FIRST PHOSPHORUS–RICH NB–TA–SN–SPECIALISED GRANITE FROM THE CARPATHIANS – DLHÁ DOLINA VALEY GRANITE PLUTON, GEMERIC SUPERUNIT, SLOVAKIA

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Abstract : First phosphorus-rich Nb-Ta-Sn-specialiced granite was found in the Dlhá Dolina valley (Spiš-Gemer ore Mts., Western Carpathians). Intrusive complex of the Dlhá Dolina is represented by two-mica medium-grained porphyritic granite and biotite granite porphyry with tourmaline in lower part. The upper one consist of protolithionite granite with tourmaline and topas-zinnwaldite granite. The highest part build up by quartz albitites and albitites with greisenised fissures and massive greisen bodies.

Key words: rare-metal granite, Gemeric superunit,

Introduction

In the Western Carpathians the rare metal granites are typically developed only in the Gemeric superunit as specialized S-type Spiš-Gemer granites (Uher and Broska, 1996). After finding and tin prospecting in the Hnilec area (Drnzík, 1982) P-, F, -Li- granite rich in Nb, Ta and Sn was discovered in the Dlhá Dolina valley near Rozňava in the Eastern part of Slovakia (Dianiška, 1983; Malachovský et al., 1983, 1992). This object represents highly evolved granitic system from barren biotite monzogranites to topaz-zinnwaldite albite granite with following albitization and greisenization. The prospecting work have included the set of boreholes, because, it is in fact a hidden granite system, crop out only fragmentally in form of small cassiterite bearing greisen cliff. The longest borehole (DD-3) was 912.9 m. This body of specialized granite can be recorded on the surface only by termic contact metamorphism indicating by patchy fyllites as well as turmalinization, locally accompanied by cassiterite mineralization.

Aim of this work is a brief description of the evolution suite of the ore-bearing granite system from Dlhá Dolina Valey and to compare this system with classical rare-metal granites with greisen mineralization in Bohemian Massif. It is based on structural borehole DD-3, which penetrated through most of the rock types in this granite body.

Geological setting

Intrusive complex of the Dlhá Dolina is emplaced within the intensively folded Lower Palaeozoic volcano-sedimentary complexes metamorphosed in the green schist facies. They are formed mainly by phyllites and meta-pyroclastic material composed from metaryolithes to metadacites as well as layers or lenses of the coarse-grained dolomites and strong steatitized magnezites. Intrusion of granite pluton has been multiphase with development of the several magmatic phases with different level of geochemical evolution. The age of the intrusion is probably analogical to the nearest Hnilec granite body, which is interpreted on the basis of zircon single grain method as Permian-Triassic (245 ± 18 ma, 255 ±22 Ma, respectively, Poller et al., 2002).

Description of granites

The Dlhá Dolina Valey pluton comprise two main constituents: the deeper complex of barren two-mica monzogranite and biotite granite porphyry, and the upper complex of more fractionated rare metal Li-F-granites. The principal granite types from the depth to the apical part have following sucsession:

(1)Two-mica medium-grained porphyritic granite with tourmaline. Porphyritic structure in these granites posses the phenocryst of K-feldspars up to 4 cm and groundmass has around 3-5 mm. The quartz is over K-feldspars, plagioclase, biotite and phengite. Volumetrically analyses is following: Qtz 42.62; KFs 29.20; Plg16.83; Bt I and II 5.51. The tourmaline (1.52 %), zircon, apatite, ilmenite, rutile ± fluorite are characteristic accessory mineral phases. ”Phengite” (3.54 %) a Bt II are identical to those in the granite porphyry. Biotite is strongly chloritized, locally bauritized.

(2)Biotite granite porphyry with tourmaline. This granite along with two-mica medium-grained porphyritic granite with tourmaline form the deeper part of granite pluton, which are situated bellow the upper Li-mica granites. Biotite granite porphyries are younger, then two-mica medium- grained porphyritic granites. This rocks have form several metres thick dykes. Phenocryst of granite porphyry are build up by carlsbad twinned K feldspars and quartz of oval and euhedral shape up to 3 resp. 1 cm (Kfs prevails). Groundmass (0.2 – 1.0 mm) consists of K-feldspar (sub-anhedral locally albitizided often with overgrowth with quartz and enclosing of subhedral quartz < 0.1 mm) and plagioclase (An_{15}), locally microporphyroblastic character (up to 5 mm) Volumetrically the average of groundmass is following: Qtz 30.98 %, Kfs 39.59, Plg 22.63, Bt 3.60, “Phengite” 2.20, Tu 0.19, others 0.81. The typical accessory minerals are biotite I (partialy chloritised), tourmaline I, apatite, zircon, garnet, fluorite. Phengite, tourmaline II, biotite II and garnet are products of Alpine overprinting.

