БЪЛГАРСКА АКАДЕМИЯ НА НАУКИТЕ • BULGARIAN ACADEMY OF SCIENCES

ГЕОХИМИЯ, МИНЕРАЛОГИЯ И ПЕТРОЛОГИЯ • 39 • СОФИЯ • 2002
GEOCHEMISTRY, MINERALOGY AND PETROLOGY • 39 • SOFIA • 2002

Buergerite in pegmatites from the Plana Cretaceous pluton, Western Bulgaria

Vassil Arnaudov, Svetoslav Petrussenko, Chavdar Karov

Abstract. Buergerite, a rare tourmaline, first described from Mexquitic, San Louis Potosi, Mexico, was found in thin (3-10 cm) aplite-pegmatite veins, cutting quartz-monzodiorites of the Plana polyphase pluton. It forms dark-brown, almost black grains, tiny prismatic crystals (2-3 mm) and aggregates, in association with quartz, pale-pink K-feldspar, oligoclase, albite, biotite, magnetite, hematite, ilmenite, garnet, beryl, cyrtolite, allanite, titanite, epidote, adularia, muscovite and stilbite. Buergerite is a relatively late mineral, crystallized after feldspars, magnetite, biotite and garnet, and before the hydrothermal quartz, adularia, muscovite and stilbite. EPMA analyses of a zonal buergerite grain (core-rim) and of a single prismatic crystal gave (wt. %): SiO_2 33.10-32.98; 34.16, TiO_2 1.39-1.09; 1.19, Al_2O_3 24.49-25.15; 26.90, Cr_2O_3 0.00-0.11; 0.00, V_2O_3 0.00-0.15; 0.15, Fe_2O_3 (total) 23.39-22.48; 20.57, MnO 1.23-1.10; 1.19, MgO 0.64-1.07; 1.07, CaO 0.38-0.39; 0.34, Na_2O 2.38-2.71; 2.59, K_2O 0.12-0.00; 0.03. Wet chemical analysis for Fe of two mineral separates of buergerite shows (wt. %): Fe_2O_3 20.75, FeO 0.58 and Fe_2O_3 20.57, FeO 0.36. The measured density is respectively 3.30 and 3.25 g/cm^3. It is supposed that the buergerite mineralization is related to the high Fe^{3+} potential of the quartz-monzodiorites. The high content of magnetite and hematite in the aplite-pegmatites supports this hypothesis.

Key words: buergerite, aplite-pegmatite veins, Cretaceous pluton

Addresses: V. Arnaudov - Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; E-mail: arnaudov@geology.bas.bg; S. Petrussenko and Ch. Karov - National Museum of Natural History, 1000 Sofia, Bulgaria

Арнаудов В., С. Петрусенко, Ч. Каров. 2002. Бюргерит в пегматити от Планския креден плутон, Западна България.- *Геохим., минерал. и петрол.*, **39**, 75-80.

Резюме. Рядко срещаният турмалин, бюргерит, установен за пръв път в Mexquitic, San Louis Potosi, Мексико, е намерен в тънки (3-10 cm) аплит-пегматитови жили, присичащи кварцмонцодиоритите на Планския наставен плутон. Бюргеритът образува тъмнокафяви, почти черни зърна, дребни призматични кристали (2-3 mm) и агрегати, в асоциация с кварц, бледорозов калиев фелдшпат, олигоклаз, албит, биотит, магнетит, хематит, илменит, гранат, берил, циртолит, аланит, титанит, епидот, адулар, мусковит и стилбит. Бюргеритът е относително късно образуван, след фелдшпатите, магнетита, биотита и граната, но преди хидротермалния кварц, адулара, мусковита и стилбита. Резултатите от ЕРМА на зонално зърно от бюргерит (централна част и периферия) и на отделен призматичен кристал, показват (тегл.%): SiO_2 33,10-32,98; 34,16, TiO_2 1,39-1,09; 1,19, Al_2O_3 24,49-25,15; 26,90, Cr_2O_3 0,00-0,11; 0,00, V_2O_3 0,00-0,15; 0,15, Fe_2O_3(total) 23,39-22,48; 20,57, MnO 1,23-1,10; 1,19, MgO 0,64-1,07; 1,07, CaO 0,38-0,39; 0,34; Na_20 2,38-2,71; 2,59, K_20 0,12-0,00; 0,03. Мокрият химичен анализ на Fe, на две отделни сборни проби от бюргерит, показва (тегл.%): Fe_2O_3 20,75, FeO 0,58 и Fe_2O_3 20,57, FeO 0,36. Измереното относително тегло на бюргерита в двете проби е съответно 3,30 и 3,25 g/cm^3. Предполага се, че образуването на минерала е свързано с висок потенциал на Fe^{3+} в кварцмонцодиоритите. Високите съдържания на магнетит и хематит в аплит-пегматитите подкрепят такава хипотеза.

