NIOBIUM-TANTALUM OXIDES IN RARE METAL PEGMATITES AND GRANITES

by

Frank Melcher

Lehrstuhl für Geologie und Lagerstättenlehre
Montanuniversität Leoben, Peter-Tunner-Straße 5, 8700 Leoben, Austria

Abstract

The occurrence and chemistry of Nb-Ta oxides in rare-element pegmatites and rare-metal granites is reviewed. Members of the columbite-tantalite group are the most common and economically important, followed by the tapiolite, wodginite and ixiolite groups and the pyrochlore supergroup. Nb-Ta oxides are characterized by considerable textural and chemical heterogeneity that is of potential use to identify mineralizing processes. Structural and chemical data are summarized and substitution mechanisms are proposed. An attempt is made to group Ta-(Nb-Sn-Li) deposits into the LCT (Li-Cs-Ta), NYF (Nb-Y-F) and mixed LCT/NYF pegmatite families using the trace element chemistry of Nb-Ta oxides.

Introduction

Tantalum (-Nb-Sn)-bearing granites and pegmatites hold an estimated 80 percent share in antalum production and occur on all continents in syn- to post-orogenic structures spanning an age range from the Archean (3000 Ma) to the Tertiary (Fig. 1; TKACHEV, 2011). Collision environments generating granite-pegmatite systems include continent-continent (e.g., the Himalayas), continent-island arc (e.g., central Svecofennian basin), possibly island arc-island arc and closures of ensialic rifts (e.g., Damara Province) (ČERNÝ, 1991). Emplacement of mineralised pegmatites is commonly related to fold structures, shears and fault systems forming bodies of variable shape and size (metres to kilometres) outside of outcropping or postulated "host" plutons; many pegmatites lack outcropping parental granitic intrusions. Pegmatites hosted by granitic rocks are less abundant. Various investigations provided conclusive evidence of systematic variations in degree of fractionation, concentration of rare elements, and distance from the assumed host pluton (VARLAMOFF, 1972). ČERNÝ & ERCIT (2005) defined four classes of granitic pegmatites bearing Ta-Nb-Sn mineralisation (abyssal, muscovite-rare-element, rare-element and miarolitic classes). In the LCT family (Li-Cs-Ta) of the rare-element class, which is economically important for Ta, four pegmatite types and further on, six subtypes are distinguished.
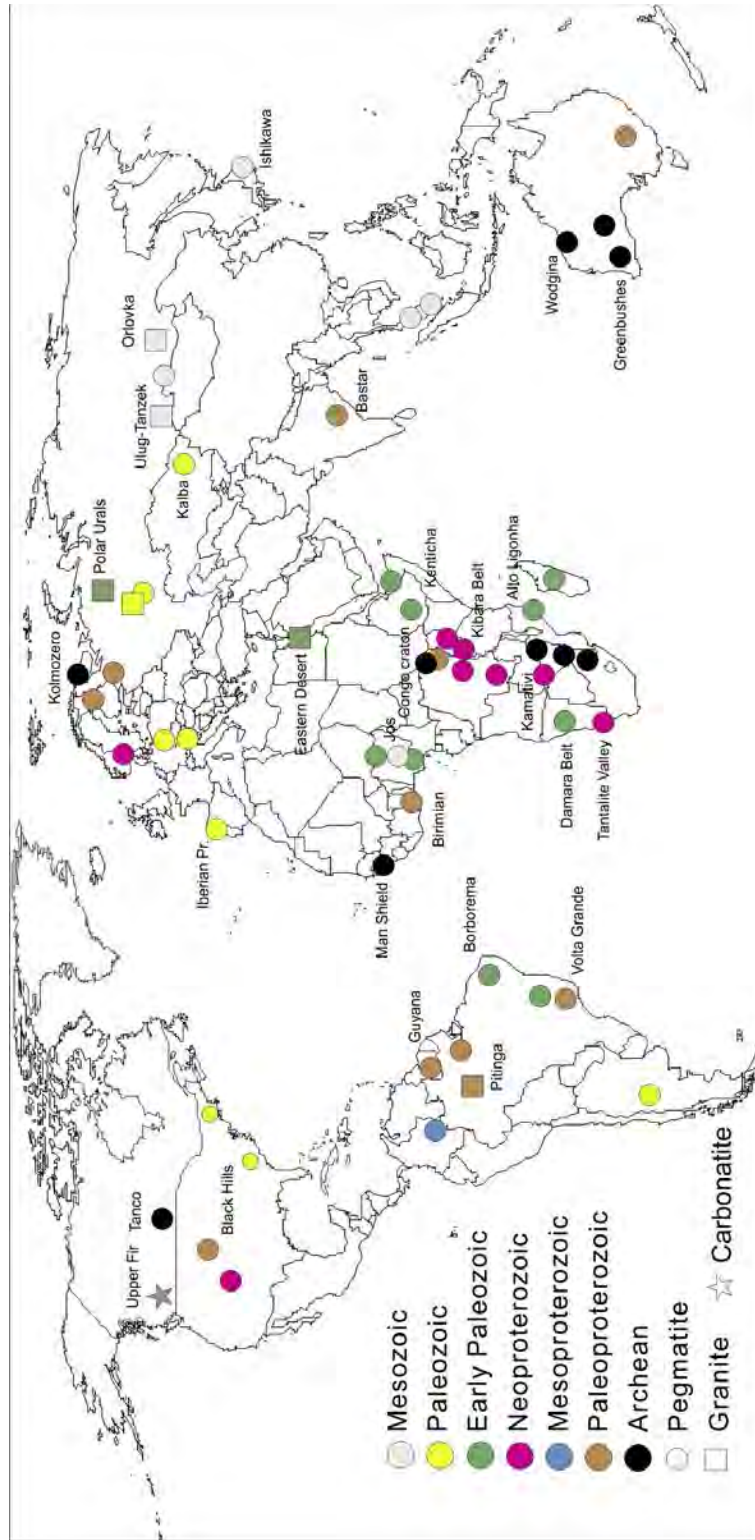
Fig. 1
Ta-(Nb-Sn) provinces investigated by the BGR