(3)Protolithionite granite with tourmaline forms the lower part of the ore-bearing complex. This is grey, coarse to medium grained leucogranite with common khaki tourmaline in form of aggregate 5 - 15 mm large. Grain size is between 3-8mm, K-feldspars locally up to 12 mm. Typical modal composition is following: Qtz 39.9 % (30.2-45.2 %), K-feldspar 36.3 % (29.5-43.7), albite 14.4 % (9.7-18.2), Li-phengite 3.5 % (1.2-8.0), protolitionite 2.9 % (0.6-5.0), tourmaline 2.7 % (1.0-5.5), topaz 0.03 % (0.0-0.2). Accessory phases: zircon, apatite, monazite (with large brabantite molecule), xenotime, wolframite, wolframixiolite, columbite, cassiterite, uraninite, thorite, goyazite, fluorite, etc. have been identificated by microprobe (Malachovský et al., 1983, 1992; Dianiška, unpublished data).

(4) Topas-zinnwaldite granite represents the youngest intrusion of the plutons and form typical cupolas. While the uppermost part of the cupola was later affected with strong metasomatism, the lower part is preserved in primary shape. This granite is fine-(medium) grained, leucocratic, with typical zinnwaldite flakes (0.x – 4.0 mm). Grain size varies between 0.5-2.0 (-5.0) mm. Modal composition: Qtz: 30.7 % (25.1-34.9 %), K-feldspar – 28.4 % (25.3-35.7 %), albite – 30.2 % (21.5-37.5 %), zinwaldite – 3.5 % (0.9-8.2 %), topaz – 3.0 % (0.0-5.9 %), ”Li-phengite” – 1.9 % (0.2-3.6 %), tourmaline – 1.7 % (0.0-3.7 %). K-feldspar shows Na-metasomitic alteration, which is locally resulted as a new albite. K-feldspar is enriched in phosphorus up to 0.3 wt% of P_2O_5. P-content in albite is substantially lover and albite contains many small inclusions of apatite. Zircon, apatite I, apatite II, fluorite, monazite

(-Ce), xenotime, wolframite, columbite, Fe-columbite, volfrámixiolit, ilmenite, cassiterite, uraninite, Bi-sulfosalts etc. Discontinuity planes are filled with fluorite.

(5) *Quartz albitites and albitites* originated by late processes from the albite-zinnwaldite granite in the uppermost part of the cupola. Modal composition of this grea and white undeformed rocks : Qtz (lesser than 40 %), Ab (more than 60 %, max. 95.2 %). The size of subhedral albite plates varies between 0.3-1.0 mm, anhedral quartz 1.5-4.0 mm. Major constituent of all albitites is apatite in form of inclusions in albite. Origin of this apatite was probably connected with albitization. Phosphorus and calcium originally bounded in feldspar were liberated and formed apatite. Part of this apatite may be also product of Alpine remobilisation. The accessory mineral phases: cassiterite, Nb-Ta minerals (tantalocolumbite, Mn-tantalocolumbite, struverit), U-minerals (uraninite, brannerite),etc.

(6) Greisenised fissures and massive greisen bodies were found inside the albitised upper part of the granite cupola. The thickness of the greisenised zone around the granite fissures rich several dm and x meters. The apatite-albite-quartz and apatite-quartz (472.4-473.0 m) as well as muscovite-albite-quartz, quartz-muscovite and also muscovite greisens (462.0-462.8 m, 490.5-496.0 m a 554.0-552 m) have been recognise. Accessory minerals: cassiterite, Nb-Ta minerály (mainly tantalocolumbite, Mn-tantalocolumbite, Mn-columbite, microlite, bizmutite.

To complete the whole suite of granite phases of the Dlhá Dolina pluton, also dykes of Li-mica and topas – Li-mica microgranites and pegmatites emplaced in the Li-F granites should be mentioned. These dyke rocks were not encountered within the drillhole DD-3.

Geochemistry

Both the lower and upper granite complexes have different geochemical characteristic.