Introduction

Buergerite, $NaFe_3^{3+}Al_6(BO_3)_3Si_6O_{18}(O,F)_4$, is the Fe^{3+} analogue of schorl, $NaFe_3^{3+}Al_6(BO_3)_3Si_6O_{18}(OH)_4$. First it was found in hydrothermally altered tuffs and clayey rhyolites near Mexquitic, San Luis Potosi, Mexico. It was initially described as a Fe^{3+}-tourmaline (ferric tourmaline, Mason et al., 1964) and two years later was specified as a new mineral species of the tourmaline group (Donay et al., 1966). In a study of tourmalines from pegmatites of Plana Mountain, tourmaline was found with a chemical composition similar to those of the buergerite from Mexico.

Geological setting

The Plana pluton (~400 km^2) is situated 30 km to the south of Sofia in the Western Sredna Gora. According to Boyadjiev (1971), it was formed by two consecutive magma impulses. During the first impulse, small bodies of gabbro-pyroxenites, gabbro and gabbro-diorites, were emplaced into Paleozoic high-grade metamorphic rocks. The second impulse, built-up of diorites, quartz-diorites, quartz-monzodiorites, granodiorites and leucogranites, forms the major part of the pluton. Related to the second impulse are pegmatites of microcline, oligoclase-microcline and oligoclase-albite-microcline composition (Boyadjiev, Ivanov, 1975). Commonly the pegmatites are presented as veins, more rarely as lenticular bodies, some of them zonal and well differentiated. In the western part of the pluton, aplite-pegmatite veins prevail. The typomorphic accessory minerals in most of pegmatites in the pluton are magnetite, tourmaline and zircon. Apatite, titanite, garnet and epidote are constantly present. Additionally were determined: hematite, ilmenite, allanite, monazite, betafite, pyrite, molybdenite (Boyadjiev, Ivanov, 1975), uraninite and thorogummite (Hisina, 1966).

Preceding studies of Plana tourmalines

The presence of tourmaline in the Plana pluton was mentioned for the first time by Bonchev (1923). He described the morphology of black, prismatic tourmaline crystals (schorl) in quartz and pegmatite veins near the villages of Belchin, Shiroki dol, Gorni Okol and Dolni Okol. Vergilov (1955) studied the mineral composition of zonal pegmatite veins near the village of Kalkovo. He related tourmaline (schorl) formation to two high themperature phases. He assumed that the second tourmaline generation replaced the microcline in the graphic quartz-feldspar zones. In the pegmatites described by Vergilov (1955), tourmaline was associated mainly with quartz, microcline, oligoclase, albite, biotite and allanite. Breskovska and Eshkenazy (1961) performed the first chemical and X-ray diffraction study of tourmaline from a pegmatite of the Plana pluton. A black tourmaline from a pegmatite vein near the village of Dolni Okol, as well as all the tourmalines from Vitosha, Sredna Gora, Rhodopes and Sakar Mountains, studied by these authors, have been determined as members of the schorl-dravite series.

Morphology and mineral composition of buergerite-bearing pegmatites

Buergerite was found in several thin, 1.5-10 cm up to 1.6-2 m long, aplite-pegmatite veins, which intersect strongly weathered to gruss quartz-monzodiorites in the western periphery of the pluton. The deposit lies in the southern outskirts of Kovachevtsi village, in the scarp of the road to Samokov. Immediately to the north of this place Neogene-Pliocene sediments outcrop.

