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GENETICAL TYPES OF THE TITANIUM MINERALIZATIONS IN THE METAMORPHIC AND BASIC ROCKS OF THE RHODOPE MASS IN SERBIA (YUGOSLAVIA)

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INTRODUCTION

Various types of titanium mineralizations in the Serbian portion of the Rhodope geotectonic unit are described in this paper. The data presented are based on complex field and lab. examinations carried out in the 1973—1980 period. Field work including the sampling of the ores and the rocks were mainly carried out by V. VUJANOVIĆ and M. TEOFILOVIĆ, and laboratory examinations by mineralogists and chemists. Ore microscopic examinations were performed by V. VUJANOVIĆ, petrographic ones by V. ĆEBIĆ, chemical analysis by Z. ČERVENJAK and V. OCOLOKJIĆ and spectrographic ones by S. MAKSIMOVIĆ and M. ARSENIJEVIĆ. X-ray diagrams were explained by V. VUJANOVIĆ and M. VUKASOVIĆ.

The geologic-tectonic study was done by M. TEOFILOVIĆ.

The collected data, the synthesis as well as the petrologic, geochemical, mineralogical and metallogenetic study were carried out by the authors.

RHODOPE MASS

The Rhodope geotectonic unit *(Fig. 1)* starts east of Beograd, south of the Danube (i.e. of the Pannonian Basin) passing throughout Serbia in the SSE direction about 300 km. in lenght (air distance). In SE Serbia and NE Macedonia Rhodope mass turns eastward passing over Bulgaria ending in Asia Minor.

The Rhodope geotectonic unit was mainly formed during Hercynian movements in form of a complex anticlinorium which was relativelly stable throughout later geological events. In fact, in the Posthercynian and especially within the period of the Alpine movements the Rhodope mass represented a mountain barrier which separated the eastern Balkan (Carpatho-Balkan range) from the western one (Dinarids), both of which were raising during the Alpine orogenesis [K. PETKOVIĆ and P. PAVLOVIĆ, 1976].

The crystalline core of the Rhodope mass consists prevailingly of high crystalline schists and also of the lower ones. The former include migmatite gneisses, para—and ortho-amphibolites, amphibole schists, biotite, mica and two mica schists, marbles, cipolines, quartzites etc. In the stratigraphic column these rocks are multiply alternating. The formation described is Prepaleosoic and is overlain by schists of lower crystallinity such as various types of phyllites and "green schists" which are often felsparized and, in a lesser degree, by limestones and quartzites [K. PETKOVIĆ and P. PAVLOVIĆ, 1976].

Most of the mountains in the Rhodope mass in Serbia are built up of the described crystalline schists, such as the mountains Crni Vrh, Juhor, Stalać Hills,

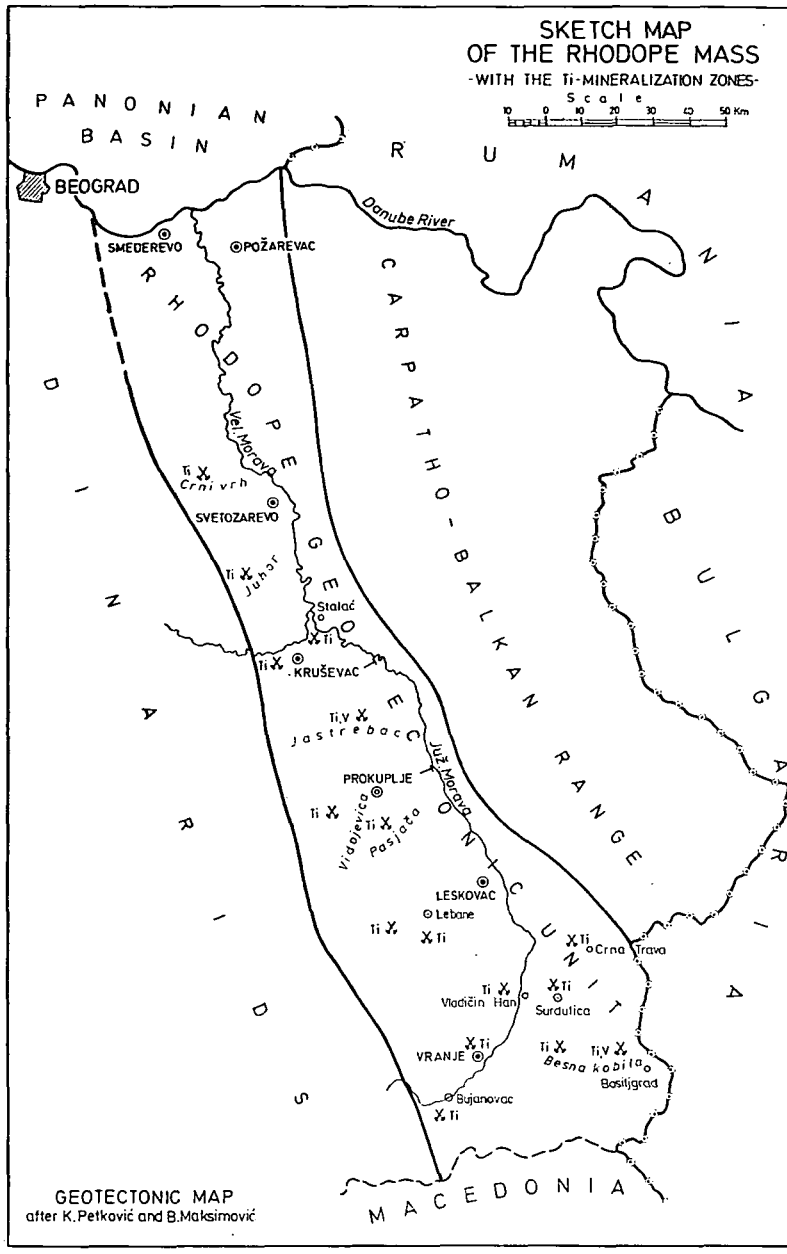

Fig. 1

Jastrebac, Vidojevica, Pasjača, and the Jablanica and the Vranje areas, further on Crna Trava, Besna Kobila, Kriva Feja, the vicinity of Bosiljgrad and others.