18

A large number of Nb-Ta oxides are known from pegmatites and granites (ČERNÝ & ERCIT, 1989). Especially the members of the columbite-tantalite, tapiolite, wodginite and ixiolite groups share a number of features that make them interesting from both, an economic and a scientific point of view. Due to their large grain size in pegmatites (commonly in the 0,5 to 5 mm range, but reaching up to several decimetres), hardness and mechanical resistivity, Nb-Ta oxides are easily concentrated by simple gravitational methods that are commonly applied in artisanal mining operations in Africa and South America. The current production of Ta (934 metric tons Ta_2O_5 in 2012; REICHL et al., 2014) is mainly from Rwanda (28 %), the Democratic Republic of the Congo (22 %), Ethiopia (13%), Brazil (13 %), followed by Burundi, Nigeria and Russia. From a scientific point of view, the chemical resistivity of most Nb-Ta oxides allows the preservation of delicate growth textures. A large number of trace elements may enter into the structure and finally, some Nb-Ta oxides are amenable to radiometric U-Pb dating using solution-TIMS or LA-ICP-MS techniques (GÄBLER et al., 2011). Textures, mineral associations, mineral chemistry and radiometric ages may be used to fingerprint the processes of formation and the regional origin of Nb-Ta oxides (MELCHER et al., 2008, 2009, 2014).

Mineralogy of Nb-Ta oxides

Solid solution members of the orthorhombic columbite-tantalite group with the general formula AB_2O_6 (A = Fe^{2+}, Mn^{2+} and B = Nb^{5+}, Ta^{5+}) are the most important source of Ta, commonly making up the major proportion of Nb-Ta oxides in a deposit (MELCHER et al., 2014). The end-members are columbite-(Fe), columbite-(Mn), tantalite-(Mn) and tantalite-(Fe). Their composition is traditionally expressed as molar ratios #Mn = 100*Mn/(Mn+Fe) and #Ta = 100*Ta/(Ta+Nb), and plotted in the "columbite quadrilateral". The structures of both ordered and disordered columbite-tantalite accommodate minor quantities of Ti, Sn, Zr, Hf, Sc, REE and other elements.

Tapiolite is a tetragonal modification of AB_2O_6, with tapiolite-(Fe) being much more abundant than tapiolite-(Mn). A miscibility gap exists between these phases and orthorhombic columbite-tantalite. Tapiolite is quite common in many pegmatite deposits and may even form a major phase. It is structurally related to rutile and cassiterite, which explains elevated Ti and Sn concentrations commonly observed. Wodginite and ixiolite are compositionally related complex phases that usually contain Sn in the weight-percent range and often also Li, Ti, Zr, Hf, Sc, W and U.

Ixiolite has an orthorhombic unit cell corresponding to a disordered structure derived from that of columbite. Heating of ixiolite induces ordering into a wodginite-type structure, which has a monoclinic unit cell. The general wodginite formula (ACB_2O_8) implies the following distribution of cations at the three crystallographic sites: A = Mn, Fe^{2+}; C = Sn, Ti, Fe^{3+}, Ta; B = Ta, Nb.

Minerals of the pyrochlore supergroup with a cubic structure are second in abundance only to columbite-tantalite. In some deposits, including NYF-family (Nb-Y-F) pegmatites, alkaline granites and especially in carbonatites, they are more abundant than columbite-tantalite group minerals. Their general formula is $A_{2-m}B_2X_{6-w}Y_{1-n}$, where: A[8] = Ca, Na, Ag, Mn, Sr, Ba, Fe^{2+}, Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}, Sc, U, Th, REE+Y, vacancy, H_2O; B[6] = Nb, Ta, Ti, V^{5+}, Sb^{5+}, W, Fe^{3+}, Sn^{4+}, Zr, Hf, Mg, Al, Si; X = O, subordinate OH and F, and Y = O, OH, F, vacancy, H_2O, K, Cs, Rb (ATENCIO et al., 2010). The nomenclature approved by the CNMNC-IMA is based on the ions in the A, B and Y sites, and five groups are recommended based on the B-site occupancy: pyrochlore (Nb), microlite (Ta), roméite (Sb), betafite (Ti), and elsmoreite (W).

In pegmatites, the most important minerals of the pyrochlore supergroup are members of the microlite group [$(Ca,Na)_{2-x}Ta_2O_6(OH,F,H_2O)_{1-y}$]. They are either present as a primary phase or more commonly replace columbite and other primary Nb-Ta oxides. Microlite may accommodate appreciable concentrations of U or Pb ("uranmicrolite", "plumbomicrolite", both now discredited), Th, and REE. In many deposits, U-rich microlite is the major source of radioactivity.

A number of somewhat poorly defined, often metamict and altered, REE+Y- and often U-Th-bearing Nb-Ta oxides are known mainly in NYF-family pegmatites and granites, but also as accessories in assemblages of the LCT family. These include members of the aeschynite and euxenite groups characterized by a general formula of $AB_2(O,OH)_6$, with A = Ca, REE+Y, U, Pb; B = Ti, Nb, Ta; the aeschynite structure shows a preference for larger A cations than the euxenite structure. The samarskite and the fergusonite groups share a general formula of ABO_4, where A = REE+Y and B = Ta, Nb. In samarskite, significant Ca, U and Fe enters into the A position, and Ti into the B position. Tantalian rutile ("strüverite") and niobian rutile ("ilmeno-rutile") are regarded as solid solutions of rutile and "mono-tapiolite". These phases are usually heterogeneous with exsolved columbite or ilmenite. Stibiotantalite [$SbTaO_4$] and bismutotantalite [$Bi(Ta,Nb)O_4$] are minor phases known from only a few pegmatites. Rare Nb-Ta oxides occurring in a few pegmatite deposits also include members of the solid solution series foordite-thoreaulite, simpsonite, rankamaite, cesplumtantite, fersmite, rynersonite, liandradite, petscheckite and others.

