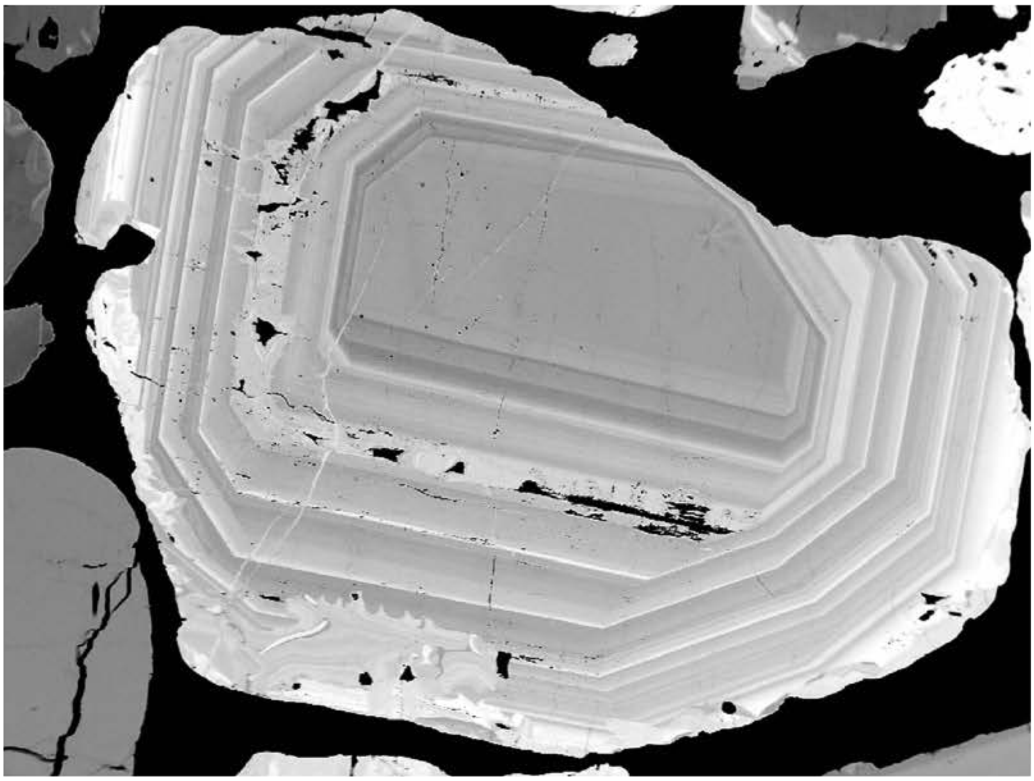
PEGMATITE

Erste Österreichische Arbeitstagung

Montanuniversität Leoben
11. April 2014

Zusammenfassung der Beiträge



Interne Zonierung eines Columbit-Kristalls aus einem Erzkonzentrat aus der DR Kongo, BSE Bild, Aufnahme F. Melcher

MITT.ÖSTERR.MINER.GES. 160 (2014)

PEGMATITE - ERSTE ÖSTERREICHISCHE ARBEITSTAGUNG

von

Johann G. Raith & Frank Melcher

Department Angewandte Geowissenschaften und Geophysik
Montanuniversität Leoben, Peter-Tunner-Straße 5, 8700 Leoben, Austria

Am 11. April 2014 fand an der Montanuniversität Leoben die 1. Arbeitstagung zum Thema Pegmatite statt. Die Veranstaltung wurde vom Department Angewandte Geowissenschaften und Geophysik (Lehrstuhl für Rohstoffmineralogie und Lehrstuhl für Geologie und Lagerstättenlehre) organisiert.

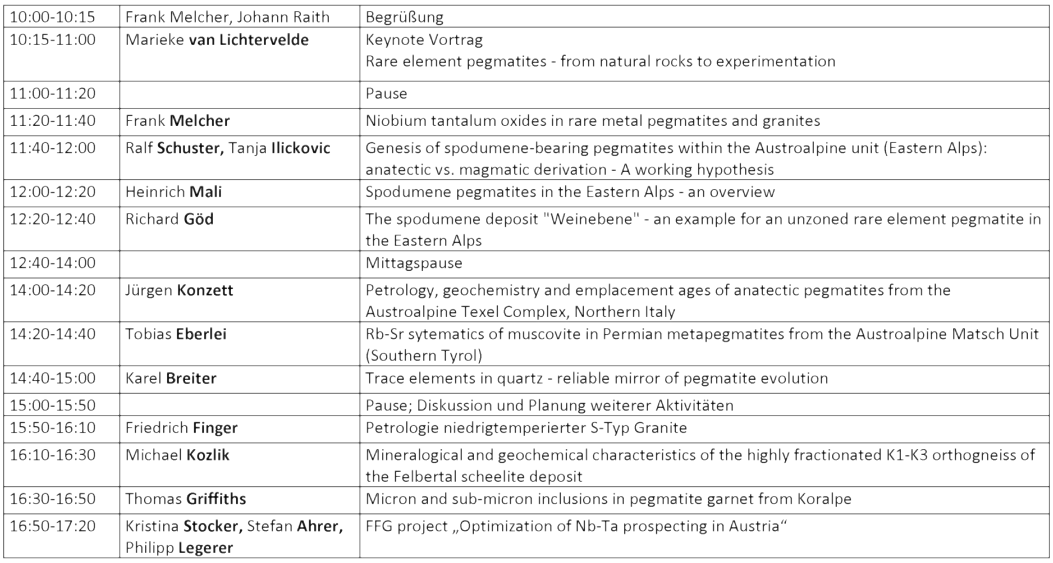
Pegmatite sind sowohl aus wirtschaftlichen als auch wissenschaftlichen Gesichtspunkten verstärkt in den Fokus der geowissenschaftlichen Forschung gerückt. Sie sind wichtige Ressourcen für Hochtechnologie-Metalle wie Li, Be, Ta, W, Sn etc. aber auch Industrieminerale und Edelsteine. Auch in Österreich gibt es in letzter Zeit wieder verstärkte Aktivitäten, pegmatitische Rohstoffvorkommen zu explorieren bzw. deren Rohstoff-Potenzial neu zu bewerten.

Aus wissenschaftlicher Sicht sind die Bildungsprozesse von Pegmatiten nach wie vor unzureichend verstanden. Klassischen genetischen Modellen, die von einer extremen Fraktionierung granitischer Schmelzen ausgehen, stehen alternative Modelle einer partiellen Aufschmelzung bei hochgradiger Metamorphose gegenüber. Gerade die Pegmatite in den Ostalpen stellen ein Musterbeispiel für dieses Paradoxon dar.

Diese Arbeitstagung sollte Interessierte, die sich mit diversen Aspekten von Pegmatiten beschäftigen, zu einem Informationsaustausch zusammenbringen. Die TeilnehmerInnen präsentierten dazu Kurzvorträge. Ein einleitender Keynote Vortrag von Marieke van Lichtervelde, Toulouse, gab einen Überblick über Seltenelementpegmatite, von Geländeaspekten bis zu experimentellen Studien.

Die weiteren Beiträge befassten sich mit Pegmatiten and Graniten als Rohstoffquellen für die Sondermetalle und kritischen Rohstoffe Lithium, Niob, Tantal und Wolfram, die Mineralogie von Pegmatiten, Spodumenpegmatite und Nb-Ta-führende Pegmatite in den Ostalpen und deren Genese, Optimierung von Prospektionsmethoden für Niob und Tantal usw. Für Details sei auf das Programm verwiesen (Tabelle 1).

Von einigen Vorträgen sind nachfolgend Zusammenfassungen veröffentlicht. Die Organisatoren bedanken sich bei der Österreichischen Mineralogischen Gesellschaft (ÖMG) für die Möglichkeit diese Zusammenfassungen in ihren Mitteilungen zu publizieren und für die finanzielle Unterstützung dieser Veranstaltung.



10:00-10:15	Frank Melcher, Johann Raith	Begrüßung
10:15-11:00	Marieke **van Lichtervelde**	Keynote Vortrag Rare element pegmatites - from natural rocks to experimentation
11:00-11:20		Pause
11:20-11:40	Frank **Melcher**	Niobium tantalum oxides in rare metal pegmatites and granites
11:40-12:00	Ralf **Schuster,** Tanja **Ilickovic**	Genesis of spodumene-bearing pegmatites within the Austroalpine unit (Eastern Alps): anatectic vs. magmatic derivation - A working hypothesis
12:00-12:20	Heinrich **Mali**	Spodumene pegmatites in the Eastern Alps - an overview
12:20-12:40	Richard **Göd**	The spodumene deposit "Weinebene" - an example for an unzoned rare element pegmatite in the Eastern Alps
12:40-14:00		Mittagspause
14:00-14:20	Jürgen **Konzett**	Petrology, geochemistry and emplacement ages of anatectic pegmatites from the Austroalpine Texel Complex, Northern Italy
14:20-14:40	Tobias **Eberlei**	Rb-Sr sytematics of muscovite in Permian metapegmatites from the Austroalpine Matsch Unit (Southern Tyrol)
14:40-15:00	Karel **Breiter**	Trace elements in quartz - reliable mirror of pegmatite evolution
15:00-15:50		Pause; Diskussion und Planung weiterer Aktivitäten
15:50-16:10	Friedrich **Finger**	Petrologie niedrigtemperierter S-Typ Granite
16:10-16:30	Michael **Kozlik**	Mineralogical and geochemical characteristics of the highly fractionated K1-K3 orthogneiss of the Felbertal scheelite deposit
16:30-16:50	Thomas **Griffiths**	Micron and sub-micron inclusions in pegmatite garnet from Koralpe
16:50-17:20	Kristina **Stocker,** Stefan **Ahrer,** Philipp **Legerer**	FFG project „Optimization of Nb-Ta prospecting in Austria“

Tabelle 1
Wissenschaftliches Programm der 1. Pegmatit Arbeitstagung am 11. April 2014 an der Montanuniversität Leoben

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RARE-ELEMENT PEGMATITES - FROM NATURAL SYSTEMS TO THE EXPERIMENTAL LAB

by

Marieke Van Lichtervelde

Institute for Research and Development
Laboratoire Géosciences Environnement Toulouse, France

Rare-element pegmatites are sources of strategic metals used in the high-tech industry (tantalum in micro-capacitors, lithium in ion batteries, rare-earth elements in green technologies such as photovoltaic panels or wind turbines; see Linnen et al. 2012 for a review). Two main types of pegmatites can be distinguished: the Lithium-Cesium-Tantalum-bearing (LCT) pegmatites, which are peraluminous in composition and are generally emplaced in late to post-orogenic settings, and the Niobium-Yttrium-Fluorine (NYF) pegmatites, which are peralkaline and generally emplaced in anorogenic settings. The ASI (aluminosilicate index = Al/alkali ratio) and the flux content (Li-F-B-P) are therefore important compositional parameters influencing rare-metal enrichment in pegmatitic melts. In particular, fluxes considerably lower melt viscosity and solidus temperature, allowing pegmatitic melts to travel kilometres away from their source before crystallisation starts.

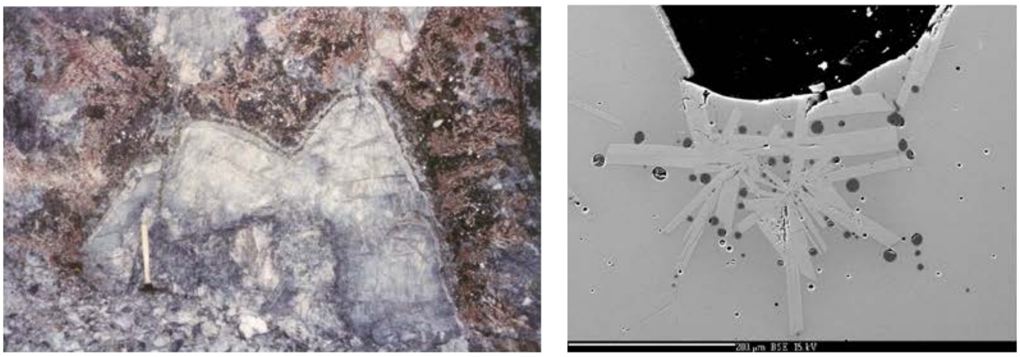

Fig. 1
left: giant K-Feldspar surrounded by red dendritic amblygonite in the Tanco pegmatite; right: Albite laths surrounded by bubbles of immiscible melt (dark grey) in an experiment at 600°C-200MPa. Both pictures illustrate boundary layer processes with incompatible components being concentrated at the crystallization front of rapidly growing crystals.

The most fractionated pegmatites are characterised by large (kilometre scale) dykes, complex internal structures, giant crystal size, and complex mineralogical textures and assemblages. These characteristics are the result of rapid, disequilibrium crystallisation from undercooled, flux-rich melts. Fluxes decrease the nucleation rates by preventing the formation of crystal nuclei, and increase the growing rates by promoting high element diffusivities. Therefore, flux-rich pegmatitic melts may keep low viscosity down to low temperatures (300-400°C), and aqueous fluids may not be the principal controller of pegmatite evolution like stated in old models (Jahns and Burnham 1969). In newly-invoked models of pegmatite formation (London 2009 and references therein), elevated flux concentrations enable extremely high water solubilities in the melts, therefore promoting low melt viscosity, high element mobility and low solidus temperatures. By inhibiting nucleation, they enable the melt to be cooled down to temperatures well below its solidus, a process known as supercooling or undercooling. Such melts can form at the crystallisation front of the consolidating pegmatite through the exclusion of incompatible elements, a process known as boundary layer process. Boundary layers may also concentrate rare metals as their solubilities considerably increase with flux contents and alkali/alumina ratios.

