personal computer with the 64-bit operating system may require the msflexgrd adjustment (see explanations in the Supplementary Material). The self-extracting setup file is ~14 Mb and can be obtained from the Supplementary material (see below) (i.e. the *WinClbclas* setup.exe file).

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