Textures

Back scatter electron images of Nb-Ta oxides reveal complex textures displaying various types of zoning (LAHTI, 1987), intergrowth, exsolution and replacement. Commonly, Nb-rich cores are rimmed by more Ta-rich zones, often in an oscillatory pattern, while Mn-Fe ratios remain almost constant. Trace elements in zoned grains often behave conservatively, and do not correlate with changes in Nb-Ta ratios. Especially the REE are not fractionated within zoned grains and chondrite-normalized REE patterns remain parallel to each other (MELCHER et al., 2014). Wodginite and tapiolite are frequently intergrown with columbite-tantalite, sometimes resembling exsolutions, and in other cases displaying replacement textures.

Mineral chemistry

The chemical composition of Nb-Ta oxides in pegmatites and rare-element granites is characterised by a strong variability (MELCHER et al., 2014). However, major as well as trace elements show regional characteristics that, in many cases, allow for the distinction of ore provinces based on the composition of a representative number of grains. The major element variations in columbite-tantalite, tapiolite, wodginite and ixiolite reflect differentiation of, and fractional crystallization from melts. The degree and type of the variation of trace element concentration in Nb-Ta oxides is complex and depends on multiple factors, including crystal-chemical parameters (e.g., ion radius, charge), melt chemistry (e.g., presence of fluxing elements), internal differentiation of the melt, reaction with host rocks, and probably melt source characteristics. All these factors are superimposed on each other and result in characteristic trace element signatures for Nb-Ta oxides from different ore provinces.
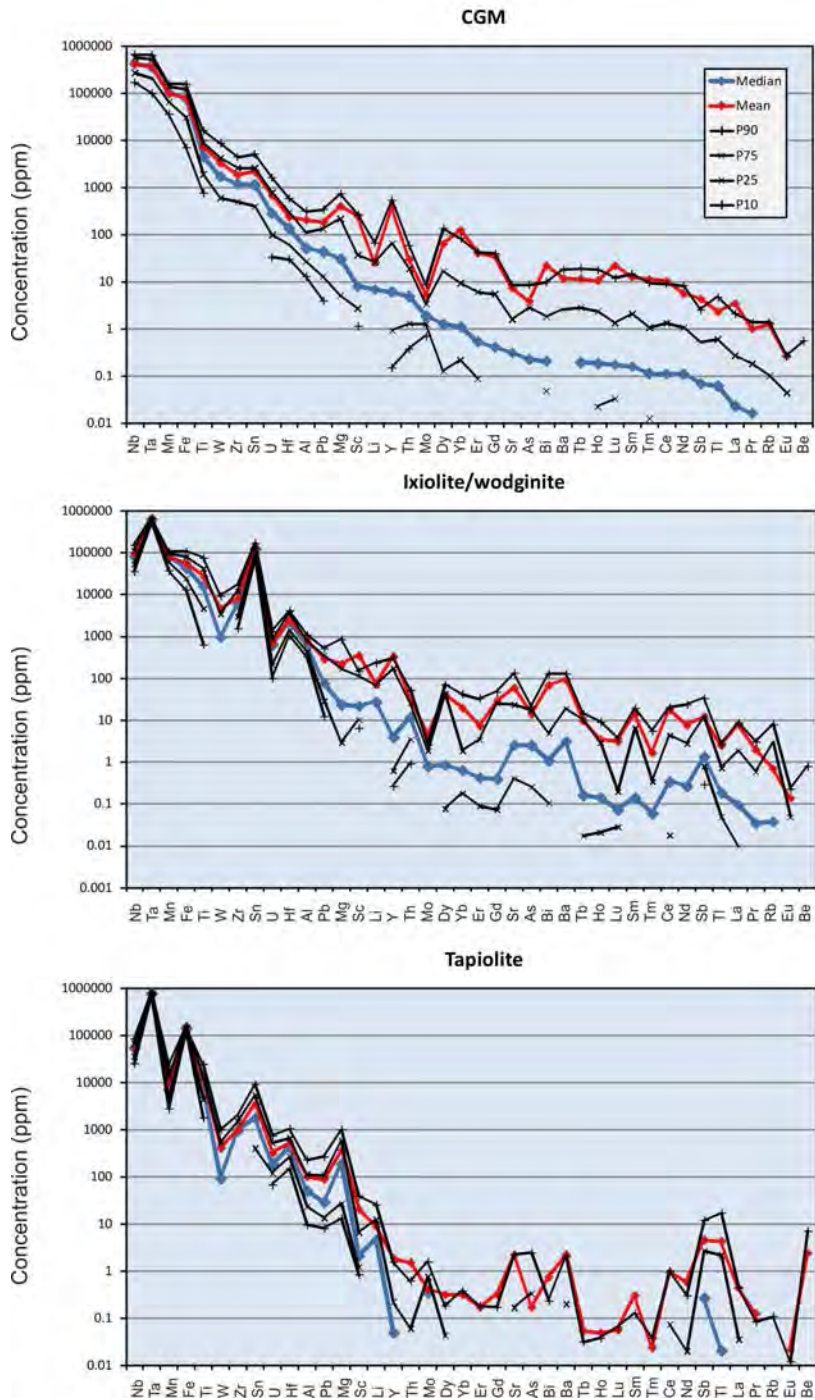
20

Fig. 2
Concentration levels of major and trace elements in columbite-tantalite group minerals (CGM), ixiolite/wodginite and tapiolite, arranged in decreasing order of abundance in CGM. Percentile values indicate ranges for 50 % (P75, P25) and 80 % of the data (P90, P10). Note that element order is the same for the three mineral groups.