In complement to investigating individual pegmatites and their petrography/mineralogy, experimentation may bring relevant information to pegmatite formation processes, such as viscosity and solubility measurements, crystallisation kinetics or interactions between metals. Our experimental studies in Hanover (Bartels et al. 2010, Fiege et al. 2011, Van Lichtervelde et al. 2010) using flux-rich water-saturated pegmatitic melts at 200 MPa and temperatures ranging between 700 and 1200°C, demonstrate that the ASI (Al/alkali) ratio is more important than any other parameter (flux content, temperature, fO_2) in influencing rare metal solubilities. An interesting observation comes from the comparison of the zircon and manganotantalite solubility products where zircon and manganotantalite are dissolved alone or in association in a pegmatitic melt. Solubility products are systematically lower where both minerals are dissolved together compared to where they are dissolved alone. This solubility difference is more strongly marked in peralkaline melts than in peraluminous melts. This not only shows that Zr and Ta metals compete for the same structural sites in the melt, but also that this competition is in favor of Ta over Zr in peraluminous conditions and in favor of Zr over Ta in peralkaline conditions (Van Lichtervelde et al. 2011). These results may explain why Zr mineralisations are generally associated with peralkaline systems whereas Ta mineralisations are associated with peraluminous pegmatites, and show the importance of investigating metal interactions in order to understand rare-metal enrichment processes in granitic melts.

In flux-rich pegmatitic melts, crystallization experiments successfully result in the formation of rare metal-bearing minerals such as Nb-Ta oxides, zircon or rutile (Van Lichtervelde et al. 2011). With various degrees of supercooling imposed to the experiment, one can reproduce the different textures observed in pegmatites: small undercooling rates (< 50°C) result in medium-grained equant crystals representative of granitic textures, whereas large undercooling rates (> 200°C) result in coarse-grained dendritic crystals typical of some pegmatitic textures (Fig. 2). Immiscibility processes were also observed by Bartels (2012) in dehydrated conditions (Fig. 1, right), at the crystallization front of albite crystals. This is evidence that many complex interrelated processes are involved in pegmatite formation, which still deserve further investigation, using both natural systems and experimentation.

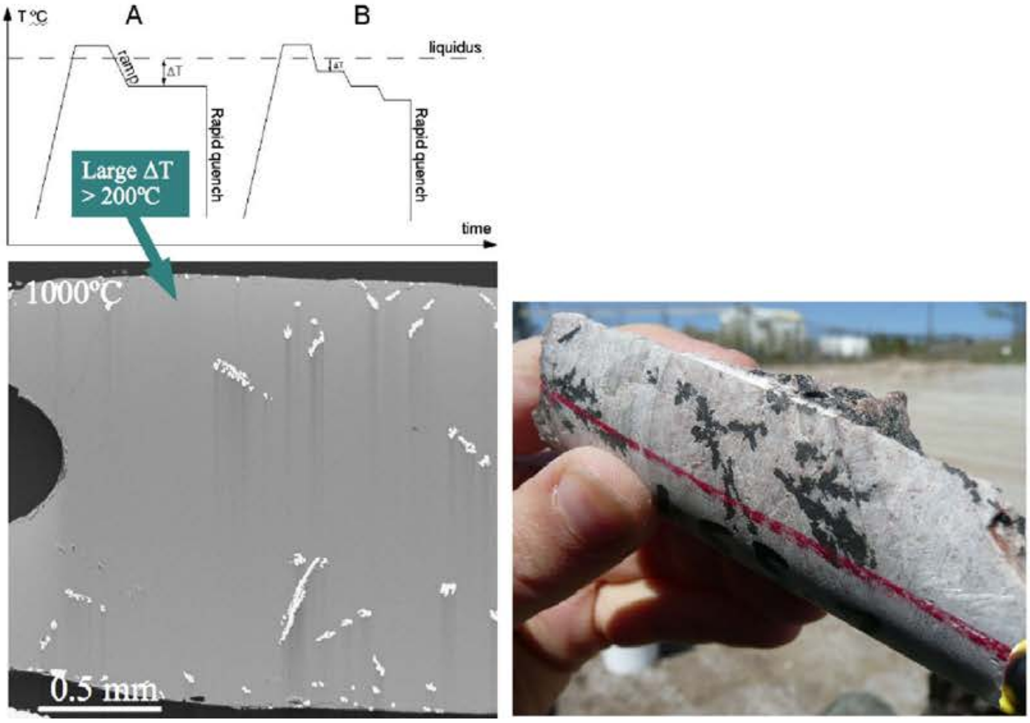

Fig. 2
Crystallisation experiment reproducing dendritic textures for manganotantalite using large supercooling. Such textures are comparable to dendritic Nb-Ta oxides observed in the Tanco pegmatite (right).

References

BARTELS, A. (2012): The influence of fluorine, boron, phosphorus and lithium on the viscosity of hydrous pegmatitic melts, PhD thesis, Hannover.

BARTELS, A., HOLTZ, F. & LINNEN, R. L. (2010);: Solubility of manganotantalite and manganocolumbite in -pegmatitic melts. Am. Mineral. 95, 537-544.

FIEGE, A., KIRCHNER, C., HOLTZ, F., LINNEN, R.L. & DZIONY, W. (201): Influence of fluorine on the solubility of manganotantalite ($MnTa_2O_6$) and manganocolumbite ($MnNb_2O_6$) in granitic melts - An experimental study. Lithos, 122, 165-174.

JAHNS, R.H. & BURNHAM, C.W. (1969): Experimental studies of pegmatite genesis. I. A model for the derivation and crystallization of granitic pegmatites. Economic Geology, 64, 843-864.

LINNEN, R.L., VAN LICHTERVELDE, M. & ČERNÝ, P. (2012): Granitic pegmatites as sources of strategic metals. Elements, 8, 275-280.

LONDON, D. (2009): The origin of primary textures in granitic pegmatites. Can. Mineral., 47, 697-724.

VAN LICHTERVELDE, M., HOLTZ, F., DZIONY, W., LUDWIG, T. & MEYER, H.-P. (2011): Incorporation mechanisms of Ta and Nb in zircon and implications for pegmatitic systems. American Mineralogist, 96, 1079-1089.

VAN LICHTERVELDE, M., HOLTZ, F. & HANCHAR, J.M. (2010): Solubility of manganotantalite, zircon and hafnon in highly-fluxed peralkaline to peraluminous pegmatitic melts. Contrib. Mineral. Petrol., 160, 17-32.

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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.

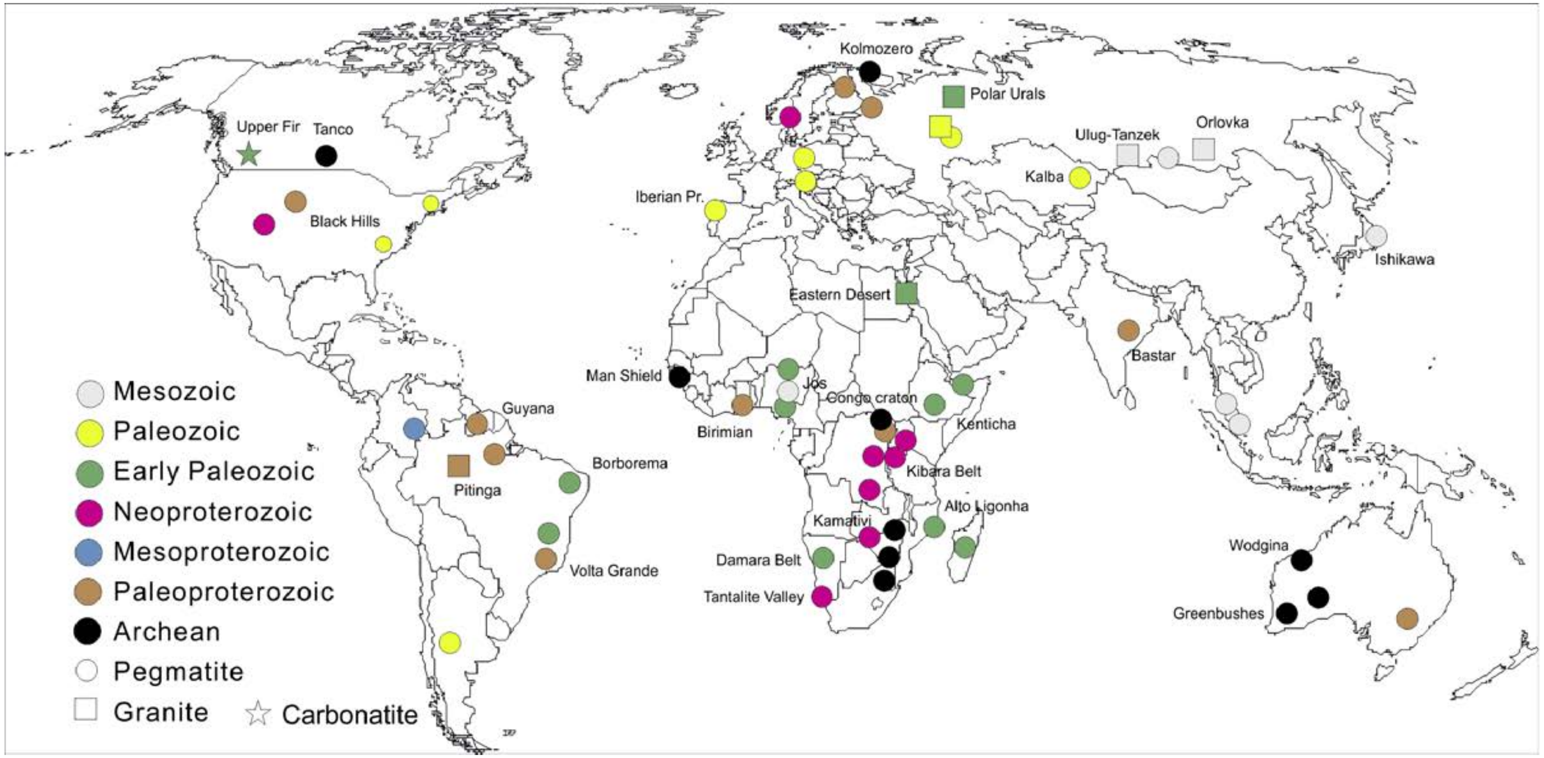

Fig. 1
Ta-(Nb-Sn) provinces investigated by the BGR

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.

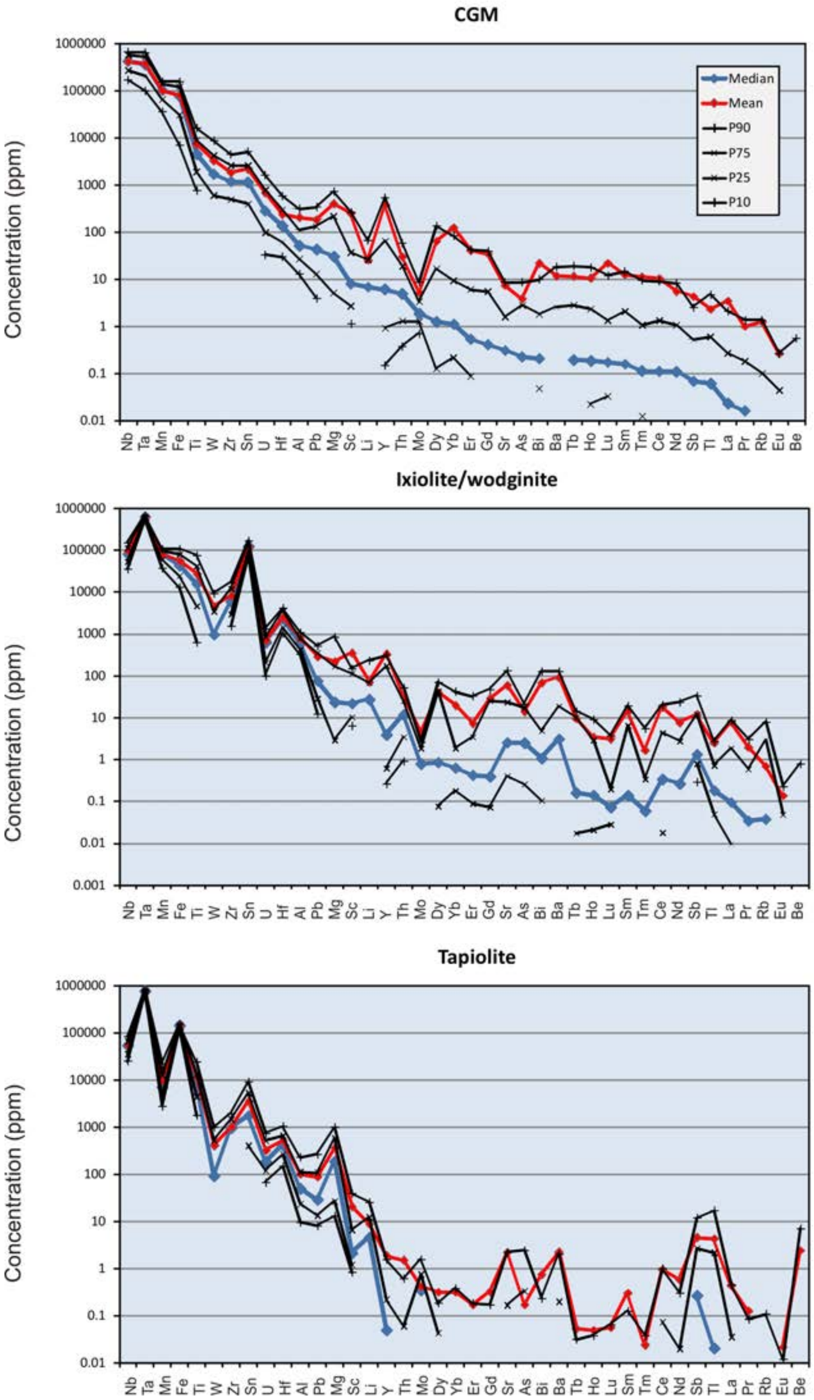

Fig. 2

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 ($B^{5+}_4Fe^{2+}_{-1}W^{6+}_{-3}$).