The lower complex of biotite and two-mica granites is peraluminous and calc-alkaline (SiO_2 75-76 %, Na_2O 2.8-3.2 %, K_2O 4.8-5.3 %, P_2O_5 0.1-0.14%, F about 0.2%). Contents of trace elements are comparable with other biotite and two-mica granites in Gemeric unit namely in its western part (area Hnilec): Rb about 400 ppm, Sr 20-30 ppm, Nb aprox. 10 ppm and Sn 20 ppm. Contents of fluxing elements F, P and Li is relatively low - F about 0.1-0.2 wt. %, P_2O_5 approx 0.15 wt. %, Li_2O 0.01 wt. %.

The upper ore-bearing intrusive suite as a whole shows much higher grade of geochemical specialisation. In can be classified as true rare-metal granite (Dianiška,1983, Malachovský et al. 1983 a 1992). In comparison with foregoing granites, the suite is enriched in P (0.5-0.6% P_2O_5), F, Li, Cs, Sn, Nb, Ta, W etc. and depleted in Si, K, Fe, Mg, Zr, REE etc. Some chemical elements show spectacular internal fractionation from the relatively less evolved protolithionite- to the more evolved zinnwaldite granite: F from 0.5 to 1.5%, Li_2O from 0.05 to 0.20 %, Rb from 700 to 1700 ppm, Nb from 30 to 50 ppm. Late albitization is chemically marked by extreme Na-enrichment (up to 10.67 % Na_2O) accompanied by depletion of K_2O (less than 1% K_2O). Destruction of Kfs and micas caused rapid depletion of Li, Rb, F. In contrast, albitites are strongly enriched Sn (in cassiterite). Greisenised parts of granite are enriched in Si and strongly depleted in Na along with Al. Content of K is much higher then in albitites.

Discussion and concluding remarks

The granites occurred in the Dlhá dolina represents the only example of strong evolved granite in the Western Carpathians with intensive fluid reworking. The similarities among the specialized S-type granites in the Spiš-Gemer region are resulted from the similar protolite offering enough volatilies (H_2O, B, F) for the evolved differentiation and postmagmatic alteration.

Direct comagmatic origin of the lower barren and the upper rare-metal granite complexes should be matter of further geochemical study. Both granitic suites are generally similar, representing late-orogenic peraluminous crustal melts. Nevertheless, a rather large chemical gap in P, F, Li, Sn, Nb etc. indicate rather two more-less independent melting episodes of the same protolith than fractionation of all rock types from one parental melt.

In geochemical characteristic, overall shape of the granite cupola and style of greisen mineralisation, the Dlhá Dolina pluton is comparable with well-known Sn-W deposit Krásno in western Bohemia (Jarchovský in Breiter et al. 2001) and other deposits in Krušné Hory/Erzgebirge Mts., e.g. Cínovec, Altenberg),. The major difference should be seen in relation between greisen and feldspatitic rocks. In Krásno, the massive greisen builds up the whole upper part of the cupola. The about 200 m thick position below the greisen is occupied by leucocratic mica-poor granite with individual layers of feldspatites in its deeper part. Within the feldspatites, facies with very different K/Na-ratio occur (K_2O 2-8 wt%, Na_2O 3-8wt%). Standard Li-F granite occurs below the feldspatites. Feldspatization is geologically younger than, or is of the same age, as greisenisation. In contrast, only Na-rich feldspatites was found in Dlhá Dolina, forming the uppermost part of the cupola. Greisen stringers and bodies cut the albitete, this means, that here the greisenisation is younger than the origin of feldspar-rich rocks.

Specialised S-type granites in the Gemeric superunit are Permian-Triassic in age and so there are probably the youngest tin-bearing granites found in the Variscan orogenic unit (Poller et al., 2002). On the contrary, the highly fractionated S-type granites of the European Variscides are usually formed during the Late Carboniferous and Early Permian. Example include the Homolka granite (319 Ma ± 7 Ma, Breiter and Scharbert, 1995), Nebelstein granite (311 ± 1.4 Ma, Scharbert, 1987) in the Czech Republic, Massif Beavoir (305 Ma, Douthou and Pin, 1987) in the French Massif Central. The known granites from the Krušné Hory Mts. (Saxothuringian zone) formed 330-310 Ma. They are product of the post-collisional evolution with dextral transtension regime and gravitationally collapse. It is not fully understand process but it is accompany with underplate magmatic activity. In Bohemian massif, the generally S-type chemistry of P, F-rich granites (Krásno, Podlesí) suddenly changed at about 310 Ma into A-like type F-rich, P-poor granites of Cínovec type. The Gemeric granites, although distinctly younger, still have S-type phosphorus-rich chemistry.