About 15,000 electron microprobe and ca. 10,000 LA-ICP-MS datasets from rare element pegmatite and rare metal granite deposits ranging in age from the Archean to the Mesozoic and covering all continents except Antarctica were evaluated and demonstrate variations over two to four orders of magnitude for most trace elements (MELCHER et al., 2014 and in prep.). The compositionally most important minor elements in columbite-tantalite are Ti, W, Zr and, Sn (Median for the dataset is > 1000 ppm), followed by U, Hf (100-500 ppm), Al, Mg, Pb (10-100 ppm), Sc, Li, Mo, Y, Th and, Tl (1-10 ppm). The median concentrations of the REE, As, Sb, Bi, and Sr are below 2 ppm, and concentrations of Be, Rb and Ba in CGM are below the detection limit of the LA-ICP-MS method (Fig. 2).

Compared to columbite-tantalite, tapiolite has a rather invariable major element composition close to $[FeTa_2O_6]$. The major elements range from 9.3-16.5 wt.% for FeO, < 3.8 wt.% for MnO, < 14 wt.% for Nb_2O_5 and 61-88 wt.% for Ta_2O_5 for the data set. The maximum #Mn value is close to 25, and the lowest #Ta is close to 74. Maximum and median concentrations of the minor elements are: TiO_2 (12.7 wt.%, 0.80 wt.%); SnO_2 (5.4 wt.%, 0.18 wt.%); WO_3 (1.1 wt.%, 0.01 wt.%), respectively. Trace elements that are frequently detected by LA-ICP-MS include (in ppm; minimum – maximum; median): Li (< 1-140; 4.6); Mg (< 1-4500; 189); Sc (< 1-1100; 2.2); Y (< 1-180; 0.05); Zr (23-16500; 902); Hf (12-4000; 416); U (1-4500; 187); Pb (1-900; 29), respectively (Fig. 2). Tapiolite does not accommodate significant amounts of trivalent cations (Al, As, Sb, Bi, and REE).

The chemical composition of wodginite-ixiolite is highly variable. Manganese-Fe substitution is complete (Median #Mn = 66), whereas #Ta commonly ranges from 65 to 95. The SnO_2 concentrations in phases classified as wodginite-ixiolite range from 0.1 to 33 wt.%, with an average and median of 12 wt.%. The concentrations of TiO_2 (up to 21 wt.%; median 1.60 wt.%), WO_3 (median 0.10 wt.%), ZrO_2 (up to 10 wt.%; median 0.59 wt.%) and Hf (up to 8500 ppm; median 2300 ppm) are often significant, with average concentration levels commonly higher than in columbite-tantalite and tapiolite. Zr/Hf ratios in wodginite are lower (1 to 4) than in coexisting columbite-tantalite (6 to 13). Trace elements that may be present in significant concentrations in wodginite-ixiolite include Li (up to 0.9 wt.% in lithiowodginite, up to 1100 ppm in ordinary wodginite-ixiolite; median 27 ppm), Mg (up to 2200 ppm; median 24 ppm), Sc (up to 1.7 wt.%; median 22 ppm), Th (up to 825 ppm; median 12 ppm), U (up to 6743 ppm; median 633 ppm), As (up to 1200 ppm), Sb (up to 300 ppm) and Bi (up to 3200 ppm) (Fig. 2). Considering Goldschmidt´s rules, most trace elements are likely incorporated by simple or heterovalent substitution into the columbite structure (Fig. 3). Lead is continuously produced by radioactive decay of U and Th. Unusually large ions such as Rb, Sr, Ba, Bi, U, Th and small ions such as Be, Al and As should not be accomodated in the columbite structure. The positive detection of such "unlikely" elements by EPMA and LA-ICP-MS might be explained by the accidental analysis of finely dispersed silicates in the analysed sample volume, e.g., introducing Al, Rb, Sr and probably Be. Nevertheless, the absence of visible contaminants on the μm-scale in most of the analysed grains, and correlations with major and minor elements, indicate that elements plotting outside of the limits calculated from Goldschmidt´s rules may be incorporated in trace amounts in the structure of columbite-tantalite.

The incorporation of minor elements (Ti, Fe^{3+}, Sn) in the cation sites of the columbite structure has been well established (ERCIT, 1994). A rutile-type substitution is responsible for Ti in the columbite structure ($A^{2+}B^{5+}_2Ti^{4+}_{-3}$). Hexavalent cations such as W may enter the structure via a wolframite-type substitution ($B^{5+}_4Fe^{2+}_{-1}W^{6+}_{-3}$).
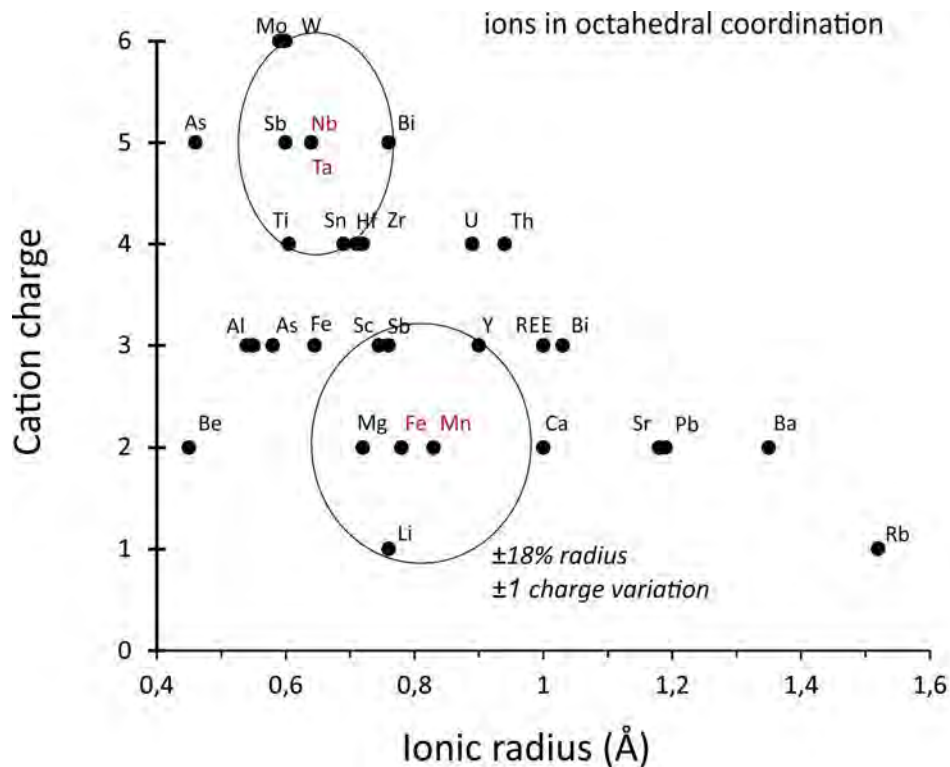
Fig. 3
Ionic radius versus cation charge for ions in octahedral coordination that were detected by in-situ analysis of columbite-tantalite grains.