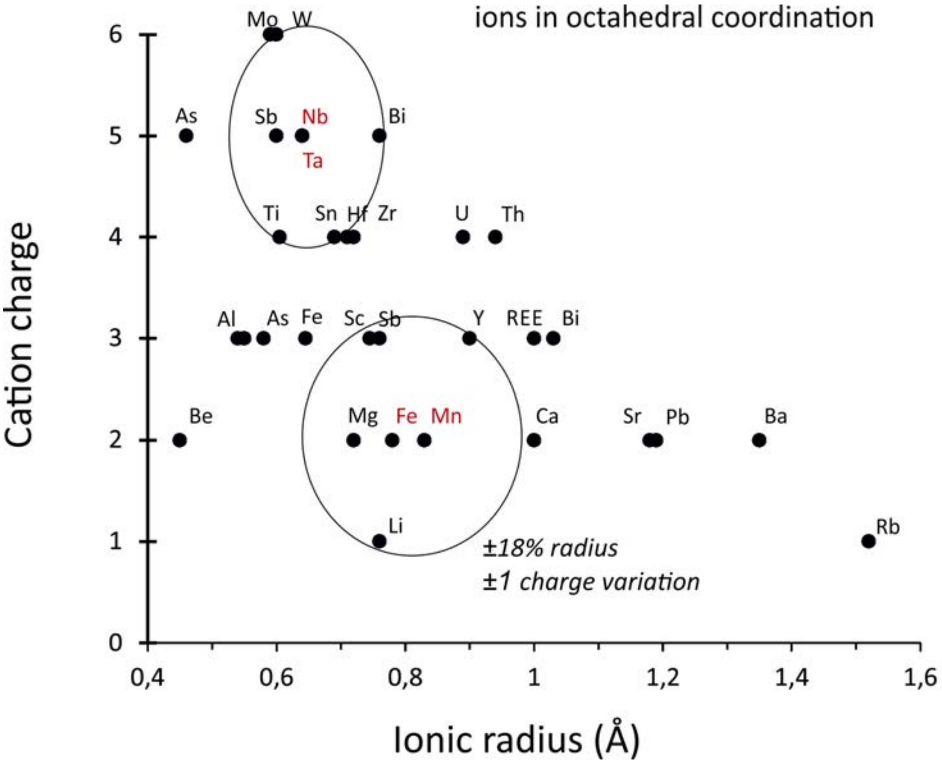

Fig. 3

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 ($B^{5+}{}_3M^{3+}{}_{-1}W^{6+}{}_{-2}$, 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 $A^{2+}{}_2B^{5+}(REE+Fe)^{3+}{}_{-3}$, 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.

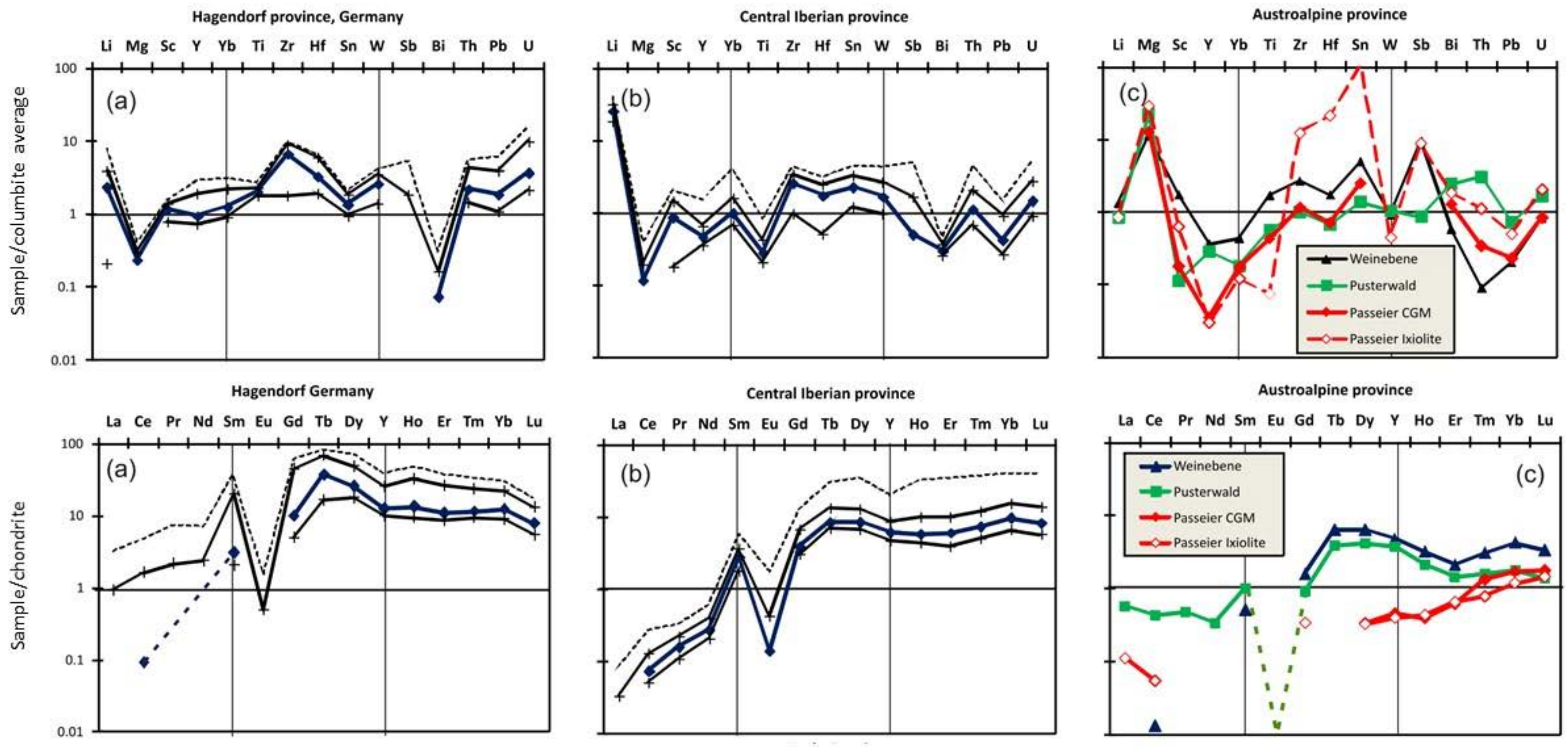

Fig. 4

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 $\mathrm{MREE_N}$ and $\mathrm{HREE_N}$. 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 microlite 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.

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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.

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GENESIS OF SPODUMENE-BEARING PEGMATITES WITHIN THE AUSTROALPINE UNIT (EASTERN ALPS): ANATECTIC VS. MAGMATIC DERIVATION

by

Ralf Schuster[1], Kostas Petrakakis[2], Tanja Ilickovic[3], Heinrich Mali[1], Rainer Abart[3], Frank Melcher[4] & Gerhard Hobiger[1]

[1]Geological Survey of Austria
Neulinggasse 38, 1030 Vienna, Austria
[2]Department of Geodynamics and Sedimentology
University of Vienna, Geozentrum, Althanstraße 14, 1090 Wien, Austria
[3]Department of Lithospheric Research
University of Vienna, Geozentrum, Althanstraße 14, 1090 Wien, Austria
[4]Chair of Geology and Economic Geology
Montanuniversität Leoben, Peter-Tunner-Straße 5, 8700 Leoben, Austria

In the Austroalpine unit of the Eastern Alps pegmatites containing the Li-pyroxene spodumene ($LiAl[Si_2O_6]$) occur heterogeneously distributed over a distance of more than 400 km. They are spatially associated with barren pegmatites lacking rare element mineralizations.
There is a debate about the genesis of the pegmatites: Mining geologists argue for a development of spodumene bearing pegmatites by fractionation of granitic parent plutons (GÖD, 1989; MALI, 2004), whereas metamorphic petrologists consider barren pegmatites as products of anatexis of metapelitic country rocks (STÖCKERT, 1987; THÖNI & MILLER, 2000; ERTL et al., 2010). In the first case the absence of co-genetic fertile granites render the model problematic, whereas in the second case the formation of suitable Li-enriched pegmatitic melts is not yet understood.

A new understanding of the Austroalpine basement and mapping during the past years gives the opportunity to reinvestigate this problem: The pegmatites developed in Permian time when the area was affected by lithospheric extension, causing basaltic underplating, high temperature / low pressure metamorphism and intense magmatic activity (SCHUSTER & STÜWE, 2008). The Permian P-T-t path is characterized by heating at slightly decreasing pressure. Mapping revealed units of migmatitic mica schists with lots of interlayed barren pegmatites, representing areas with aborted melt generation. Other areas with spodumene bearing pegmatites and other enriched pegmatites represent structurally higher levels, where fractionated melts crystallized. Some of the dykes can be traced over several hundred meters and allow to study processes of internal fractionation.

Due to these facts we would like to investigate the genesis of the spodumene-bearing pegmatites in a research project. Even if we will go on searching for potential Permian parent granites we think it is possible to create Li-rich pegmatitic melts by anatexis and we want to investigate this problem starting with a petrological and geochemical approach, based on the new field geological data. In our working hypothesis we propose the following model for melt genesis: As source rocks for the pegmatitic melts we expect Al-rich metapelites derived from marine shales. During their metamorphic evolution these rocks passed through mineral assemblages including paragonite/muscovite, albite, quartz, chlorite, staurolite and minor biotite and plagioclase. During the Permian event a temperature increase at more or less constant pressures caused melting of white mica, feldspar and quartz with additional H_2O at 650-700°C and 0.4–0.6 GPa, within the sillimanite stability field. Breakdown of staurolite served as additional source for Li in the primary melts. Subsequent internal fractionation lead to further Li-enrichment and crystallization of spodumene from the most evolved melts, whereas less enriched/fractionated melts formed co-genetic barren pegmatites.

The validation of our working hypothesis would contribute to our understanding of (1) the regional (Austroalpine) evolution that is still considered as "non-anatectic", (2) the alternative formation modes of rare element pegmatites and (3) the strategies of exploration of these economically valuable rocks.

References

ERTL, A., MALI, H., SCHUSTER, R., KÖRNER, W., HUGHES, J.M., BRANDSTÄTTER, F. & TILLMANNS, E. (2010): Li-bearing, disordered Mg-rich tourmalines from the pegmatite-marble contact from the Austroalpine basement units (Styria, Austria). - Mineralogy and Petrology, 99, 89-104.

GÖD, R. (1989): The spodumene deposit at "Weinebene", Koralpe, Austria. – Mineralium Deposita, 24: 270–278.

MALI, H. (2004): Die Spodumenpegmatite von Brettstein und Pusterwald (Wölzer Tauern, Steiermark, Österreich). - Joannea - Mineralogie, 2, 5-53.

SCHUSTER, R. & STÜWE, K. (2008): The Permian Metamorphic Event in the Alps. - Geology, 36/8: 303-306.

STÖCKHERT, B. (1987): Das Uttenheimer Pegmatitfeld (Ostalpines Altkristallin, Südtirol): Genese und alpine Überprägung. - Erlanger geologische Abhandlungen, 114, 83-106, Erlangen.

THÖNI, M. & MILLER, CH. (2000): Permo-Triassic pegmatites in the eo-Alpine eclogite-facies Koralpe complex, Austria: age and magma source constraints from mineral chemical, Rb-Sr and Sm-Nd isotopic data. - Schweizerische Mineralogische und Petrographische Mitteilungen, 80, 169-186.

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TRACE ELEMENTS IN QUARTZ FROM LI-ENRICHED PEGMATITE

by

Karel Breiter[1], Martin Svojtka[1], Jana Ďurišová[1], Lukáš Ackerman[1] & Milan Novák[2]

[1]Institute of Geology of the Academy of Sciences of the Czech Republic
v. v. i., Rozvojová 269, CZ-165 00 Praha 6, Czech Republic
[2]Department of Geological Sciences, Masaryk University
Kotlářská 2, CZ-611 37 Brno, Czech Republic

Introduction

Concentration of trace elements in rock-forming minerals is often used for evaluation of fractionation trends of magmatic rocks. However, in case of granitoids, the most common minerals like feldspar or mica are often altered during post-magmatic fluid-related processes. Quartz is more resistant and its magmatic trace-element signature is usually preserved.

Improvement of microanalytical methods in last two decades stimulated numerous studies focused on trace element composition of granitic (e.g. Jacamon and Larsen, 2009; Breiter and Müller, 2009; Deans, 2010; Breiter et al., 2012, 2013) and pegmatitic (Larsen et al., 2000, 2004; Götze et al., 2005; Müller et al., 2008) quartz. Nevertheless, detailed studies about evolution of quartz in complex pegmatites are still scarce (Beurlen et al., 2011, Breiter et al. in print).

Aims of this contribution are:

(i) to describe evolution of the trace-element pattern in quartz during crystallization of fractionated Li-enriched pegmatite body,
(ii) to evaluate the influence of mineral assemblages to distribution of trace elements in quartz,
(iii) to compare contents of trace elements in quartz from pegmatites and granites.

Analytical conditions

Trace element (Al, B, Ba, Be, Cr, Fe, Ge, Li, Mn, P, Rb, Sn Sr, and Ti) contents in quartz were analyzed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Institute of Geology, Academy of Sciences of the Czech Republic using a Thermo-Finnigan Element 2 sector field mass spectrometer coupled with the 213-nm NdYAG laser (New Wave Research UP-213). The isotopes ^{29}Si and ^{30}Si were used as the internal standards based on presumption that the analyzed quartz contains 99.95 wt% SiO_2. The data were calibrated against the external standard of synthetic silicate glass NIST SRM 612. For more details see Breiter et al. (in print). Homogeneity of quartz grains was controlled prior the analyses with the cathodoluminescence.

Results and discussion

We studied samples of quartz from all major textural zones from two complex pegmatites from western Moravia, Bohemian Massif, Czech Republic (Cháb et al., 2009): the Rožná lepidolite pegmatite (Novák and Cempírek, 2010), and the beryl-columbite Věžná I pegmatite (Dosbaba and Novák, 2012). Both selected pegmatites are of peraluminous LCT-type. For description of individual samples and contents of the genetically most important trace elements see Table 1.

Locality	Sample no.		Li	Ge	Al	Ti
Rožná	RO-1	coarse-grained border unit with biotite	4.9	1.3	109	22
	RO-2	graphic unit with muscovite	6.6	2.6	153	16
	RO-3	granitic unit with schorl	7.5	3.4	147	11
	RO-4	coarse-grained albite subunit with schorl to Fe-rich elbaite	32	4.2	320	8.9
	RO-5	albite subunit with lepidolite and Fe-rich elbaite	4.2	9.6	121	1.5
	RO-6	quartz core	23	10	235	1.4
Věžná	Věž-1	granitic unit with biotite	14	0.78	72	29
	Věž-2	granitic unit-to-coarse-grained unit with biotite	14	0.73	114	25
	Věž-3	graphic unit	20	1.2	140	39
	Věž-5	blocky unit	24	2.6	211	43

Table 1

Description of samples and selected trace element concentrations (means in ppm) in quartz. For complete analytical data see Breiter et al. (2012a) and Breiter et al. (in print).