The specialized S-type granites of the Spiš-Gemer area are specific in this sense due to their origin not only during post-collisional extension but, in the initial Alpine rifting of the Variscan orogenic belt (Broska and Uher, 2001, Poller et al, 2002).

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References

Breiter K. & Scharbert S. 1995: The Homolka Magmatic Centre - an Example of Late Variscan Ore Bearing Magmatism in the Southbohemian Batholith. - *Jb. Geol. B. - A., 138,* 9-25.

Breiter K. et al. 2001: Phosphorus- and fluorine-rich fractionated granites. *Excursion guide. CGS Praha,* 108p.

Broska I. & Uher P. 2001: Whole-rock chemistry and genetic typology of the West-Carpathian Variscan granites. *Geol. carpath.* 52, 79-90.

Dianiška I. 1983 : Endo and exo contact post-magmatic alteration of granites from the eastern part of Spiš-Gemer Ore Mts. *Unpublished PhD thesis, Comenius University,* Bratislava (in Slovak).

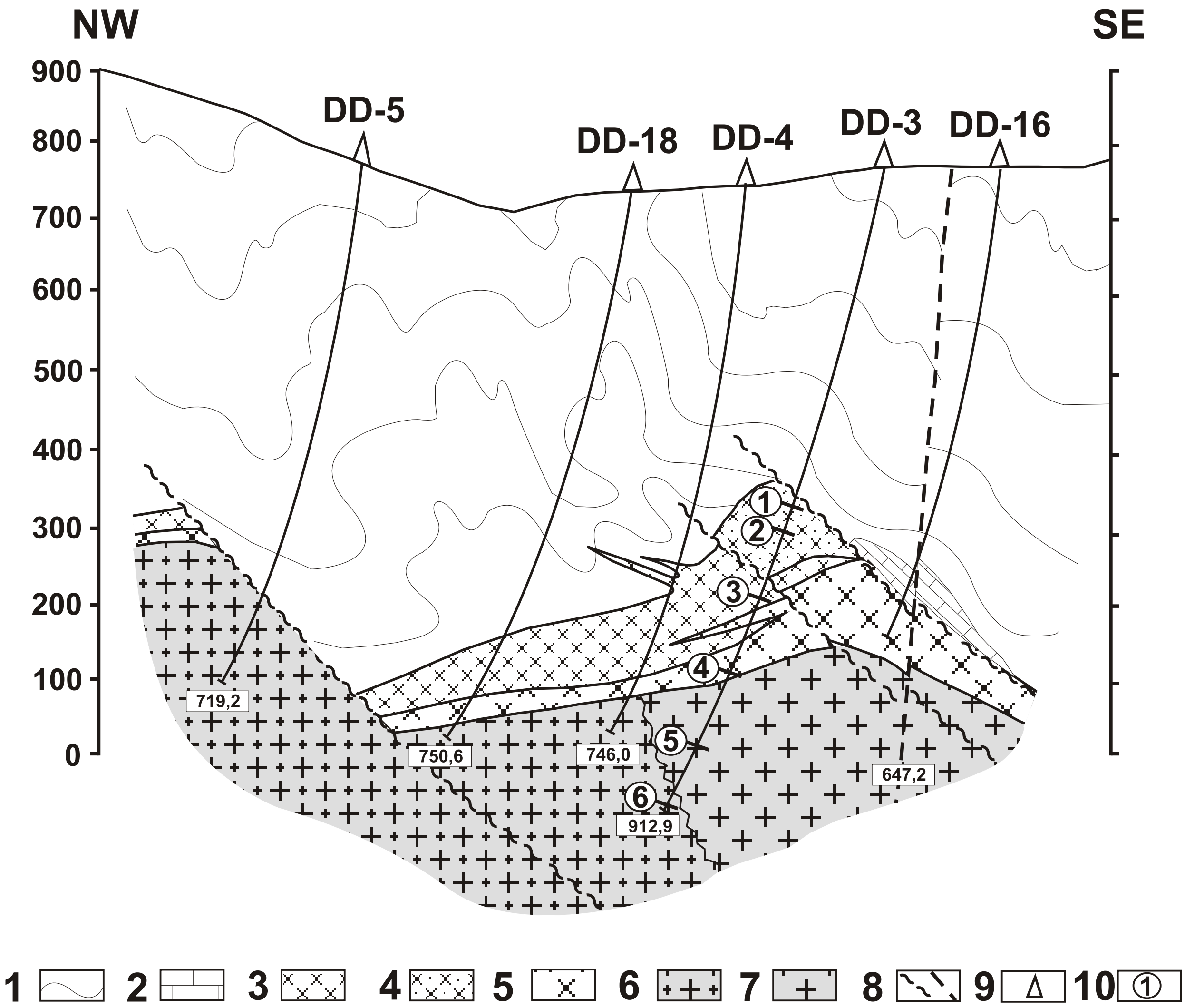
Drndzík E. 1982: Factor controling the tin mineralization in the Hnilec tin ore field. *PhD thesis, Technical University,* Košice, 1-142, (in Slovak).