An alternative is the substitution of W^{6+} into the B site ($B^{5+}_3 M^{3+}_{-1} W^{6+}_{-2}$, where M = metal, e.g., Fe^{3+}). ERCIT (1994) described the effects of Fe-Mn and Nb-Ta fractionation on the concentrations of Mg, Ca, Sc, REE, tetravalent cations and W in NYF-family pegmatites. For Zr and Hf, heterovalent substitutions in both A and B sites such as $(Nb,Ta)^{5+}_2 (Fe,Mn)_2^{+1}(Zr,Hf)^{4+}_{-3}$ have been discussed (ČERNÝ et al., 2007), implying the existence of a solid solution towards srilankite (ixiolite-structured ZrO_2). Scandium incorporation is favoured in highly disordered structures via the euxenite-type substitution $A^{2+} B^{5+} M^{3+}_{-1} Ti^{4+}_{-1}$ (WISE et al., 1998); the same substitution scheme may apply to REE+Y. REE can also enter the structure via the coupled substitution $A^{2+}_2 B^{5+}(REE+Fe)^{3+}_{-3}$, eventually leading to samarskite ABO_4, where A = REE+Y, Ca, U, Fe; B = Ta, Nb, Ti (WARNER & EWING, 1993).

Pegmatites of Paleozoic age hosting Nb-Ta oxides in Europe are used to illustrate the heterogeneity of columbite-tantalite compositions between different pegmatite provinces (Fig. 4). Each diagram illustrates the median and the variation around it for populations of several grains from a number of pegmatites in each province. Note the variation in absolute concentration levels of Li, Mg, Y and the REE and different shapes of chondrite-normalized REE distribution curves. In Permian pegmatites within the Austroalpine basement units of the Eastern Alps, columbite-tantalites have lower Sc, Y and REE and higher Mg concentrations than in the Hagendorf and Central Iberian Provinces.
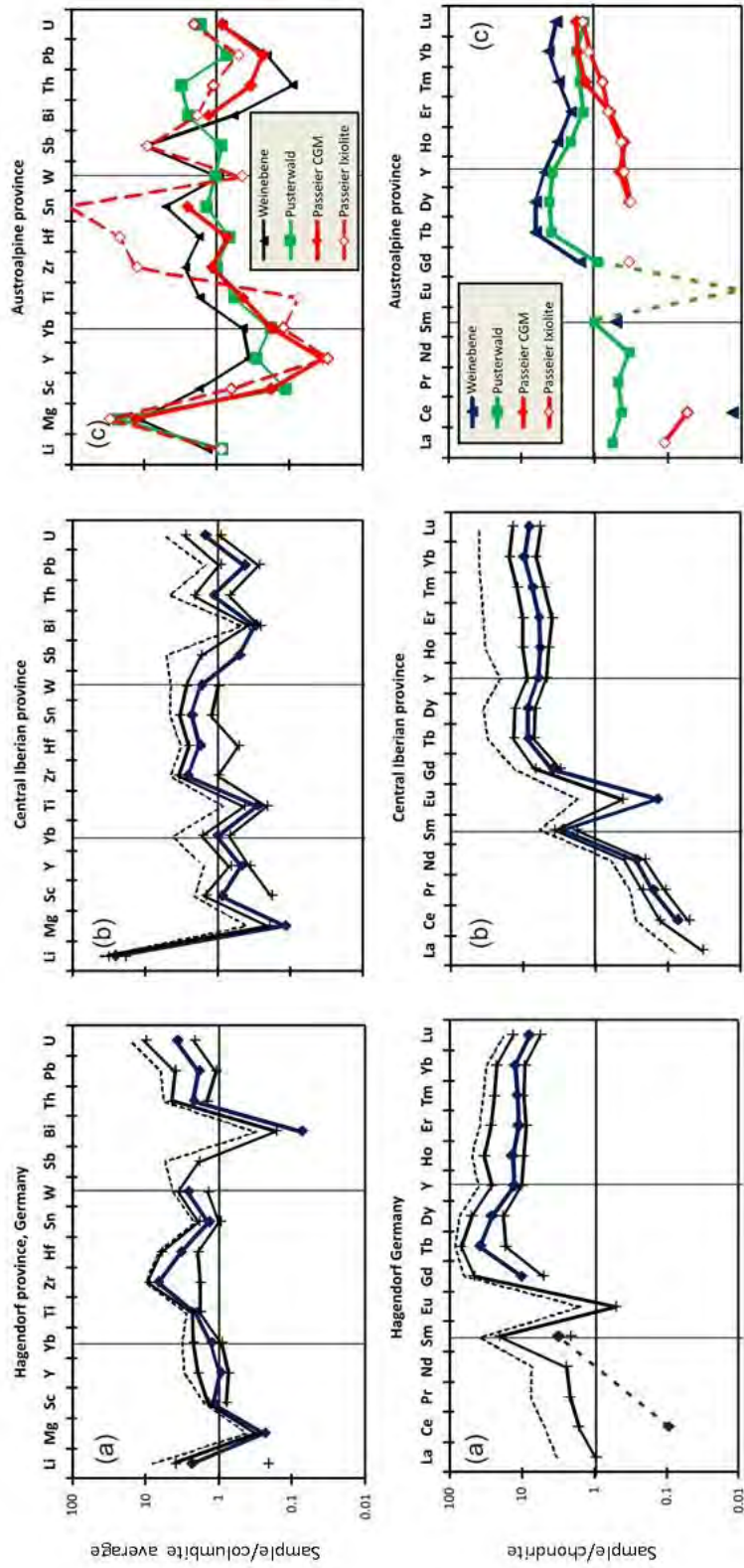
Fig. 4