Among all analyzed trace elements, contents of Al are the highest and systematically increase from the margin to the core zones in Rožná and Věžná pegmatites (109 to 235 ppm and 72 to 211 ppm, respectively). Contents of the second most abundant element, Ti, decrease systematically from margin to core in Rožná, but scattered in Věžná. Because the increasing Al/Ti ratio in quartz is generally accepted as reliable indicator of granitic magma fractionation (Jacamon and Larsen, 2009, Breiter et al., 2012b), this ratio is used for demonstration of evolution of other trace elements in Figs. 1 and 2.

Germanium has similar crystallochemical parameters like Si and is, in very small amount, present in all silicate minerals. Contents of Ge in quartz well correlate with Al/Ti ratios (Fig.1a) and it is concentrated predominantly in the latest stages of the Rožná pegmatite fractionation – in the albite-lepidolite zone and in the quartz core. This is consistent with theoretically predicted behavior of disseminated incompatible trace element. Contents of Ge in Věžná are lower, but the trend is similar.

Distribution of Li strongly differs from those of Ge (Fig. 1b), although the tendency to increase in the late phases of crystallization is also well visible. Lithium, unlike Ge, is able to form its own minerals like lepidolite.

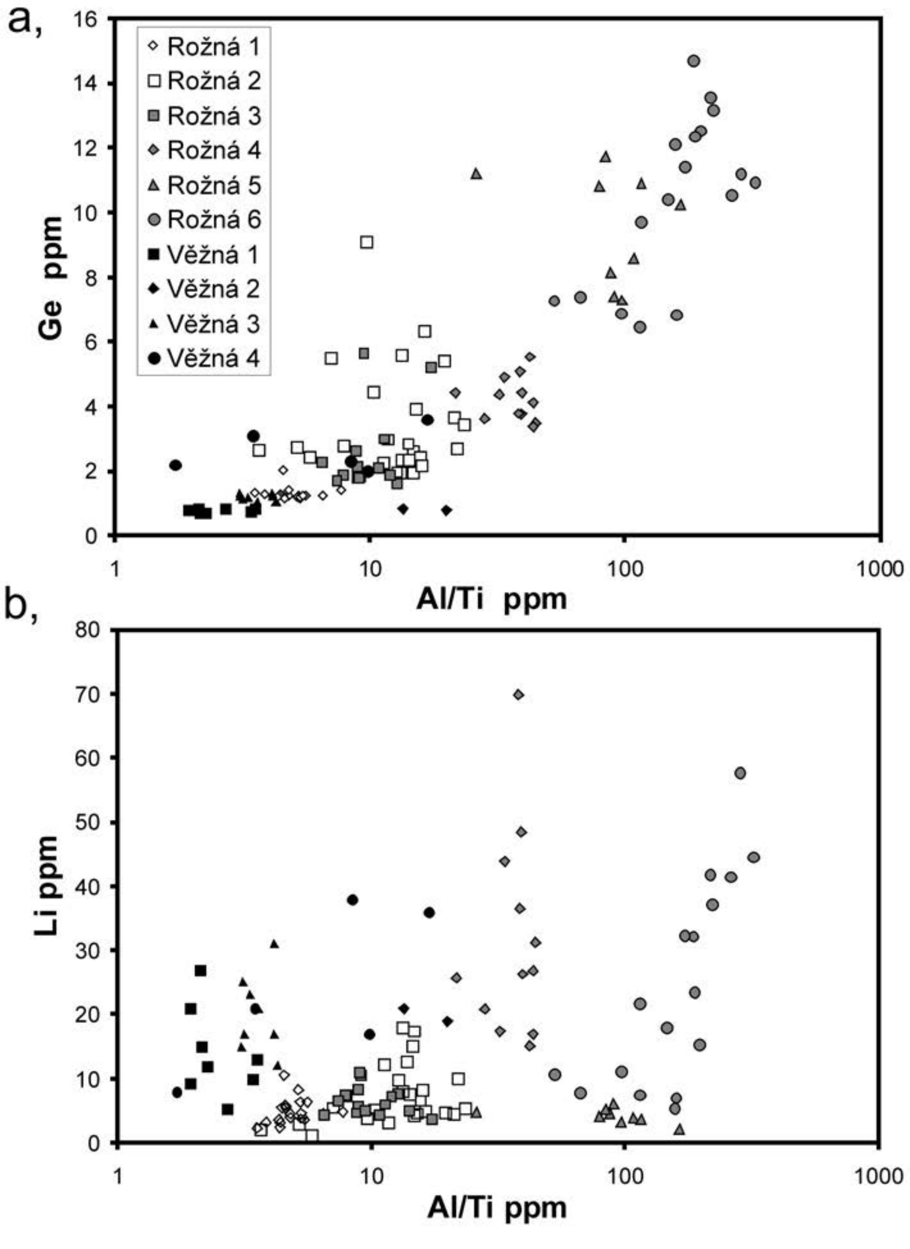

Fig. 1
Contents of Ge and Li in quartz from individual textural zones (from the margin to the core) in complex LCT pegmatites.

The Li contents in quartz increase systematically in lepidolite-free zones (= activity of Li in melt is high and Li enter quartz lattice), but strongly decrease in the lepidolite-bearing zone, where all Li preferentially incorporate into lepidolite and its activity in melt dropped. Thus, minerals crystallized from melt along with quartz may strongly influence the distribution of trace elements between quartz and melt.

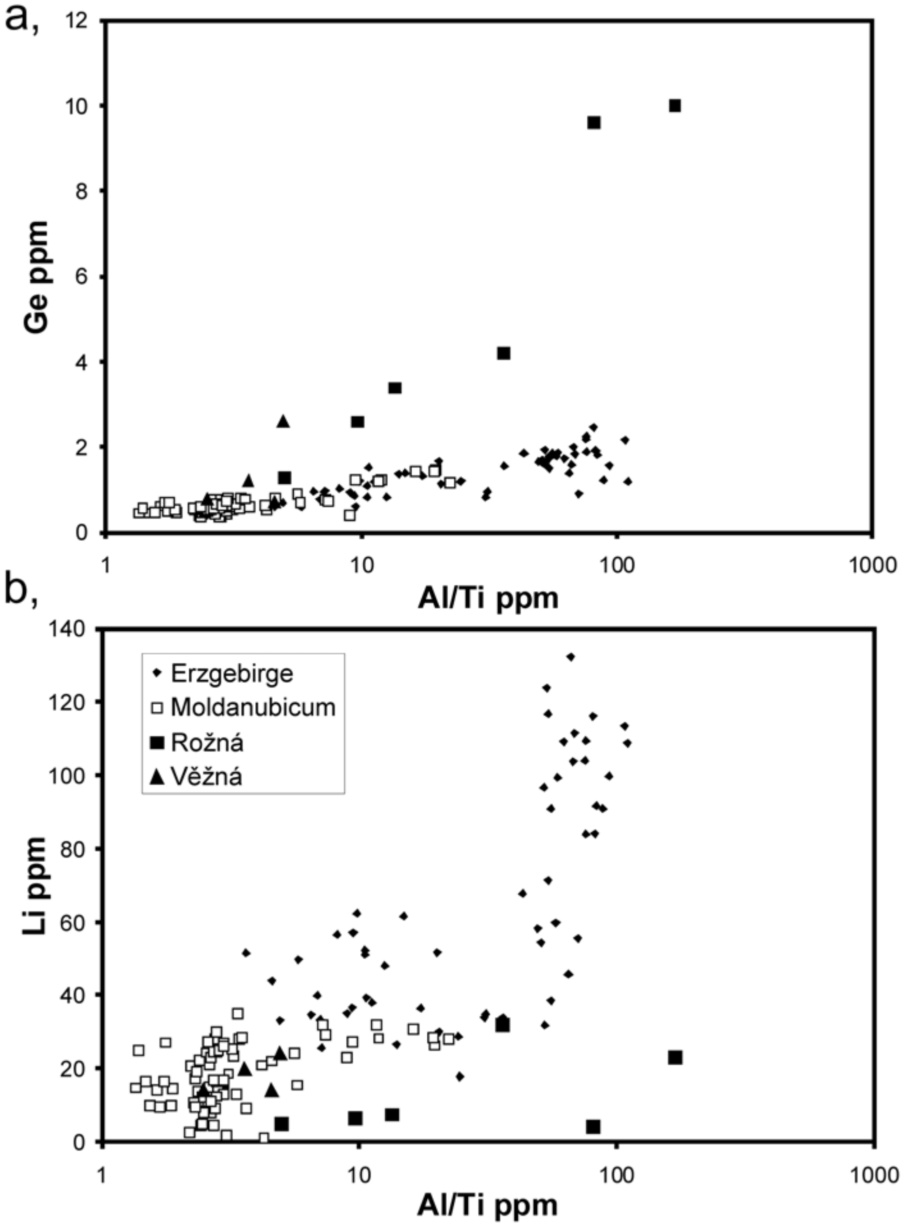

Fig. 2

Comparison of the Ge- and Li-contents in quartz from complex LCT pegmatites and peraluminous granites.

Fig. 2 illustrates comparison of Ge and Li contents in quartz from LCT-pegmatites and peraluminous granites. Contents of Ge in granites are mostly lower than 2 ppm. On the other hand, pegmatitic quartz, especially from the later stage of crystallization, tends to be strongly enriched in Ge with the concentrations up to 10-11 ppm in the albite-lepidolite zone and quartz core of Rožná pegmatite.

In case of Li, quartz from fractionated peraluminous granites in Erzgebirge contains 2-3 times more Li in comparison to late-stage zones of both studied pegmatites: crystallization of zinnwaldite in granitic melt was not able to block the entry of Li into quartz lattice.

Conclusions

Quartz from complex LCT pegmatites has similar evolutionary trend as quartz from fractionated granites: systematic increase of Al, Li, and Ge. In comparison with the most fractionated peraluminous granites, pegmatitic quartz is relatively depleted in Li, but strongly enriched in Ge. Minerals associated with crystallizing quartz may strongly influence the distribution of trace elements between quartz and melt. This influence is stronger in the pegmatitic than granitic melt.

Acknowledgement

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Referenecs

BEURLEN, H., MÜLLER, A., SILVA, D. & SILVA, M.R.R.D. (2011): Petrogenetic significance of LA-ICP-MS trace-element data on quartz from the Borborema pegmatite province, northeast Brazil. Mineralogical Magazine, 75, 2703-2719.

BREITER, K. & MÜLLER, A. (2009): Evolution of rare metal-specialised granite melt documented by quartz chemistry. European Journal of Mineralogy, 21, 335-346.

BREITER, K., SVOJTKA, M., ACKERMAN, L., ĎURIŠOVÁ, J., MATOUŠKOVÁ, Š., ŠVECOVÁ, K. & LOUN, J. (2012a): Trace elements in quartz from pegmatite Věžná I (Česká Republika). Bulletin Národního muzea, 20, 218-222. (in Czech)

BREITER, K., SVOJTKA, M., ACKERMAN, L. & ŠVECOVÁ, K. (2012b): Trace element composition of quartz from the Variscan Teplice caldera (Krušné hory/Erzgebirge Mts., Czech Republic/Germany): Insights into the volcano-plutonic complex evolution. Chemical Geology, 326-327, 36-50.

BREITER, K., ACKERMAN, L., SVOJTKA, M. & MÜLLER, A. (2013): Behavior of trace elements in quartz from plutons of different geochemical signature: A case study from the Bohemian Massif, Czech Republic. Lithos, 175-176, 54-67.

BREITER K., ACKERMAN, L., ĎURIŠOVÁ, J. & SVOJTKA, M. (2014): Chemical composition of quartz from pegmatites of different types: A case study from the Moldanubian Zone of the Bohemian Massif (Czech Republic). Mineralogical Magazine, in print

CHÁB, J., BREITER, K., FATKA, O., HLADIL, J., KALVODA, J., ŠIMŮNEK, Z., ŠTORCH, P., VAŠÍČEK, Z., ZAJÍC, J. & ZAPLETAL, J. (2009): Outline of the geology of the Bohemian Massif. 295p. Praha.

DEANS, J.R.L. (2010): Trace element and calculated temperature variation in quartz and titanite in the 36 Ma Harrison Pass pluton, Ruby Mountains NE Nevada. MSc Thesis, Texas Tech. University.

DOSBABA, M. & NOVÁK, M. (2012): Quartz replacement by "kerolite" in graphic quartz-feldspar intergrowths from the Věžná I pegmatite, Czech Republic; A complex desilicification process related to episyenitization. Canadian Mineralogist, 50, 1609–1622.

GÖTZE, J., PLÖTZE, M. & TRAUTMANN, T. (2005): Structure and luminescence characteristics of quartz from pegmatites. American Mineralogist, 90, 13-21.

JACAMON, F. & LARSEN R.B. (2009): Trace element evolution of quartz in the charnockitic Kleivan granite, SW-Norway: The Ge/Ti ratio of quartz as an index of igneous differentiation. Lithos, 107, 281-291.

LARSEN, R.B., POLVÉ, M. & JUVE, G. (2000): Granite pegmatite from Evje-Iveland: trace element chemistry and implications for the formation of high-purity quartz. NGU Bulletin, 436, 57-65.

LARSEN, R.B., HENDERSON, I., IHLEN, P.M. & JACAMON, F. (2004): Distribution and petrogenetic behaviour of trace elements in granitic pegmatite quartz from South Norway. Contribution to Mineralogy and Petrology, 147, 615-628.

MÜLLER, A., IHLEN, P.M. & KRONZ, A. (2008): Quartz chemistry in polygeneration Sveconorwegian pegmatites, Froland, Norway. European Journal of Mineralogy, 20, 447-463.

NOVÁK, M. & CEMPÍREK, J. (Eds, 2010): Granitic pegmatites and mineralogical museums in Czech Republic. IMA 2010, Budapest, Hungary. Acta Mineralogica -Petrographica, Field guidebook serie, 6, 1-56.

