MITT.ÖSTERR.MINER.GES. 160 (2014)

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

by

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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).

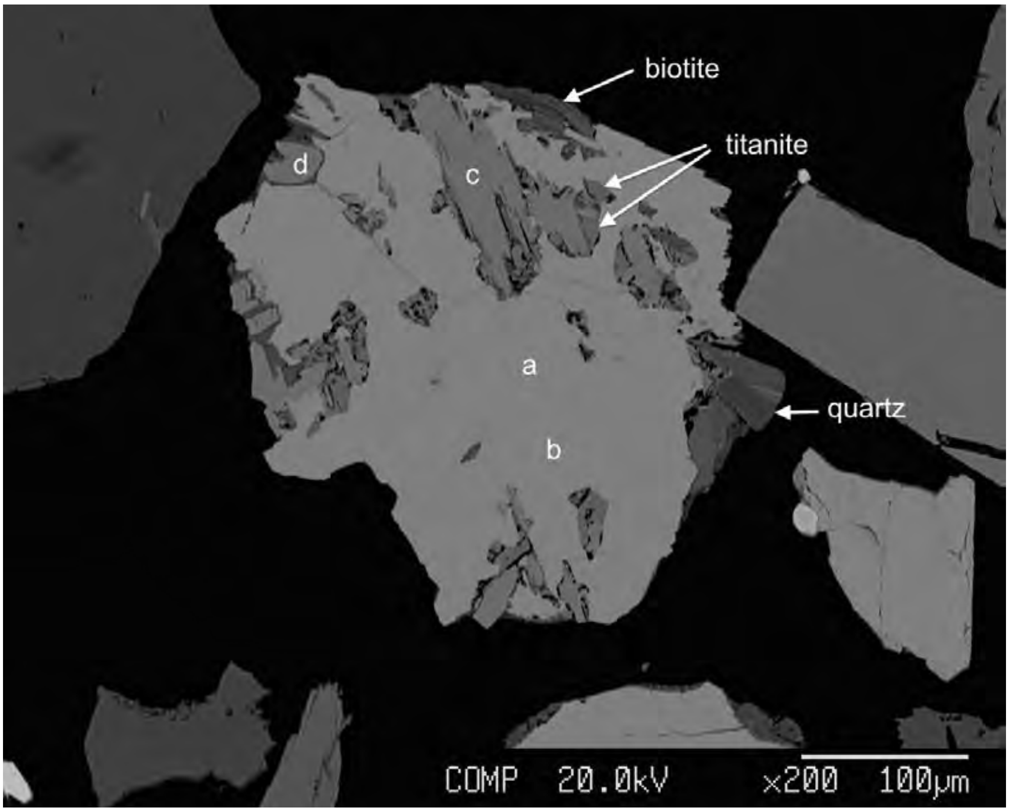

Fig. 1

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.

Acknowledgements

We thank Helmut Mühlhans and Federica Zaccarini for assistance with electron microprobe analyses. Cooperation with GBA Vienna, namely A. Schedl, is greatly acknowledged. K. Stocker, S. Ahrer, H. Mali and F. Melcher are thanked for various inputs in this project. This project including the first author's master thesis is financially supported through FFG project number P062-F-01-05 to Johann G. Raith.

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