Trace element concentrations in columbite-tantalite and ixiolite from Paleozoic pegmatites in Europe. Upper diagrams are normalized to an average columbite-tantalite composition (MELCHER et al., 2014); lower diagrams are normalized to C1 chondrite. Median (thick blue lines), P25 and P75 (thick black lines) and P90 (stippled lines) are given in (a) and (b); median values are given in (c).

Nb-Ta oxides on a global scale

Following a comprehensive study of Nb-Ta oxides from pegmatite and granite deposits with a focus on Africa (MELCHER et al., 2014) and examples from other continents (MELCHER etal., in prep.), the following conclusions are made:

(1) Pegmatite-hosted Ta-(Nb-Sn) mineralization covers a time span from the Archean to the Cenozoic. The most important pegmatites and pegmatite fields investigated include (Fig. 1):

- Archean: Man Shield (Sierra Leone; 2.85 Ga); Zimbabwe and Kaapvaal Cratons, Bikita (Zimbabwe, South Africa; 2.6 Ga); Congo Craton (2.49 Ga); Tanco (Manitoba, Canada; 2.64 Ga); Wodgina (Western Australia; 2.9 Ga); Greenbushes (Western Australia, 2.53 Ga); Kolmozero (Kola, Russia; 2.52 Ga)
- Paleoproterozoic: Birimian (Ghana; 2.08 Ga); NE Congo Craton (1.9-2.05 Ga); Volta Grande (Brazil; 2.0 Ga); Guyana Shield (2.0 Ga); Black Hills (USA; 1.7 Ga); Finish Lapland (1.8-2.05 Ga); Somero-Tammela (Finland; 1.8 Ga); Karelia (Russia; 1.65-1.86 Ga); Bastar-Malkangiri Belt (India; 2.1 Ga)
- Mesoproterozoic: Eastern Colombia (1.27-1.45 Ga)
- Early Neoproterozoic: Kibara Belt (DR Congo, Rwanda, Burundi, Uganda; 0.9-1.0 Ga); Kamativi Belt (Zimbabwe; 1.0 Ga); Sveconorwegian Province (Sweden, Norway; 1.0 Ga); South Platte District (USA; 1.0 Ga); Orange River Belt/Tantalite Valley (South Africa, Namibia; 0.9-1.0 Ga); Grenville Belt (Canada; 1.0 Ga)
- Late Neoproterozoic to Early Paleozoic ("Pan-African"): Kenticha (Ethiopia; 0.53 Ga); Alto Ligonha Province (Mozambique; 0.44-0.48 Ga); Madagascar (0.5 Ga); Damara Belt (Namibia; 0.5 Ga); Older Granites (Nigeria; 0.45-0.56 Ga); Eastern Brazilian Pegmatite Province (0.5 Ga); Borborema Province (Brazil; 0.5 Ga)
- Paleozoic: Pampean Province (Argentina; 0.45 Ga); Central Iberian Province (Portugal, Spain; 0.2-0.3 Ga); Hagendorf Province (Germany; 0.3 Ga); Austroalpine Province (Austria, Italy; 0.2-0.3 Ga); Appalachian Belt (0.27-0.39 Ga); Kalba (Kazakhstan; 0.25 Ga)
- Mesozoic and Cenozoic: Thailand, Malaysia and Burma (22-149 Ma); Ishikawa (Japan; 110 Ma); Malkhany Field (Transbaikalia, Russia; 125 Ma)

(2) Granite-hosted mineralization covers a time span from the Paleoproterozoic to the Cenozoic, with most examples studied being Paleozoic or younger. Specimen from the following areas have been investigated (Fig. 1): Pitinga (Brazil; 1.82 Ga); Eastern Desert (Egypt; 0.5-0.6 Ga); Polar Urals (Russia; 0.6 to 0.25 Ga?); Ilmen (Russia; 0.24-0.29 Ga); Jos (Nigeria; 150-210 Ma); Yichun (China; 178 Ma); Ulug Tanzek (Siberia, Russia; 209-219 Ma); Orlovka (Transbaikalia, Russia; 143 Ma).

(3) Carbonatite-hosted mineralization was investigated from the Paleozoic Upper Fir carbonatite (Canada; 0.33 Ga; Fig. 1).

(4) Minerals of the columbite-tantalite group are the most abundant Ta-Nb minerals in all pegmatite provinces. However, their compositions are extremely variable. The evaluation of the mineral chemical data of columbite-tantalite demonstrates that two major groups exist, which may be related to the LCT and NYF families, and a third group, which may be related to a mixed LCT-NYF type (ČERNÝ & ERCIT, 2005).