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CHEMICAL CHARACTERISTICS OF THE K1-K3 METAGRANITOID IN THE FELBERTAL SCHEELITE DEPOSIT (AUSTRIA)

by

Michael Kozlik & Johann G. Raith

Chair of Resource Mineralogy, Department of Applied Geosciences and Geophysics
Montanuniversität Leoben, Peter-Tunner-Straße 5, 8700 Leoben, Austria

Introduction

In 2012 Austria produced 706 metr. t W (tungsten), representing a share of 0.87% of the global tungsten market (REICHL et al., 2014). This output originated entirely from the Felbertal scheelite deposit, the only active tungsten mine in Austria. Since its discovery 50 years ago by Rudolf Höll and a group of students from the University of Munich, the genesis of the Felbertal deposit is still controversially discussed with two contrasting models trying to explain the ore forming processes.

According to the syngenetic/synsedimentary stratabound model, scheelite precipitated from exhalative hydrothermal fluids released during Early Palaeozoic submarine mafic volcanism (e.g., HÖLL, 1975). On the contrary, the epigenetic model links the mineralisation to the intrusion of a highly differentiated orthogneiss of Early Carboniferous age (K1-K3 orthogneiss) and subsequent hydrothermal overprint by circulating granite-derived fluids (e.g., BRIEGLEB, 1991). Similar geological models relating W-mineralisation with silicic magmatism are proposed for a great number of deposits worldwide (e.g., Erzgebirge-Slavkovský les, BREITER et al., 1999; Shizhuyuan, JINGWEN et al., 1996; Cantung, RASMUSSEN et al., 2011), where tungsten mineralisation is associated with the emplacement of highly evolved granitic melts, enriched in volatiles (F, Li, Be), and subsequent hydrothermal alteration of the country rocks.

Anyway, both genetic models for the Felbertal deposit highlight the importance of magmatic-hydrothermal fluids from which scheelite precipitated to form stockwork-like scheelite-quartz-veins and masses. This study presents new chemcial data for the mineralised K1-K3 metagranitoid in the Felbertal deposit and its related scheelite-quartz veins and discusses the results in the context of granite and fluid chemistry.

The K1-K3 orthogneiss

The K1-K3 orthogneiss is a fine- to medium-grained felsic microcline-phengite monzogranite with low-grade mineralisation in form of scheelite-quartz veinlets and disseminations of scheelite.

In the past high-grade ores were mined from quartz-rich ore zones (K1, K3) developed at the contacts of the orthogneiss with the host rocks. The orthogneiss is exposed underground in the western ore field where two varieties of the K1-K3 metagranitoid can be distinguished in the field. The dark K1-K3 orthogneiss type is characterised by a higher biotite content compared to the bright variety with less biotite but higher modal abundances of phengitic muscovite. Additionally, dm- to m-thick layers of leucocratic aplite gneisses are intercalated in the metabasic host rocks. All three gneisses are distinct in terms of various geochemical criteria but they display a common evolutionary trend.

When studying granitic rocks, the aluminium saturation index (ASI, ratio of molar $Al_2O_3/[Na_2O+K_2O+CaO]$) is an important parameter to draw conclusions on possible magma sources and the melting history of the granite (FROST et al., 2001). The ASI for the dark K1-K3 orthogneiss variety ranges from 0.93 to 1.03 (one outlier at 1.14) with $Al_2O_3 > Na_2O+K_2O$, indicating a metaluminous to transitional peraluminous character (Fig. 1a). In the bright orthogneiss variety the ASI increases to values between 0.99 and 1.08 (one outlier at 1.19) and achieves its maximum in the aplite gneiss (ASI = 1.11-1.12). Both the bright K1-K3 and the aplite gneiss can therefore be classified as weakly peraluminous.

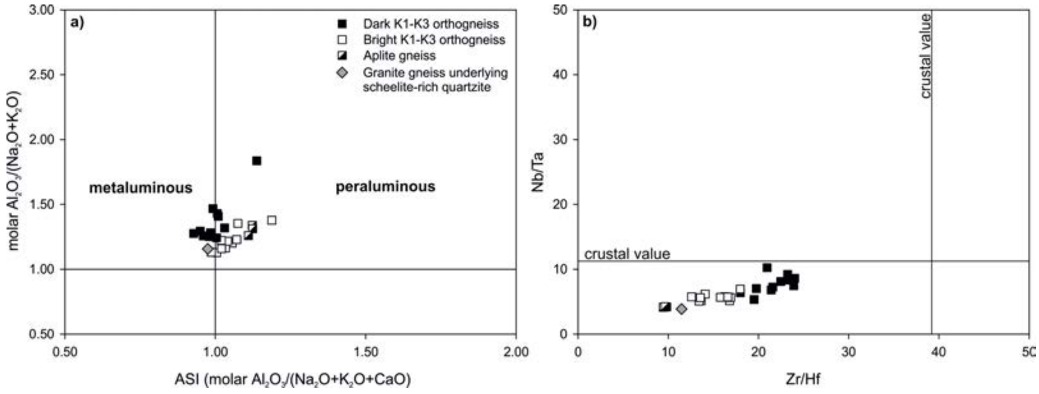

Fig. 1a

ASI vs. molar $Al_2O_3/(Na_2O+K_2O)$ displaying an increase in the ASI from the dark K1-K3 orthogneiss (0.93-1.03) to the bright K1-K3 orthogneiss (0.99-1.08) and the aplite gneiss (1.11-1.12). b): plot of Zr/Hf vs. Nb/Ta showing a linear trend and decreasing ratios from the dark K1-K3 to the bright variety and the aplitic gneiss.

A systematic trend becomes apparent when plotting Zr/Hf vs. Nb/Ta (Fig. 1b). Both ratios decrease from the dark K1-K3 orthogneiss (Zr/Hf = 18-24, Nb/Ta = 6-10, n = 11) to the bright K1-K3 variety (Zr/Hf = 13-18, Nb/Ta = 5-7, n = 11). The aplite gneiss is characterised by the lowest values (Zr/Hf = 9-10, Nb/Ta = 4, n = 3). Additionally, one published analysis for a leucogranitic gneiss underlying the laminated scheelite-quartz ores (“scheelite-rich quartzite”) in the eastern ore field (HÖLL & EICHHORN, 2000; p. 244 therein, rightmost sample) is included in the data set due to its close chemical similarities with the K1-K3 orthogneiss.

The systematic variation within the K1-K3 series is also illustrated in the following multielement-spiderplots and REE-distribution diagrams (Fig. 2). Normalized to average upper continental crust, the dark K1-K3 metagranitoid shows a more or less uniform distribution of many elements except for Cs, Rb, U, and Ta. These elements are enriched, in the case of U up to 10 times, whereas Sr and Ti are slightly depleted. When comparing the bright K1-K3 orthogneiss to the dark K1-K3 variety, we observe a decrease in Ba, Sr, P, Zr, Ti, and the LREE in the bright variety. Only Ta and Si (not shown here) increased slightly and the other elements roughly remained constant. The aplite gneiss is strongly depleted in Ba, K, LREE, Sr, P, and Ti. Tantalum increased significantly but also Nb, Hf, and the HREE are enriched as compared to both K1-K3 orthogneiss varieties. The pattern of the granite gneiss underlying the scheelite-rich quartzite in the eastern ore field matches exactly those of the aplite gneisses from the western ore field. A striking feature of all samples is the unusual high U concentration (up to 74 ppm), which is unique for granites known from the Tauern Window.

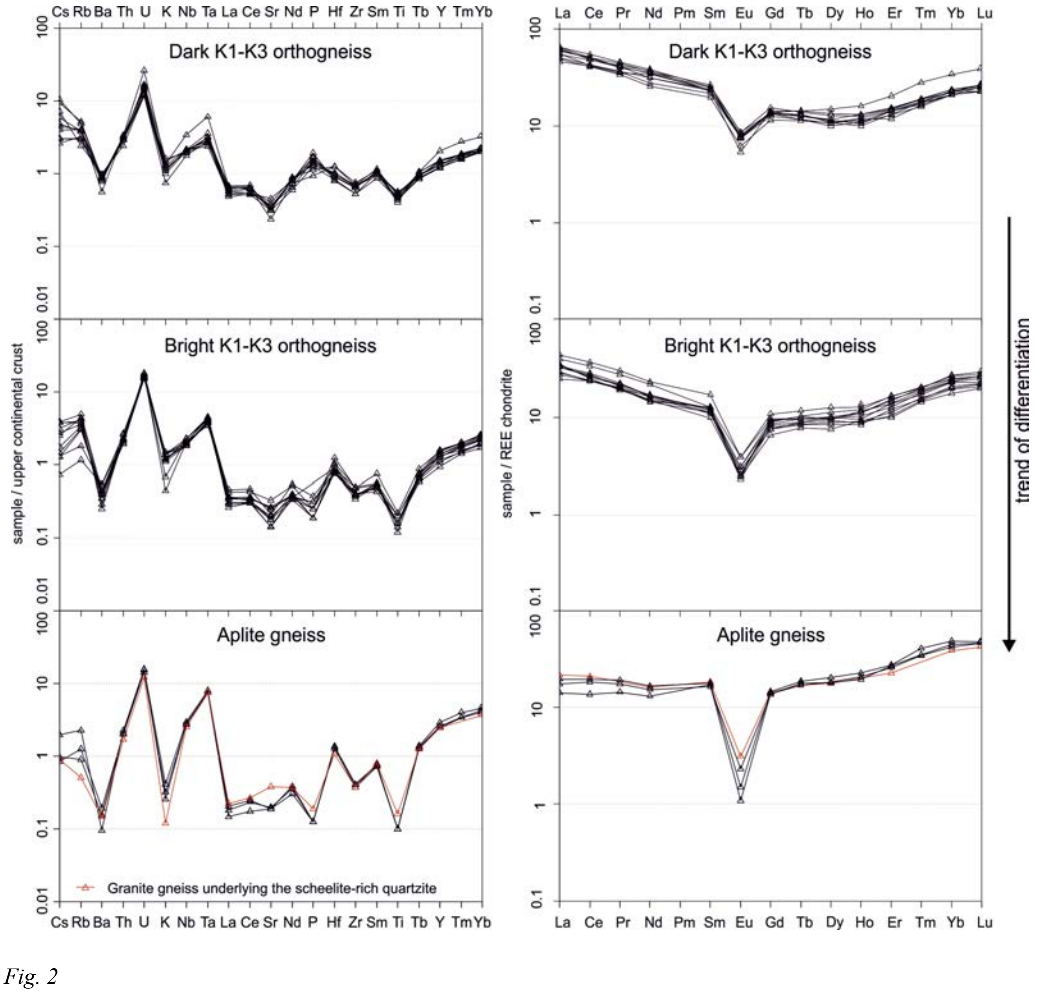

Fig. 2

Multielement-spiderplots and REE patterns for the dark and bright K1-K3 orthogneiss, the aplite gneiss and the granite gneiss underlying the scheelite-rich quartzite.

Differences among the orthogneiss varieties and the aplitic gneiss are also expressed in the chondrite-normalized REE-distribution plots. All K1-K3 gneiss samples are characterised by a distinct negative Eu-anomaly (Eu/Eu* = 0.013-0.026) and decreasing concentrations of the LREE with evolution of the metagranitoids from the dark to the bright variety. The most pronounced negative Eu-anomaly (Eu/Eu* = 0.004-0.009) is developed in the aplite gneiss. The progressive decrease in LREE concentrations with the evolution of the gneisses due to magmatic differentiation is significant when comparing the dark K1-K3 orthogneiss (La_N/Yb_N = 1.93-3.11) with the aplitic gneiss (La_N/Yb_N = 0.33-0.41). The correlation of the granite gneiss underlying the scheelite-rich quartzite with the aplite gneiss is also revealed by its REE pattern.

Discussion

It is often recognised that very felsic granitic rocks may be weakly peraluminous, whereas more mafic granites belonging to the same suite are metaluminous. CHAPPELL (1999) showed for fractionated felsic I-type granites from the Lachlan Fold Belt that their abundant peraluminous character (ASI= 1.06) results from mineral fractionation and that initially Al-undersaturated melts may become saturated in Al with progressive fractionation.

Concluding therefrom (and other chemical paramters), the bright K1-K3 orthogneiss and the aplite gneiss were derived by mineral-melt fractionation processes from the more mafic K1-K3 melt. The variation in ASI of the K1-K3 orthogneiss series displays a close to Al-saturated source for the least fractionated K1-K3 melt (ASI= 0.93-1.01 of the dark K1-K3 orthogneiss variety). The K1-K3 melt became saturated in Al with increasing differentiation, reflected by the weakly peraluminous character of the higher evolved orthogneisses. Partitioning of trace elements between main/accessory minerals and the melt is also responsible for producing the systematic variation observed in the multielement-spiderplots and REE-distribution patterns. The low P concentrations of the leucocratic varieties are a consequence of apatite fractionation. Crystallisation of feldspar and biotite controls the variation in Ba, Sr, Eu, and K furthermore. The decrease in the LREE contents is related to early segregation of allanite, being the main carrier of the LREE in the more primitive dark K1-K3 orthogneiss. The variation of the high field strength elements (HFSE) Zr, Hf, Nb, and Ta and the HREE can be attributed to fractionation of zircon and late crystallisation of Nb-Ta-Ti-U-oxides.

The latter are frequently associated with the granite-related scheelite-quartz veins. The occurrence of niobium- and tantalum-mineralization also suggests extreme fractionation processes that are necessary to reach Ta-saturation in a peraluminous residual granitic melt (LINNEN, 1998). The Nb/Ta ratios decrease with ongoing differentiation from the dark K1-K3 orthogneiss to the aplite gneiss, while Nb- and Ta-concentrations systematically increase during melt evolution. The shift in melt composition towards lower Nb/Ta ratios reflects the higher solubility of manganotantalite over manganocolumbite in granitic melts (LINNEN, 1998). This means that Ta gets fractionated over Nb due to different solubilities of their respective oxides, irrespective of the similar incompatible geochemical behaviour of Nb and Ta. Additionally, the chemical composition of the melt acts as an influencing factor. High fluorine concentrations of the melt also contribute to the behaviour of Nb and Ta in granitic melts, since F will increase the solubility product of Ta-oxides and therefore delays the precipitation of the respective oxides (LINNEN, 1998).