Duthou J. L. & Pin C. 1987: Etude isotopique Rb/Sr de l'apex granitique d' Echassières. *Géol. Fr.*, 2-3, 63-68 (in French).
Malachovský P. et al. 1983: Final report, high-temperature mineralisation, *VP. Manuscript, Geofond Bratislava* (in Slovak).
Malachovský P. et al.1992: Final report, Gemerská Poloma Sn, *VP. Manuscript, Geofond Bratislava* (in Slovak).
Poller U., Uher P., Broska I., Plašienka D. & Janák M. 2002: First Permian-Early Triassic zircon ages for tin-bearing granites from the Gemeric unit (Western Carpathians, Slovakia): connection to the post-collisional extension of the Variscan orogen and S-type granite magmatism. *Terra nova,* 14, 41-48.
Scharbert S. 1987: Rb-Sr- Untersuchungen granitoider gesteine des Moldanubikums in Österreichs. *Mitt. Österr. Miner. Ges.,* 132, 21-37 (in German).
Uher P. & Broska I. 1996: Post-orogenic Permian granitic rocks in the Western Carpathian-Panonian area: geochemistry, mineralogy and evolution. *Geol. carpath.,* 47, 311-321.

Table 1 The representative whole-rock analyses from the borehole DD-3

Fig. 1. Cross-section through the granite body in the Dlhá dolina area with the location of the boreholes. The analyses of the representative samples from the borehole DD-3 are in the Explanation:
1- metasediments of the Gelnica group, 2 -coarse-grained dolomites, 3-topaz-zinnwaldite albite granite, 4 - albitite with fissure greisens, 5 - protolithionite granite, 6-biotite fine-grained granite porphyry, 7- two-mica medium-grained porphyritic granite, 8 - faults, 9 - boreholes, 10 - position of the samples in the borehole DD-3 (see table 1)

Pos	1	2	3	4	5	6
depth (m)	460	488	580	686	785	910
type rock	topaz-zinwaldite albite granite	topaz-zinwaldite albite granite	albitites with fissure greisens	protolithionite granite	biotite granite porphyry	Ms-Bt coarse granite to porphyritic granites
SiO_2	72.81	79.69	71.68	73.24	75.41	75.57
TiO_2	0.01	0.02	0.03	0.06	0.17	0.14
Al_2O_3	15.80	11.33	15.66	14.11	12.38	12.21
Fe_2O_3	0.05	0.26	0.18	0.47	0.50	0.82
FeO	0.09	0.33	0.51	0.58	0.94	1.19
MnO	0.01	0.02	0.05	0.02	0.03	0.06
MgO	0.14	0.66	0.02	0.26	0.19	0.18
CaO	0.43	0.87	0.72	0.70	0.58	0.56
Li_2O	0.01	0.02	0.28	0.05	0.01	0.01
Na_2O	9.37	0.92	4.13	3.57	2.91	2.85
K_2O	0.61	3.46	4.36	4.66	5.09	4.87
P_2O_5	0.30	0.52	0.49	0.27	0.14	0.12
F	0.08	0.31	1.38	0.48	0.23	0.21
LOI	0.46	1.74	1.15	1.08	0.83	0.89
H_2O-	0.04	0.06	0.05	0.06	0.05	0.04
Total	100.17	100.08	100.11	99.40	99.36	99.62
Rb ppm	106	669	1720	709	370	385
Zr ppm	20	23	15	45	77	79
Nb ppm	62	120	53	22	11	11
Sn ppm	575	794	80	47	25	19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