Similarly to the host quartz-monzodiorites, the pegmatite veins are heavily weathered in places to gruss. They have an aplitoid appearance. Fine-grained (0.15 mm to 1.5-2 mm) quartz-feldspar mass prevails, consisting of potassium feldspar, oligoclase, quartz and biotite. Isolated microcline crystals of pale-pink colour, up to 3×1.5 mm long and up to 2-3 mm thick, can be observed, as well as nests of pegmatoid or micro-block texture consisting of perthitic microcline (sized up to 2×2 cm), fine grained albite (up to 3×3 mm), grey quartz (0.5×1 mm) and biotite (1-5 mm). Aggregates (up to 0.5×1 cm) of fine-grained, black buergerite, are found often in these nests along with quartz. In some veins, small cavities in the central part of the pegmatite nests, are filled with fine quartz crystals and nontransparent adularia, growing on earlier crystallized potassium feldspar. In such cavities also rosette-shaped aggregates of pale-green, fine-flaked muscovite and of stilbite occur. In the contact zones of some aplite-pegmatite veins, small micrographic quartz-feldspar complexes are observed, which alternate with apographic complexes towards the vein centre. A tarry-black, very fine (1-2 mm) buergerite is found replacing often the feldspars. It forms characteristic graphic or apographic inter-growths with quartz. The relationships of buergerite to the other minerals in the aplite-pegmatite veins attest its relatively later formation, after magnetite, biotite, feldspars and garnet, but before hydrothermal quartz, adularia, stilbite and fine-flaked greenish muscovite. In places, fine buergerite veinlets intersect also quartz grains of the main aplite-pegmatite mass. The most frequent accessory mineral is magnetite, found in all zones of the veins. It forms both fine (<0.1 to 2-3 mm) irregular grains and octahedral crystals of same size, usually strongly oxidized. In addition to the uniformly presented zircon and apatite often hematite, almandine, cyrtolite, allanite, titanite and epidote occur. In a micro-block zone, in the central part of a non-massive aplite-pegmatite vein, an aquamarine grain, sized 3×3 mm, was found at a boundary between quartz and potassium feldspar. This is the first beryl finding in pegmatites, related to a Cretaceous intrusion of the Sredna Gora structural zone. Buergerite was found also in a quartz-tourmaline lens to the south of Dolni Okol village.

Chemical composition of buergerite

Microprobe analyses of a small grained (2×2 mm) tourmaline aggregate (sample 1, Table 1), associated with quartz, plagioclase, potassium feldspar and magnetite in a thin (~3 cm) aplite-pegmatite vein near the Kovachevtsi village, as well as of an elongated prismatic (0.7×0.2 mm) tourmaline crystal (sample 2) from the quartz-tourmaline lens near Dolni Okol village, determine the samples studied as high-iron varieties of iron-containing tourmalines. In tourmaline from Kovachevtsi village a zonation, perpendicular to the three-fold axis, can be observed. The inner crystal part (1-core, Table 1) shows higher Fe, Ti and Mn content, whereas the outer part (1-rim) is characterised by higher Al, Mg and Na content. In the peripheral zone Cr and V are present too. The chemical composition of the tourmaline from the quartz-tourmaline lens near Dolni Okol village is similar (Table 1).