- LCT family: In individual pegmatites and pegmatite provinces, columbite-tantalites are characterized by Mn-rich compositions (50% > #Mn 60), low to intermediate REE (5-500 ppm), intermediate to high Zr/Hf (6-11) and high U/Th ratios (> 20). REE patterns are frequently $MREE_N$-dominated. Typically enriched minor and trace elements are Li, Zr, Hf, Sn and Sb, less frequently also Mg, Bi and U. Other elements such as Sc, Y, the REE, W and Th are commonly depleted compared to the global average

columbite-tantalite composition. In some of the LCT family pegmatites, significant concentrations of As, Be and Ba were measured. Columbite chemistry can also be used to infer the prevailing pegmatite type according to the ČERNÝ & ERCIT (2005) classification: beryl type (#Mn ca. 20; e.g., Hagendorf); spodumene-albite and complex spodumene types (#Mn = 30-40; e.g., Austroalpine, Kamativi, Bastar, Back Hills, Greenbushes); complex types with spodumene (#Mn = 60; e.g., Kibara, Kolmozero); complex types, often with amblygonite, lepidolite, petalite, elbaite (#Mn >80; e.g. Volta Grande, Bikita, Tanco, Alto Ligonha, Kenticha, Birimian, Borborema, Tantalite Valley, Wodgina, Kalba, Iberian Province, Damara).

- NYF family: Columbite-tantalite minerals in pegmatites are Fe-rich (92% <#Mn 40) or intermediate Fe-Mn columbite and always have Nb > Ta. REE concentrations are intermediate to high (100-8000 ppm), and U/Th ratios are low (< 60). Zr/Hf ratios scatter from 4 to 18. REE patterns are dominated by both, the $MREE_N$ and $HREE_N$. Scandium, Y, HREE, W and Th are abundant trace elements, whereas Li, Sn, Sb and U are usually lower than in LCT-family pegmatites.

  In some rare metal granites that chemically resemble NYF family pegmatites, CGM are Fe- or Mn-rich or both, but always have Nb > Ta. REE are high (300-6000 ppm), and U/Th is very low to low (< 13). Zr/Hf is either very low (< 4 = highly fractionated; Orlovka, Egypt) or very high (> 13 = less fractionated; Polar Urals, Jos, Altai), thus defining two extreme subtypes of the "granite" NYF family. Molybdenum is commonly present in elevated concentrations in the NYF granite group compared to NYF and LCT pegmatites.

- Columbite-tantalite in mixed LCT-NYF family pegmatites is either Fe-rich (Guyana, Appalachians, Svecofennian) or Mn-rich (Alto Ligonha, Malkan); their #Ta values are within the range typical of LCT pegmatites, but their REE concentrations are higher and U/Th is lower (ca. 10). Minor and trace element patterns in columbite-tantalite resemble NYF-types regarding their high Sc, Y, REE and W concentrations, and LCT-types in their Sb, Zr, Hf and Mg values.

- Carbonatite: Columbite-tantalites from the Upper Fir carbonatite are Fe- and Nb-dominated, with low REE (40 ppm) and extremely low U/Th (Md, 0.14), but display very high (suprachondritic) Zr/Hf (42). The columbite-tantalite group minerals could be classified as similar to a REE-poor NYF pegmatite system.

(5) Tapiolite is abundant in the Kibara Belt and the Congo Craton and is of minor importance in the Kamativi and Damara Belts and in Nigeria. Major occurrences are recorded from Greenbushes, Marowgne (Guyana), Finish Lapland, Bastar and Borborema,

(6) Wodginite and ixiolite are generally less abundant Sn-, Ti-, W- and Li-rich minerals, but are quite common constituents in pegmatites of Zimbabwe and are locally abundant in the Kibara Belt, Older Granites of Nigeria, Damara Belt, Tanco, Wodgina, Greenbushes, Volta Grande, Bastar, Black Hills, Eastern Colombia, the Austroalpine Province (e.g. Wölz) and in rare-metal granites of the Eastern Desert.

(7) All provinces carry microlite and other pyrochlore-supergroup minerals. However, "primary" microlite is mainly restricted to Alto Ligonha, the Eastern Desert of Egypt and, Orlovka (Russia). Pb-rich pyrochlore dominates at Pitinga, Brazil, and U-bearing pyrochlore in the Upper Fir carbonatite.

(8) Accumulations of rare Ta-Nb phases occur in some provinces (e.g., bismutotantalite at Alto Ligonha; stibiotantalite at Lema, Nigeria, Kola Peninsula and Greenbushes, Australia; fersmite in the Lachtal pegmatites (Austroalpine Perovince); foordite at Kubitaka, Kibara Belt; and an extremely unusual assemblage of simpsonite, cesplumtantite, lithiowodginite and Ba-rich micro-lite at Mumba, Kibara Belt).

(9) U-Y-REE-rich Ta-Nb minerals are abundant only in NYF-family pegmatites and, thus, are rare in the studied African deposits. However, significant proportions of these minerals were encountered in the Alto Ligonha Province, Jos Plateau, at Lutenga in the Kibara Belt and at Orlovka (Transbaikalia).

(10) Nb-Ta-rich rutile is the major Ta-Nb phase in placer deposits of the Man Shield, whereas Ta-rich rutile occurs in some areas within the Kibara Belt.

(11) Cassiterite is present in large quantities in pegmatites of the Kibara Belt, Kamativi Belt, Congo Craton, Damara Belt, Older Granites of Nigeria and in mineralised granites in the Eastern Desert and Jos Plateau, as well as at Tanco, Wodgina, Greenbushes, Volta Grande and many others. Its occurrence coincides partly with Sn-rich Nb-Ta oxides (wodginite, ixiolite, foordite) and with elevated Sn concentrations in columbite-tantalite. On the other hand, some provinces (e.g., Alto Ligonha, Sveconorwegian, Hagendorf) and deposits like Kenticha, Tantalite Valley and Kolmozero are virtually cassiterite-free.