The consequence is that the Ta-concentration will increase with progressive differentiation. The common presence of fluorite in scheelite-quartz veins as well as the high F concentrations of biotite and titanite from the K1-K3 metagranitoid confirms that F was present in the granitic melt and mineralising hydrothermal system (KOZLIK & RAITH, 2013). Moreover the occurrence of minute fluorite inclusions within Nb-Ta-Ti-U-oxides documents the influence of fluorine on Nb-Ta-oxide precipitation. The higher solubility of hafnon relative to zirconium causes the decrease in the Zr/Hf ratio of the granitic melt with increasing fractionation, similar to the decrease of the Nb/Ta ratio (LINNEN, 1998).

Conclusions

The K1-K3 orthogneiss in the Felbertal scheelite deposit represents a geochemically highly evolved metagranitoid, which has clearly undergone extensive magmatic differentiation processes. The systematic trend in a multitude of elements and their respective ratios indicates that crystal-melt fractionation controlled the evolution of the K1-K3 magma during differentiation. The source for the more primitive dark K1-K3 orthogneiss was undersaturated or nearly saturated in aluminium, but the melt attained Al-saturation and became peraluminous with increasing evolution. The close geochemical similarities between the granite gneiss underlying the laminated scheelite-quartz ores in the eastern ore zone and the aplite gneisses in the western ore zone reveal the presence of highly evolved K1-K3 equivalent material also in the eastern ore field. The precipitation of Nb-Ta-Ti-U-oxides in scheelite-quartz veins indicates that granite-derived magmatic-hydrothermal fluids were enriched in HFSE together with W and that both Nb and Ta fractionated into the fluid phase during transition from the magmatic to the hydrothermal stage.

References

BREITER, K., FÖRSTER, H.-J., SELTMANN, R. (1999): Variscan silicic magmatism and related tin-tungsten mineralization in the Erzgebirge-Slavkovský les metallogenic province. - Mineral. Deposita, 34, 505-521.

BRIEGLEB, D. (1991): Ein epigenetisches Modell der Scheelitlagerstätte Felbertal (Land Salzburg). - Ber. Deutsch. Miner. Ges., Beih. Europ. J. Mineral, 3, 43.

CHAPPELL, B.W. (1999): Aluminium saturation in I- and S-type granites and the characterization of fractionated haplogranites. - Lithos, 46, 535-551.

FROST, R.B., BARNES, C.G., COLLINS, W.J., ARCULUS, R.J., ELLIS, D.J., FROST, C.D. (2001): A geochemical classification for granitic rocks. - J. Petrol, 42, 2033-2048.

HÖLL, R. (1975): Die Scheelitlagerstätte Felbertal und der Vergleich mit anderen Scheelitvorkommen in den Ostalpen. – Abh. Bayer. Akad. Wissensch., Mathemat. Naturwiss. Kl., 157a, 1-114.

HÖLL, R., EICHHORN, R. (2000): Tungsten mineralization and metamorphic remobilization in the Felbertal scheelite deposit, Central Alps, Austria. - In: Spry, P.G., Marshall, B., Vokes, F.M. (eds): Metamorphosed and metamorphogenic ore deposits. Society of Economic Geologists, 233-264.

JINGWEN, M., HONGYAN, L., SHIMAZAKI, H., RAIMBAULT, L., GUY, B. (1996): Geology and metallogeny of the Shizhuyuan skarn-greisen deposit, Hunan Province, China. - Intern. Geol. Rev., 38, 1020-1039.

KOZLIK, M., RAITH, J.G. (2013): Hydrothermally induced fluorine enrichment in metagranitoids of the Felbertal scheelite deposit (Austria). Proceedings to the 12th SGA Biennial Meeting 2013, 1271-1274.

LINNEN, R.L. (1998): The solubility of Nb-Ta-Zr-Hf-W in granitic melts with Li and Li + F; constraints for mineralization in rare metal granites and pegmatites. - Econ. Geol., 93, 1013-1025.

RASMUSSEN, K.L., LENTZ, D.R., FALCK, H., PATTISON, D.R.M. (2011): Felsic magmatic phases and the role of late-stage aplitic dykes in the formation of the world-class Cantung Tungsten skarn deposit, Northwest Territories, Canada. - Ore Geol. Rev., 41, 75-111.

REICHL, C., SCHATZ, M., ZSAK, G. (2014): World-Mining-Data, 29, 251.

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OPTIMIZATION OF NIOBIUM TANTALUM PROSPECTING IN AUSTRIA - ROUTINES FOR SAMPLING, PREPARATION ANA ANALYSIS

by

Kristina Stocker & Johann G. Raith

Chair of Resource Mineralogy, Department of Applied Geosciences and Geophysics
Montanuniversität Leoben, Peter-Tunner-Straße 5, 8700 Leoben, Austria

Introduction

Niobium and tantalum are classified as critical raw materials by the European Union and the Austrian government. These metals show an extreme country and market concentration (Herfindahl-Hirschmann-Index (HHI) FeNb & Ta = 8.559), and have to be imported into the EU to 100%. In 2010 Austria imported 1061 t of ferroniobium (FeNb) and 17 t Ta; the latter figure is about 1% of the total world production of Ta (LUIDOLD, 2013). Main ore minerals for niobium and tantalum are columbite and tantalite, which form a solid solution series known as "coltan"-group. About 40% of the global coltan production derives from countries in Central Africa (LINNEN et al. 2014). In these countries coltan is mainly produced by artisanal mining under adverse conditions and might be used to finance military conflicts and civil wars in politically unstable countries for instance in the Democratic Republic of Congo.

Niobium is dominantly used to produce ferroniobium, which is used in high-strength low alloy (HSLA) steels. The light weight and high strength of HSLA steel make it suitable for use in vehicle bodies, ship hulls, railway tracks and oil and gas pipelines. The primary use of Ta is in capacitors, particularly for wireless devices and touch screen technologies (BARDT, 2010). It is also added to superalloys, because of its resistance to high temperature and corrosion and is among other applications used in high-temperature turbines. Furthermore, Ta is biocompatible with human tissue and thus is used in prosthetic joints and pacemakers (LINNEN et al., 2014).

Primary Nb-Ta deposits are mainly associated with carbonatites, alkaline to peralkaline granites and syenites as well as with peraluminous pegmatites and granites (SHAW & GOODENOUGH, 2011; LINNEN et al., 2014). Due to their resistance to chemical and mechanical weathering and high specific gravities tantalum and niobium minerals may also accumulate in alluvial placers.

Coltan in Austria?

As shown in the study on “Critical raw materials for high-technology applications in Austria” there exists a poorly investigated geological potential for coltan in Austria (LUIDOLD et al., 2013). This potential is indicated by the occurrence of spodumene (lithium) pegmatites in some metamorphic units in the Eastern Alps, from which coltan minerals were reported (e.g., at Weinebene). Additionally, the geochemical data sets for stream sediments revealed numerous geochemical niobium anomalies (Ta has not been analysed) within the Eastern Alps and the Bohemian Massif (THALMANN et al., 1989). The geological reasons for these anomalies and their potential use as prospectivity indicators for niobium and tantalum deposits are largely unclear. The ongoing pilot project “Optimization of Nb-Ta prospecting in Austria”, it is funded by the FFG through the FTI initiative “Intelligent Production”, aims for optimizing the exploration methods for coltan deposits and increasing the knowledge about the primary resources of coltan in Austria. In this contribution the sampling strategy, sample preparation and analytical routines, as developed for this project are presented.

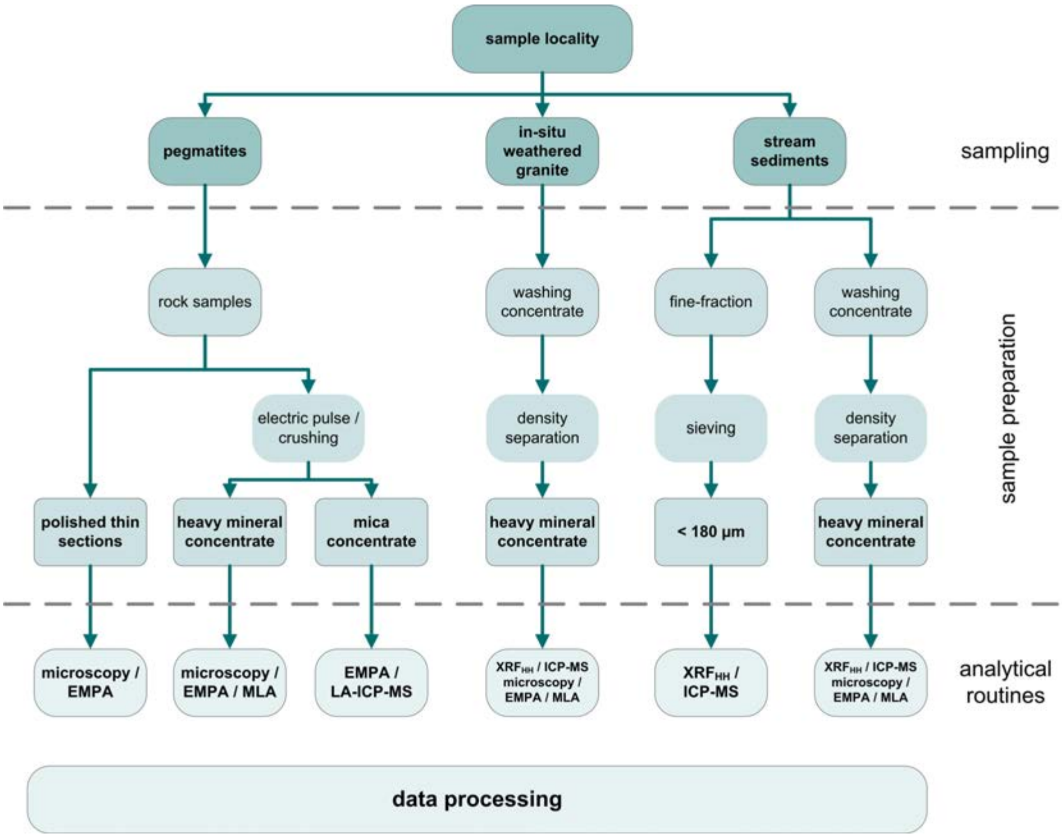

Fig. 1

Overview of preparation and analytical routines applied to the three types of media.

Sampling, preparation and analytical routines

The routines developed for sampling, preparation and mineralogical and chemical analyses are summarized in Fig. 1. For the purpose of verifying and following up known geochemical anomalies and checking pegmatites for Nb-Ta mineralization three types of media were sampled: pegmatite rock, stream sediments (heavy mineral concentrate, fine fraction < 180 μm) and eluvium material formed by the in-situ weathering of granites (”Granitgrus”).

Within the Bohemian Massif stream sediments and granite eluvium were sampled in three areas: north of Sandl and south of Weitra (see LEGERER etal., 2014) and in an area north of Heidenreichstein and Litschau. Pegmatite samples were taken at Widy Quarry, Königswiesen and Reinolz.

Studied pegmatite localities within the Eastern Alps include Hohenwart, Lachtal, Mitterberg/Übelbach, Garrach/St. Radegund and the Weinebene spodumene deposit. A few stream sediment samples were collected in the Hohenwart area and around Übelbach. The routines, which were applied for pegmatite samples are reported in more detail in AHRER & RAITH (2014).

The routines as applied to stream sediments and eluvium are as follows: At each sampling site the fine fraction (SF) and a washed heavy mineral concentrate (SM) were collected. The samples were obtained from point bars along stream channels. The SF samples were gained using a small shovel to take the upper approx. 2 cm of the stream bar after removing organic material by dispersing in shallow water. Upon retrieval, the sediment samples were transferred into paper bags, decanted and dried. If possible, multiple subsamples were aggregated to form a single sample for that site. To obtain heavy mineral concentrates, an amount of 15-20 l of active river sediment was collected into a bucket and sieved < 1.4 mm to remove coarser material. Afterwards the sample was wet panned in the field to preconcentrate the heavy minerals and to remove organic matter and clay material. The remaining sample was dried and passed through a 355 μm sieve. To remove remaining minerals of low density, the sample was treated by heavy liquid separation using sodium-poly-tungstate (ϱ=2.95 g/cm). After careful washing with bidistilled water the remaining sample was split into two halves. One portion was ground in an agate vibrating cup mill prior to chemical analysis, the other one was used for mineralogical studies. Eluvial material was dealt with in the same way as described above for heavy mineral concentrates although the processing started from about the double amount of material (about 30-40 l).

Pegmatite samples were collected considering zonation of pegmatite bodies. Depending on the mean crystal size up to 20 kg of material was collected from each zone to obtain representative samples. To separate heavy minerals from pegmatite matrix minerals the samples were crushed by electric pulse disaggregation and/or a jaw crusher, treated by heavy liquid separation and/or wet panned. Additionally, mica concentrates were prepared from crushed pegmatite material by handpicking.

Polished (thin) sections were prepared from rock samples and heavy mineral concentrates for polarisation microscopy (transmitted and reflected light) as well as for electron microprobe analysis (EMPA; electron imaging, qualitative EDS and quantitative WDS analysis, element distribution maps). EMPA analyses were done using the Superprobe JEOL JXA 8200 of UZAG Steiermark at Montanuniversitaet Leoben. This allowed mineralogical phase identification and mineral chemical analysis of Nb-Ta and associated phases.

In addition, heavy mineral concentrates obtained from stream sediments and pegmatites were analyzed by automated MLA-techniques (heavy mineral concentrates of stream sediments, TU Bergakademie Freiberg/Germany; concentrates from pegmatites, BGR Hannover/Germany). With this technique quantitative information about the mineralogical composition of samples was obtained. Combined LA-ICP-MS and EMPA analyses were applied for analysis of the main and trace element composition of micas. LA-ICP-MS analyses of micas were done at the Department of Chemistry and Department of Earth Sciences, Karl – Franzens – University, Graz using a New Wave UP 213 laser unit combined with an ICP-MS Agilent 7500 ICP quadrupole mass spectrometer. Each processing step of stream sediments and eluvium granite material was monitored by handheld XRF analysis using a Niton XL3t RF Analyzer at the Chair of General and Analytical Chemistry, Montanuniversitaet Leoben. Chemical compositions were then determined by ICP-MS and ICP-ES techniques at AcmeLabs/Canada.