The interpretation of the major components data from the microprobe analyses for the general formula of the tourmaline group minerals, $XY_3Z_6(BO_3)_3Si_6O_{18}(OH)_4$, places the tourmaline from the two deposits in Plana close to the Fe-tourmalines - schorl and buergerite. Wet chemical phase analysis of Fe, performed by B. Karaivanova in two mineral samples of fine aggregate grains from neigh-bouring thin aplite-pegmatite veins near Kovachevtsi village, determines the tourmaline as buergerite. The first mineral separate of buergerite includes that tourmaline aggregate, on a grain of which the microprobe analyses 1-core and 1-rim were performed. It contains 20.75 wt. % Fe_2O_3 and 0.58 wt. % FeO. The second sample contains 20.57 wt. % Fe_2O_3 and 0.36 wt. % FeO. The measured density of the first sample is 3.30 g/cm^3 and 3.25 g/cm^3 of the

Table 1. *Microprobe analyses of buergerite (wt. %): 1 and 2 - from Plana; 3 (a - range from 14 specimens and b - mean values) - from Mexquitic, Mexico, after Dunn (1976); 4 - wet chemical analysis of buergerite from Mexquitic, Mexico, after Donnay et al. (1966)*

Таблица 1. *Електронномикросондови анализи на бюргерит (тегл. %): 1 и 2 от Плана; 3 (а – вариации на съдържанията в 14 образеца, b – средна стойност) от Mexquitic, Mexico (Dunn, 1976); 4 – мокър химически анализ на бюргерит от същото находище (Donnay et al., 1966)*

Samples	1 - core	1 - rim	2	3a - range	3b - mean	4
SiO_2	33.10	32.98	34.16	32.99 - 35,15	34.22	33.86
TiO_2	1.39	1.09	1.19	0.31 - 0.80	0.55	0.55
Al_2O_3	24.49	25.15	26.90	29.33 - 31.46	30.30	30.79
Cr_2O_3	-	0.11	-	-	-	<0.01
V_2O_3	-	0.15	0.15	-	-	<0.01
Fe_2O_3	23.39	22.48	20.57	17.59 - 20.04	18.77	17.62
FeO						1.27
MnO	1.23	1.10	1.19	0.07 - 0.14	0.1	0.13
MgO	0.64	1.07	1.07	0.08 - 0.35	0.16	0.13
CaO	0.38	0.39	0.34	0.24 - 0.99	0.64	0.69
Na_2O	2.38	2.71	2.59	2.32 - 2.47	2.38	2.46
K_2O	0.12	-	0.03	-	-	0.07
Total	87.12	87.23	88.19		87.12	87.57
		Cations on the basis of 24.5 [O]				
Si	5.68	5.64	5.71		5.69	5.61
Ti	0.18	0.14	0.15		0.07	0.07
Al	4.95	5.07	5.30		5.94	6.01
Cr	-	0.01	-		-	-
V	-	0.02	0.02		-	-
Fe	3.02	2.89	2.59		2.35	2.37
Mn	0.18	0.16	0.17		0.01	0.02
Mg	0.16	0.27	0.27		0.04	0.03
Ca	0.07	0.07	0.06		0.11	0.12
Na	0.79	0.90	0.84		0.77	0.79
K	0.03	-	0.01		-	0.01
Total	15.06	15.17	15.12		14.98	15.03

Wet analyses for Fe of two mineral separates of buergerite from pegmatites near Kovachevtsi (wt. %): Fe_2O_3 20.75, FeO 0.58 and Fe_2O_3 20.57, FeO 0.36

Мокър фазов анализ на Fe в две сборни проби от бюргерит от пегматити при Ковачевци (тегл. %): Fe_2O_3 20,75, FeO 0,58 и Fe_2O_3 20, 57, FeO 0,36

second one; the density of the buergerite from Mexquitic, Mexico, is 3.31 g/cm^3.

On the Al-Fe(tot)-Mg diagram after Henry and Guidotti (1985) the investigated Plana tourmalines plot near the point of tourmaline end-members schorl and buergerite, into the area of rich in Fe^{3+} quatrz-tourmaline rocks (Fig. 1). The Mexico buergerite lies slightly above the Fe^{3+} tourmaline end-member, in the area of Li-poor granitoids and associated with them pegmatites and aplites. This is due to the higher Al content of this buergerite, compared to the theoretical buergerite composition. The buergerite samples near Kovachevtsi and Dolni Okol villages are placed just below the end-member point, due to their quite lower Al content.