Most LCT-family pegmatites are post-orogenic and post-tectonic with respect to a regional metamorphic event. The characteristic trace element associations found in Nb-Ta oxides from the LCT pegmatites may stem from the presence of a thick package of metasedimentary rocks underlying the intrusion. Some of the observed variations may be explained by contributions from felsic and mafic igneous rocks, old continental or oceanic crust, or from the upper mantle. The origin of the trace element distributions observed in the NYF and mixed LCT/NYF groups is more difficult to explain. The rare-metal granites of the Eastern Desert of Egypt were emplaced along late-orogenic structures into juvenile Neoproterozoic rocks including an early Pan-African subduction complex. The complex geochemical and mineralogical character of the pegmatites in the Alto Ligonha Province points to a heterogeneous source and a long-lived magma-generation process postdating typical post-collisional A-type magmatism. Despite textural complexities, such as complex zoning patterns and multiple mineralisation stages, the chemical compositions of columbite-tantalite, tapiolite and wodginite-ixiolite from rare-metal granite and rare-element pegmatite provinces indicate that they are cogenetic and reflect specific source characteristics that may be used to determine their origin.

References

ATENCIO, D., DE ANDRADE, M.B., CHRISTY, A.G., GIERE, R. & KARTASHEV, P.M. (2010): The pyrochlore supergroup of minerals: nomenclature. - Can. Mineral., 48, 673-698.

ČERNÝ, P. (1991): Rare-element granite pegmatites. II. Regional to global environments and petrogenesis. - Geoscience Canada, 18, 68-81.

ČERNÝ, P. & ERCIT, T.S. (1989): Mineralogy of niobium and tantalum: crystal chemical relationships, paragenetic aspects and their economic implications. - In: MÖLLER, p. et al. (eds.), Lanthanides, Tantalum and Niobium. Springer Verlag, Berlin, Germany, 27-79.

ČERNÝ, P., ERCIT, T.S. (2005): The classification of granitic pegmatites revisited. - Can. Mineral., 43, 2005-2026.

ČERNÝ, P., ERCIT, T.S., SMEDS, S.-A., GROAT, L.A. & CHAPMAN, R. (2007): Zirconium and hafnium in minerals of the columbite and wodginite groups from granitic pegmatites. - Can. Mineral., 45, 185-202.

ERCIT, T.S. (1994): The geochemistry and crystal chemistry of columbite-group minerals from granitic pegmatites, southwestern Grenville province, Canadian Shield. - Can. Mineral., 32, 421-438.

GÄBLER, H.-E., MELCHER, F. GRAUPNER, T., BAHR, A., SITNIKOVA, M., HENJES-KUNST, F., OBERTHÜR, T., BRÄTZ, H. & GERDES, A. (2011): Speeding up the analytical workflow for coltan fingerprinting by an integrated mineral liberation analysis/LA-ICP-MS approach. - Geostand. Geoanal. Res., 35, 431-448.

LAHTI, S.I. (1987): Zoning in columbite-tantalite crystals from the granitic pegmatites of the Eräjärvi area, southern Finland. – Geochim. Cosmochim. Acta, 51, 509-517.

MELCHER, F., SITNIKOVA, M.A., GRAUPNER, T., MARTIN, N., OBERTHÜR, T., HENJES-KUNST, F., GÄBLER, E., GERDES, A., BRÄTZ, H., DAVIS, D.W. & DEWAELE, S. (2008). Fingerprinting of conflict minerals: columbite-tantalite ("coltan") ores. - SGA News, 23, 1-14.

MELCHER, F., GRAUPNER, T., SITNIKOVA, M., HENJES-KUNST, F., OBERTHÜR, T., GÄBLER, H.-E., BAHR, A., GERDES, A., BRÄTZ, H. & RANTITSCH, G. (2009): Ein Herkunftsnachweis für Niob-Tantalerze am Beispiel afrikanischer Selten-Element-Pegmatite. – Mitt. Österr. Mineral. Ges., 155, 231-267.

MELCHER, F., GRAUPNER, T., GÄBLER, H.-E., SITNIKOVA, M., HENJES-KUNST, F., OBERTHÜR, T., GERDES, A. & DEWAELE, S. (2014): Tantalum-(niobium-tin) mineralization in African pegmatites and rare metal granites: constraints from Ta-Nb oxide mineralogy, geochemistry and U-Pb geochronology. - Ore Geology Reviews, doi: 10.1016/j.oregeorev.2013.09.003

MELCHER, F., GRAUPNER, T., GÄBLER, H.-E., SITNIKOVA, M., HENJES-KUNST, F., OBERTHÜR, T., GERDES, A., BADANINA, E. & CHUDY, T. (in prep.): Mineralogical, chemical and temporal evolution of tantalum-(niobium-tin) mineralisation in some pegmatites, granites and carbonatites–examples from outside of Africa. - Ore Geology Reviews (in prep.)

REICHL, C., SCHATZ, M. & ZSAK, G. (2014): World Mining Data 2014, Volume 29. – Bundesministerium für Wissenschaft, Forschung und Wirtschaft, Wien, 251 pp.

TKACHEV, A. V. (2011): Evolution of metallogeny of granitic pegmatites associated with orogens throughout geological time. In: A. N. SIAL, BETTENCOURT, J.S., DE CAMPOS, C.P. & FERREIRA, V.P. (Eds.), Granite-related ore deposits, London, Geol. Soc. Spec. Publ., 350, pp. 7-23.

VARLAMOFF, N. (1972): Central and West African rare-metal granitic pegmatites, related aplites, quartz veins and mineral deposits. - Miner. Deposita, 7, 202-216.

WARNER, J. K. & EWING, R. C. (1993): Crystal chemistry of samarskite. - Am. Mineral., 78, 419-424.

WISE, M.A., ČERNÝ, P. & FALSTER, A.U. (1998): Scandium substitution in columbite-group minerals and ixiolite. - Can. Mineral., 36, 673-680.