By applying this multi-method mineralogical and chemical approach it could be demonstrated that geochemical anomalies of Nb-Ta-(REE±W±Sn etc.) in the Bohemain Massif reflect different sources and provenance. Whereas some regional anomalies like the one N of Sandl are caused by incorporation of higher contents of Nb and Ta in Ti oxides (see LEGERER et al., 2014), others like the one north of Litschau in the Rottal area are caused by presence of distinct Nb-Ta phases. There, tiny inclusions of columbite-tantalite were observed within cassiterite as well as single larger grains of columbite (Fig. 2a, 2b).

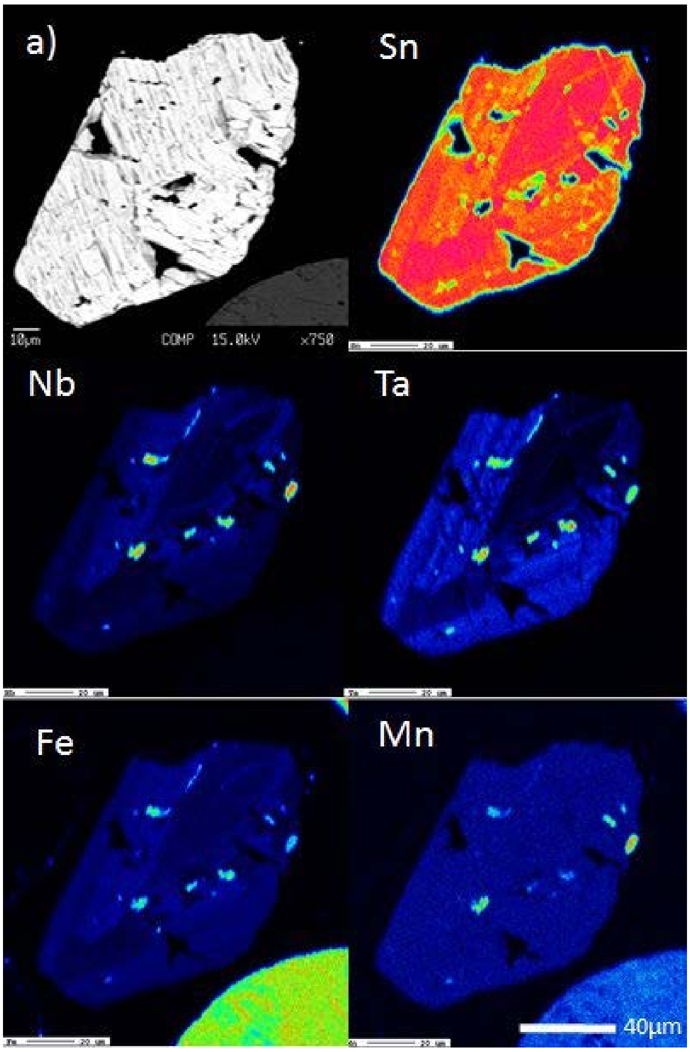

Fig. 2a
Element distribution map.
Cassiterite with tiny inclusions of columbite-tantalite, Rottal/Litschau.

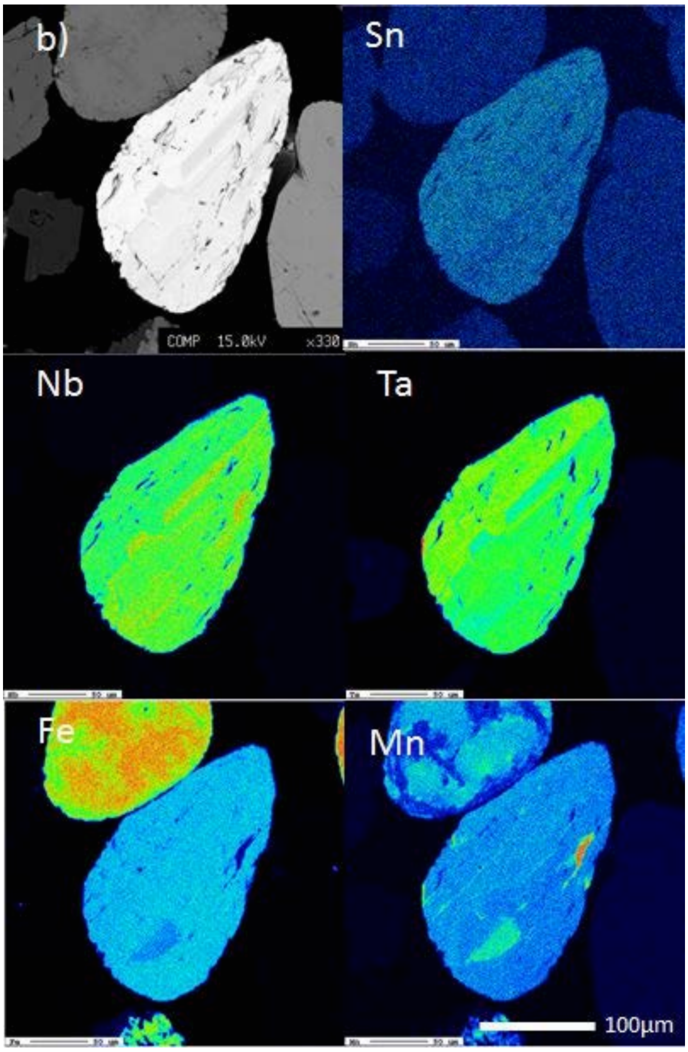

Fig. 2b
Element distribution map.
Larger columbite grain, Rottal-/Litschau.

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References

AHRER, S., RAITH, J.G. (2014): Comparing beneficiation methods for the concentration of Nb-Ta minerals in the heavy minerals fraction of pegmatites from the Eastern Alps. - Mitt. Österr. Miner. Ges., this issue

BARDT, H. (2010): Keine Zukunft ohne Rohstoffe. Strategien und Handlungsoptionen. – Urban Mining Kongress, Iserlohn. http://www.urban-mining-kongress.de/fileadmin/pdfs/vortraege/Dr_Bardt_Urban_Mining_-Iserlohn.pdf

LEGERER, P.A., NEINAVAIE, H., RAITH, J.G. (2014): Mineralogical and geochemical investigations of selected stream sediment anomalies (Nb, Ta, REE) in the Bohemian Massif.- Mitt. Österr. Miner. Ges., this issue

LINNEN, R., TRUEMAN, D.L., & BURT, R. (2014): Tantalum and niobium. In: GUNN, G. (ed.): Critical Metals Handbook. - John Wiley & Sons, 454, 361-384.

LUIDOLD, S. (2013): The situation regarding critical raw materials for the high technological sector in Austria. - In: WEBER, L. & STIFTNER, R. (eds.): Raw materials are the future. Eumicon – Contributions to a resilent raw materials policy, Vol. 2, p. 605-627, Vienna.

LUIDOLD, S. et al. (2013): Kritische Rohstoffe für die Hochtechnologieanwendung in Österreich. - Schriftenreihe 11/2013, bmvit.

SHAW, R.A. & GOODENOUGH, K.M. (2011): Niobium-tantalum. Mineral Profile. British Geological Survey. http://www.bgs.ac.uk/downloads/start.cfm?id=2033

THALMANN, F., SCHERMANN, O., SCHROLL, E. & HAUSBERGER, G (1989a): Geochemischer Atlas der Republik Österreich 1:1.000.000 (Atlasteil). - Geol. B. -A., Wien, 36 p.

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MINERALOGICAL AND CHEMICAL INVESTIGATIONS OF SELECTED STREAM SEDIMENT ANOMALIES (NB, TA, REE) IN THE BOHEMIAN MASSIF

by

Philipp A. Legerer[1], Hassan Neinavaie[2] & Johann G. Raith[1]

[1]Chair of Resource Mineralogy, Department of Applied Geosciences and Geophysics
Montanuniversität Leoben, Peter-Tunner-Straße 5, 8700 Leoben, Austria
[2]Rennfeld 28, 6370 Kitzbühel, Austria

Introduction

As part of a master thesis within the context of the FFG project "Coltan in Österreich" stream sediments and granite eluvial material ("Granitgrus") were drawn and mineralogically and geochemically examined.

On the basis of known geochemical anomalies of Ce, La, Nb, Th, Ti, U, W, Y and Zr as shown in the Geochemical Atlas of Austria (THALMANN et al., 1989) and follow-up projects by VOEST-ALPINE (1986) and "Büro Dr. Pirkl" in cooperation with GBA (1992) (SCHEDL et al., 2013) detailed investigations were performed in two selected study areas in the Bohemian Massif. The principal study area is located in the northeastern Mühlviertel north of Sandl (15 km NE of Freistadt, Upper Austria), the second one in the northwestern Waldviertel south of Weitra (Lower Austria).

The main aim of this study has been to clarify in which mineral phases niobium, tantalum and associated elements (REE, W etc.) are bound and to figure out their provenance. In this context it is of special interest to identify indicators for Nb-Ta mineralization in this region.

Geological overview

The Bohemian Massif as part of the European Variscan orogenic belt hosts the South Bohemian batholith in the Moldanubian zone. The evolution of this composite batholith begins with the partial melting of Cadomian basement series at 360 to 350 Ma (Lower Carboniferous). It is followed by the formation of large masses of geochemically diverse granitoids (Weinsberg granite, Rastenberg granodiorite) and by intrusions of small amounts of I-type granites and huge amounts of S-type granites (Mauthausen, Schrems and Eisgarn type granites) in the Middle Carboniferous (330 to 300 Ma) (KLÖTZLI et al., 1999). The study area north of Sandl is dominated by the Weinsberg granite. However, there are a few small exposures of a more leucocratic granite variety known as Plochwald granite.

This granite differs from the typical Weinsberg granite with respect to its chemical composition but also in its age. The Plochwald granite is more acidic and is strongly peraluminous (e.g., it has a higher content of white mica) and it contains zircons with a different morphology (HAUNSCHMID, 1989). U/Pb measurements of monazite and xenotime from the Plochwald granite yielded ages of 318 ± 4 and 314 ± 4 Ma, respectively (FRIEDL et al., 1992).

Methodology

Details of the sampling and preparation methology are presented by STOCKER & RAITH (2014). Alltogether 21 heavy mineral concentrates (SM), 21 fine fractions (SF) and 3 samples of material from the eluvial zone above granites ("Granitgrus", GG) were taken.

For the fine fraction > 20 g of the uppermost and finest part of a river bank were taken, dried, sieved < 180 µm and ground for chemical analysis. The SM samples were drawn from deeper parts of the streambeds to gain a higher concentration of heavy minerals. 20 kg were sieved < 1.4 mm and enriched in-situ with a gold washing pan. For sampling the eluvial zone 40 kg from the Weinsberg granite were taken. Afterwards the same procedure as with SM material was carried out.

After drying and sieving < 355 µm the SM and GG samples gravity separation with sodium polytungstate (density = 2.95 g/cm^3) was performed. One part of the heavy mineral concentrate was used for preparation of polished thin sections the other part was ground for chemical analysis. Mineral chemical analyses and electron imaging were performed with the Jeol JXA 8200 electron microprobe of UZAG Steiermark installed at Montanuniversitaet Leoben. Also MLA analyses were done at the TU Bergakadmie Freiberg using a REM Quanta 650 FEG instrument and the softwarepackage MLA-Suite 2.907.

Results

Chemistry

Using ICP-ES and ICP-MS major oxides, minor elements and 25 trace elements were analysed at ACME laboratories in Vancouver, Canada. Concentration ranges of some selected elements in the three sample types are listed in Table 1. The dataset shows high concentrations of Nb and Ta in the heavy mineral concentrates (SM) and to a lesser extent in the GG samples. The high concentrations of REE + Y in these two sample types are also remarkable (e.g., up to 1.14 mass% Ce).

[ppm]	SANDL			WEITRA		
	SF	**SM**	**GG**	**SF**	**SM**	**GG**
Nb	16 - 51	445 - 760	122 - 173	11 - 23	421 - 772	100
Ta	1 - 5	40 - 105	8 - 17	1 - 2	57 - 90	10
La	77 - 710	805 - 2160	3180 - 3840	140 - 250	1330 - 5550	1980
Ce	150 - 1550	1840 - 4680	7320 -8950	300 - 525	2750 - 11400	4470
Pr	20 - 185	254 - 580	920 - 1050	35 - 60	330 - 1330	580
Y	40 - 875	1490 - 11310	4960 - 6410	70 - 115	1490 - 4490	1710

Table 1

Concentration ranges (ICP-ES and ICP-MS) of selected elements (ppm) of the different types of samples for the two study areas.

Mineralogy

Microscopic investigation of the SM material did not reveal any distinct niobium or tantalum minerals in the heavy mineral concentrates. Also qualitative EPMA-EDS analysis, element mapping and MLA analyses failed in the identification of distinct Nb and Ta phases. However, quantitative EPMA-WDS measurements allowed identifying ilmenite and Ti-oxides as the main carriers of these two elements. Up to 2850 ppm Nb and up to 2130 ppm Ta were detected in various ilmenites by EPMA-WDS; the mean concentrations are 770 ppm Nb and 690 ppm Ta, respectively. Ilmenite also shows a strong within-grain variation of Nb and Ta (Table 2). Furthermore Nb/Ta ratio < 1 is noticed in many grains. In sample PL013001 (Fig. 1) ilmenite contains about 2.2 mass% Mn and Ti-oxide, likely rutile, contains about 0.10-0.12 mass% W (Table 2). Monazite and apatite (?) have been identified as the main carriers of the REE.

[ppm]	Nb	Ta	W	Mn	Nb / Ta
a - Ilmenite	245	400	0	22684	0,6
b - Ilmenite	585	1605	0	22120	0,4
c – TiO_2	660	1385	1055	210	0,5
d – TiO_2	690	940	1170	225	0,7

Table 2

Results of EPMA – WDS analysis and Nb/Ta values for ilmenite and Ti-oxide in sample PL013001. The position of the analysed spots (a, b, c, d) can been seen on Fig. 1.