Discussion

The microprobe analyses, toghether with wet chemical determination for Fe_2O_3 and FeO, are

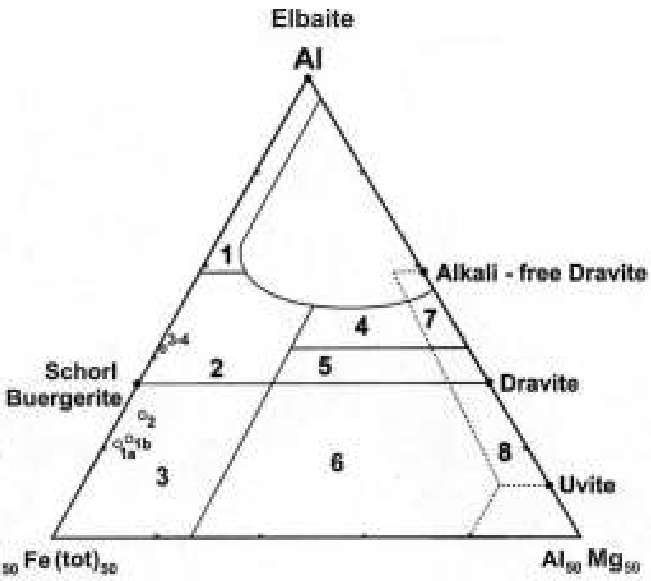

Fig.1 Al-Fe(tot)-Mg diagram (in molecular proportion) for tourmalines from various rock types (after Henry and Guidotti, 1985): 1 - Li-rich granitoid pegmatites and aplites; 2 - Li-poor granitoids and their associated pegmatites and aplites; 3 - Fe^{3+}-rich quartz-tourmaline rocks; 4 - metapelites and metapsammites coexisting with an Al-saturating phase; 5 - metapelites and metapsammites not coexisting with an Al-saturating phase; 6 - Fe^{3+}-rich quartz-tourmaline rocks, calc-silicate rocks, and metapelites; 7 - low-Ca metaultramafics and Cr, V-rich metasediments; 8 - metacarbonates and meta-pyroxenites; **O** - buergerites from Plana; ⊙ - buergerite from Mexquitic, Mexico (Donnay et al., 1966; Dunn, 1976)

Фиг. 1. Al-Fe(tot)-Mg диаграма (в молекулярни отношения) за турмалини от различни типове скали (по Henry & Guidotti, 1985): 1 - богати на Li гранитоидни пегматити и аплити; 2 - бедни на Li гранитоиди и асоцииращи с тях пегматити и аплити; 3 - богати на Fe^{3+} кварц-турмалинови скали; 4 - метапелити и метапсамити, съдържащи преситена на Al фаза; 5 - метапелити и метапсамити, несъдържащи преситена на Al фаза; 6 - богати на Fe^{3+} кварц-турмалинови и калциевосиликатни скали, и метапелити; 7 - нискокалциеви метаултраметаморфити и богати на Cr и V метапсамити; 8 - метакарбонати и метапироксенити; **O** - бюргерити от Плана; ⊙ - бюргерит от Mexquitic, Мексико (Donnay et al.,1966; Dunn, 1976)

the basis to consider the investigated tourmalines from the deposits near Kovachevtsi and Dolni Okol villages as buergerite. Their chemical composition is very similar to that of buergerite from Mexquitic, Mexico (Donnay et al., 1966), the only one deposit of the mineral we know from the literature. In addition to the wet chemical analysis of this buergerite, Dunn (1976) published data of 14 microprobe analyses of 14 separate tourmaline samples from the same deposit (Table 1). The variations in content of the major components are small.

The Plana buergerite samples have several substantial differences compared to the composition of the Mexican buergerite. They have lower Al content and correspondingly higher Fe content. The tourmaline from the quartz-tourmaline lens near Dolni Okol village has closer Al and Fe content, compared to the buergerite from Mexico. Other differences are the twice higher Ti content and almost one order of magnitude higher Mn content of the Plana buergerite. The difference in the chemical composition of the Plana and Mexican buergerites can be explained by the composition of the solutions from which they have crystallized, and respectively by the chemical composition of the embedding magmatic rocks. The rocks, including the Plana buergerite bearing pegmatites, have higher total alkaline content. To a grate extent, it determines the higher Fe^{3+} potential of the rocks. This is attested by the pink-coloured potassium feldspars, due to Fe^{3+} presence, as well as by high magnetite and hematite content in the aplite-pegmatite veins near Kovachevtsi village. The relatively high Mn content, characteristic of the Plana buergerite samples, is due to its high concentration in the pegmatite-forming fluids. Magnetite, associated with buergerite, has also increased Mn content (1.36-1.62 wt. % MnO). Mn was not found in magnetite samples from the other pegmatite veins, outcropping to north and south of Dolni Okol and Gorni Okol villages, where tourmaline is presented by schorl-dravite, dravite-schorl and an intermediate dravite-feruvite composition (according to preliminary data). These tourmalines have low Mn content, usually below 0.2 wt. %.

A small number of buergerite findings are also described by other authors (Stanek, Schnorrer, 1993; Ertl, 1995; Betti et al., 1999). However, they are characterised only by X-ray diffraction data and refraction indexes, with no information about the chemical composition, which does not allow their precise classification as buergerite.

It is possible, after correct determination of their Fe^{3+} content, some of the published Fe-tourmalines to turn out to be buergerite.

References

Betti, C., D. Paesani, G. Pagani. 1999. I minerali della cava “MAFFEY” (Campiglia Marittima, Livorno). - *Rev. Mineral. Ital.*, **3**, 176-185.

Bonchev, G. 1923. Minerals of Bulgaria. - *Ann. Univ. Sofia, Fac. Phys.-Mathem.,* **19**, 1, 1-212 (in Bulgarian).

Boyadjiev, S. 1971. Petrology of the Plana pluton. - *Bull. Geol, Inst., Ser. Geochem., Mineral., Petrogr.,* **20**, 219-242 (in Bulgarian).

Boyadjiev, S., I. Ivanov. 1975. On the pegmatites in the Plana pluton. - *Geochem. Mineral. Petrol.*, **3**, 78-87 (in Bulgarian).

Breskovska, V., G. Eshkenazy. 1961. Tourmaline from some occurrences in Bulgaria. - *Ann. Univ. Sofia, Fac. Biol.-Geol.-Geogr., 2 - Geol.*, **54**, 15-48 (in Bulgarian).

Donnay, G., C.O. Ingamells, B. Mason. 1966. Buergerite, a new species of tourmaline. - *Amer. Mineral.*, **51**, 198-199.

Dunn, P.J. 1976. Buergerite, uniformity of composition. - *Amer. Mineral.*, **61**, 1029-1031.

Ertl, A. 1995. Elbait, Olenit, Dravit-Buegerit-Mischkristalle, Dravit, Uvit und ein neuer Al-Tourmalin (?) von österreichischen Fundstellen. - *Mitt. Österr. Miner. Ges.*, **140**, 55-72.

Henry, D.J., C.V. Guidotti. 1985. Tourmaline as a petrogenetic indicator mineral: An example from the staurolite-grade metapelites of NW Maine. - *Amer. Mineral.*, **70**, 1-15.

Hisina, T. 1966. Pseudomorphic replacement of uraninite by thorogummite in the pegmatites of the Rila Mountain. - *Trav. Geol. Bulg., Ser. Geochim., Mineral., Petrogr.*, **6**, 243-246 (in Bulgarian).

Mason, B., G. Donnay, L.A. Hardie. 1964. Ferric iron tourmaline from Mexico. - *Science*, **144**, 71-73.

Stanek, J., G. Schnorrer. 1993. Phenakit und Buergerit aus dem Skarnsteinbruch Vlastejovice bei Zruc nad Sazovou in Bohmen. - *Aufschluss*, **44**, 161-164.

Vergilov, V. 1955. Mineral composition and geochemistry of pegmatites of Kalkovo by Samokov - *Izv. Geol. Inst.*, **3**, 25-45 (in Bulgarian).

Приета на 28. 12. 2002 г.
Accepted December 28, 2002