Discussion and conclusions

This study confirms regional geochemical Nb-Ta-REE anomalies in stream sediments in the Bohemian Massif, which have already been indicated in previous studies (see above). In the Sandl area higher concentrations of Nb, Ta and REE were detected over 25 km^2. The catchment area of the stream sediments is dominated by the Weinsberg granite with minor exposures of more leucocratic peraluminous granites (Plochberg granite) and other lithologies not explicitly shown on the regional scale geological map. To the south of the study area fine-grained granite ("Feinkorngranit") like the Pleßberger granite and Freistädter granodiorite are known (HAUNSCHMID, 1989).

Ilmenite and titanium-oxides are the exclusive carriers of Nb and Ta (plus W). Both ilmenite and TiO_2 polymorphs contain Nb as well as Ta in a range of several hundreds to thousands of ppm. No distinct Nb-Ta minerals have been found and there is no association of Nb, Ta with Sn. This is in contrast to other areas along the Czech-Austrian border in the Bohemian Massif where Nb-Ta minerals (columbite) have been reported together with cassiterite, wolframite and topaz in stream sediments (BREITER & SCHARBERT, 1998; STOCKER & RAITH, 2014). Hence, we conclude that the studied geochemical anomalies are not caused by distinct Nb-Ta mineralisation (e.g. pegmatites, greisen style mineralisation). It rather reflects geochemical enrichment of Nb and Ta in rock-forming Ti-oxides, which concentrate in the heavy minerals fraction during gravity concentration (panning, heavy liquid separation).

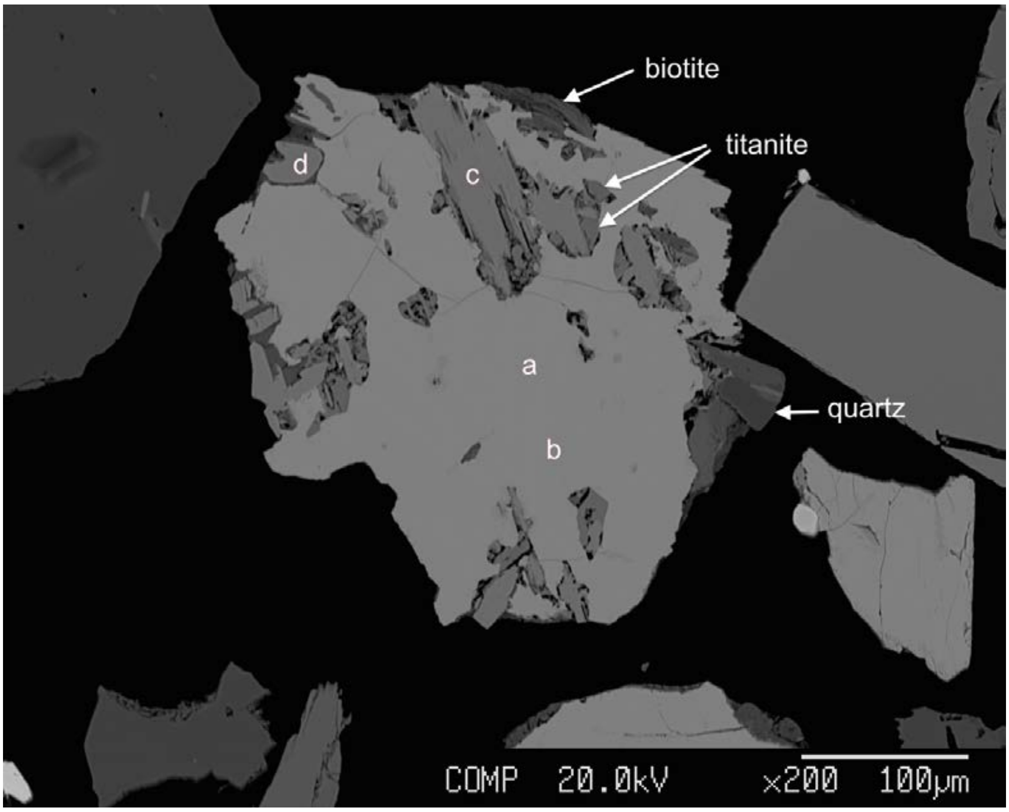

Fig. 1
Ilmenite (a, b) intergrown with Ti-oxides (c, d), titanite, biotite and quartz. For results of the quantitative measurements see Table 2; sample PL013001, grain 22.

The fine fraction of the stream sediments does not reflect the geochemical anomaly as clearly as the heavy mineral separate. Niobium and tantalum values in this sample type are comparable and slightly enriched to average crustal values. The eluvial zone above granites, which formed during in-situ weathering of the underlying granite also shows some enrichment in Nb and Ta.

At present, the provenance of the Nb-Ta bearing Ti-oxides is unclear. Possible source rocks could be the Weinsberg granite, the more leucocratic peraluminous Plochberg granite or even other (minor) lithologies like the fine-grained granites. The provenance of the polyphase grain where ilmenite and TiO_2, both with low Nb/Ta, are associated with titanite, biotite and quartz (Fig. 1) is also unknown. It is interesting that Nb/Ta is < 1 (Table 2) and thus much lower in these analyses than in typical crustal rocks, which are about 11-12 (HUI, 2011). This grain type must therefore come from a source rock characterised by a strong fractionation of Ta over Nb, what is not a very common geochemical feature. It is known that during evolved fractionation of peraluminous granitic melts rich in fluxes like Li and F, Ta is enriched in the strongly fractionated residual granitic melts (LINNEN, 1998).

Such granites may well host economic Nb-Ta-(W-Sn-Li) mineralization (LINNEN & CUNEY, 2005). Thus, although no distinct Nb-Ta phases have yet been discovered in the study area the high Nb and Ta concentrations of ilmenites and Ti-oxides with their unusual low Nb/Ta values make it worth to follow up these first findings.

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References

BREITER K. & SCHARBERT S. (1998): Latest intrusions of the Eisgarn Pluton (South Bohemia – Northern Waldviertel). - Jahrb. Geol. Bundesanst., 141, 1, 25-37.

FRIEDL, G., FRASL, G., VON QUANDT, A. & FINGER, F. (1992): Neue U/Pb Altersdaten aus der südlichen Böhmischen Masse. - Frankfurt. Geowissenschaftl. Arb. , 11, 217-218.

HAUNSCHMID, B. (1989): Das Granitgebiet um Plochwald zwischen Sandl und Windhaag im nordöstlichen Oberösterreich: Mit besonderer Berücksichtigung des dortigen Plochwalder Granit-Typs und des Pseudokinzingits. – Unveröffentl. Diplomarbeit, Univ. Salzburg, 171 S.

HUI, H., NIU, Y., ZHIDAN, Z., HUIXIN, H. & DICHENG, Z. (2011): On the Enigma of Nb-Ta and Zr-Hf Fractionation—A Critical Review. - J. Earth Sci., 22, 1, 52–66.

KLÖTZLI, U., FRANK, W., SCHARBERT, S. & THÖNI, M. (1999): Evolution of the SE Bohemian Massif Based on Geochronological Data – A Review. - Jahrb. Geol. Bundesanst., 141, 4, 377-394.

LINNEN, R. L. (1998): The solubility of Nb-Ta-Zr-Hf-W in granitic melts with Li and Li + F; constraints for mineralization in rare metal granites and pegmatites. - Econ. Geol., 93, 7, 1013-1025.

LINNEN, R. L. & CUNEY, M. (2005): Granite-related rare-element deposits and experimental constraints on Ta-Nb-W-Sn-Zr-Hf mineralization. - Short Course Notes, Geol. Ass. Canada, 17, 45-68.

SCHEDL, A., LIPIARSKI, P., NEINAVAIE, H., BENOLD, CH., PFLEIDERER, S. & BIEBER G. (2013): Bundesweite Erfassung von Rohstoffpotenzialen für kritische Rohstoffe gemäß der Kommissionsstudie, Kritische Rohstoffe für die EU (2010) – Datenaufbereitung betreffend Böhmische Masse, Ergebnisevaluierung als fachliche Basis zukünftiger Projektplanungen. Endbericht Projekt ÜLG – 63. - Geol. Bundesanstalt, Wien.

STOCKER, K. & RAITH, J. G. (2014): Optimization of Nb-Ta prospecting in Austria – routines for sampling, preperation and analysis. - Mitt. Österr. Mineral. Ges., this issue.

THALMANN, F., SCHERMANN, O., SCHROLL, E. & HAUSBERGER, G. (1989): Geochemischer Atlas der Republik Österreich 1:1.000.000 Böhmische Masse und Zentralzone der Ostalpen (Bachsedimente < 0,18 mm). - Geol. Bundesanstalt, Wien.

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COMPARING BENEFICIATION METHODS FOR THE CONCENTRATION OF NB-TA-MINERALS IN THE HEAVY MINERALS FRACTION OF PEGMATITES FROM THE EASTERN ALPS

by

Stefan Ahrer & Johann G. Raith

Chair of Resource Mineralogy, Department of Applied Geosciences and Geophysics
Montanuniversität Leoben, Peter-Tunner-Straße 5, 8700 Leoben, Austria

Introduction

Niobium-tantalum minerals have been reported from several Permian pegmatites (MELCHER et al. 2010), which occur in medium to high-grade polymetamorphic rocks of the Austroalpine tectonic unit (SCHUSTER et al., this issue). For an ongoing master thesis four different pegmatite occurrences in the Wölzer Tauern (Lachtal, Hohenwart), Gleinalpe (Mitterberg) and St. Radegund area (Garrach) have been geologically mapped and sampled in order to check for the presence of Nb-Ta mineralization.

To extract Nb-Ta-minerals out of pegmatite bulk samples different methods of comminution and beneficiation were tested and compared. Sample size was between 1-2 kg. For comminution two different methods were applied: 1) Electric pulse dissaggregation (EPD), Chair of Resource Mineralogy, Montanuniversitaet Leoben; 2) Jaw crushing, Chair of Mineral Processing, Montanuniversitaet Leoben. The second step was separation of the heavy minerals using gravity and magnetic separation. Three different methods were applied: 1) Concentration with a gold washing pan; 2) Heavy liquid separation using sodium polytungstate (SPT) (ϱ = 2,95 g/cm^3) and 3) Magnetic separation using a Frantz-magnetic separator.

Results

The goal of the first experiment was to test the effectiveness of the gold washing pan compared to the other more laborous methods of heavy mineral concentration by SPT heavy liquid separation. Two samples of Mitterberg were crushed with EPD and then concentrated with the gold washing pan to less than 1 g. The remaining material left in the gold washing pan was treated with SPT. Polished sections were prepared from the concentrates and Nb-Ta-minerals (columbites) were microscopically determined and counted. The results show that the recovery for columbite minerals using the gold washing pan is good; for the two samples it is > 92 and 82 %, respectively (Table 1).

Sample	Sample size [kg]	EPD + gold washing pan [Col in the section, #]	Left material treated with SPT [Col in the section, #]	Recovery grade for Col [%]
MB0611	0,9	72	6	92
MB0203	1,1	99	18	82

Table 1
Results of the first experiment (Col ... columbite minerals).

Different methods for separating the heavy minerals were compared in the second experiment. The two samples used are from Mitterberg and Lachtal. The samples were crushed with a jaw crusher to less than 1 mm and then a heavy mineral pre-concentrate of about 50 g was produced with the gold washing pan. With SPT the heavy mineral pre-concentrate was further concentrated to about 10-20 g. Then, this material was split into three thirds. The first third was not treated any further and a polished section was prepared directly from this material. The second third was once more panned with the gold washing pan to less than 1 g of material and the third part was additionally treated with the Frantz-magnetic separator before section preparation, mineral identification and counting (Table 2).

Sample	Sample size [kg]	Jaw crusher + gold washing pan (50g) + SPT (20-10g)					
		1/3	2/3	3/3			
		No further concentration	Gold washing pan, < 1g	Frantz-magnetic separator [A ... Ampere]			
				< 0,10A	0,10-0,25A	0,25-0,50A	> 0,50A
		[Col in the section, #]					
MB0611	1,3	6	49	32			n.a.
LA0205	1,4	2	21	3	17	3	n.a.

Table 2
Results of the second experiment (Col ... columbite minerals).

The results (Table 2) reveal considerable differences between the three separation approaches, especially between the first one and the two others for which additional processing steps have been performed. The least number of columbite minerals was found in the not further processed material (1/3); obviously the material is too diluted and if there is too much material (> 1g) quantitative determination of coltan minerals by microscopy is also problematic.

Heavy liquid separation using SPT also has its limitations. The density of 2.95 g/cm^3 normally used for separating the heavy from the light mineral fraction is too low to remove minerals with higher densities like garnet, tourmaline and spodumene. Using higher density thresholds with SPT is hampered by the dramatic increase of the viscosity of the SPT solution making the physical separation of particles infeasible. For such samples a further separation step using the Frantz-magnetic separator was applied.

It gives good results, especially for separating the non-magnetic spodumene, which is enriched in the > 0.50 A fraction. Separating columbites from garnets and tourmalines in the fractions < 0.50 A depends very much on their composition, especially their iron content.

Conclusion

The most effective combination of methods for quick separation and enrichment of Nb-Ta phases from pegmatites is crushing the bulk sample with a jaw crusher and then concentrating the material to less than 1 g by gravity separation simply using a gold washing pan. This approach yields acceptable recovery rates that are similar to separation of Nb-Ta minerals with combined heavy liquid separation with sodium polytungstate (plus magnetic separation).

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References

MELCHER, F., GÖD, R., KONZETT & J., MALI, H. (2010): Niobium-tantalum-tin-bearing minerals in pegmatites of the Eastern Alps: case studies. PANGEO 2010 Abstracts, J. Alpine Geol., 52, 178-179.

SCHUSTER, R., PETRAKAKIS, K. , ILICKOVIC, T., HEINRICH M., ABART, R. , MELCHER, F. & HOBIGER, G. (2014): Genesis of spodumene-bearing pegmatites within the Austroalpine unit (Eastern Alps): anatectic vs. magmatic derivation. Mitt. Österr. Mineral. Ges. (this issue).