Along the eastern and western borders of the Rhodope anticlinorium in Serbia, deep dislocation lines were formed in which basic magmatites intruded. They occasionally occur in the Rhodope mass in form of occurrences or as relativelly large

massifs. These rocks intruded throughout the late Caledonian and the young phases produced the Posthercynian gabbros. In the Saalian and Pfalzian phase of the Hercynian orogenesis various types of granitoids were formed, accompanied by aplites and pegmatites [K. PETKOVIĆ and P. PAVLOVIĆ, 1976].

During the Alpine movements strong granitization of the metamorphic, granitoid and gabbroic rocks took place and by this process the large migmatite complex was produced within the whole Rhodope mass in Serbia. Throughout the granitization processes the granitoids were alkalized, dacites and andesites were felsparized or granitized, whereas meta-gabbros were alkalized or converted into diorites, quartz-diorites and plagiogranites.

In the Tertiary/Quaternary period the latest granitization took place and produced the mineralizations of the titanium metasomatic front, and this was followed by the later alkaline metasomatism. These titanium mineralizations are the most widespread in the whole Rhodope mass in Serbia.

TITANIUM MINERALIZATIONS

Examinations described have demonstrated that the highest concentrations of titanium show such rocks as meta-gabbros, granitized gabbros, amphibole gneisses and amphibolites, occasionally also biotitized and garnetized schists, whereas serpentinites, as a rule, show very low contents of the mentioned metal.

On the basis of the field investigations and the laboratory examinations numerous titanium mineralizations have been detected throughout the Rhodope mass in Serbia, including a number of titanium deposits.

The mineralizations described, depending on their genetical features, occur in various rocks and differ in size and way of appearance.

In general, there exist four genetical types of the titanium occurrences such as:

1. Titanium minerals as accessory constituents in the gabbroic and metamorphic rocks. The dominant titanium mineral has usually been ilmenite, but occasionally also rutile, or sphene or both of them. In the gabbroic rocks these minerals often occur as minute grains, or crystals (ilmenite, rutile), which are often elongated with cleavages of Fe—Mg minerals. The relatively coarse ilmenite grains are in many cases partly or totally transformed into leucoxene, in much less degree in rutile and sphene.

In some localities also ilmenite-hematite and hematite-ilmenite have been recognized, accompanied by some hematite-rutile. The primary accessory minerals had been ilmeno-hematite and hemato–ilmenite, later transformed into the above cited associates. The latter as a rule occur in the gabbroic rocks, the amphibolites and in the „greenschists". Hematite from the associates described is usually cream-white, showing rate internal reflections as well as lower reflectivity, indicating the presence of some unexsolved $FeTiO_3$. In the dioritized amphibolites situated near the town of Lebane, beside ilmenite-hematite and hematite-ilmenite also accessory sphene occurs namely as numerous minute "droplets" forming relativelly large patches. The primary hemato–ilmenite and ilmeno–hematite, as well as the sphene "droplets" are high-temperature products of the remobilization of the accessory titanium, and the latter process took place during the dioritization of the amphibolites.

Finally, in some cases also Ti-magnetite has been recognized as the accessory mineral, sometimes accompanied by some magnetite.

2. The titanium mineralizations in the gabbroic rocks are detected in many cases in the studied region and are genetically related to these rocks. The dominant titanium mineral has always been ilmenite frequently converted into leucoxene or

into rutile and sphene. As a rule, ilmenite is coarse but rarely also crystalline. In the polished sections ilmenite concentrations may reach up to 80%, and its average contents in the ore bodies is up to 10%. The average vanadium contents in this type of deposit reach up to 0.15%.

In the gabbroic rocks ilmenite is rarely associated with the other metallic minerals like magnetite and Ti-magnetite and the latter minerals are scarce. Occasionally sulphide assemblages may occur sparsely, namely in form of small grains disseminated in the host rock. These assemblages include pyrrhotite, pyrite, pentlandite, cubanite, valleriite, chalcopyrite and quartz.

The largest deposit of this type is the Bodevik, situated on the top of the Jastrebac mountain, north of the town of Prokuplje, south Serbia, where the ore body may be traced about 0.5 km in lenght, is 200 m large and sinks 200 m at least. The average contents of TiO_2 are about 5%, those of vanadium 0.13%.

3. The occurrences of leucoxene have been detected in the vicinity of the town of Bosiljgrad, SE Serbia, namely in the granitized gabbro. This gabbro appeared in form of large massif in which the Ti-mineralizations were present occasionally. The primary titanium mineral was ilmenite, and its associates were not detected. The gabbro described is of Paleozoic age and throughout the Alpine tectonics it was metamorphized and granitized, whereas the ilmenite was mostly converted into leucoxene. The late granitization (granitization II) which is of Tertiary/Quaternary age introduced some titanium (ilmenite, sphene) and caused the greisenization of the granitized gabbroic rocks introducing tourmaline and the associates [V. VUJANOVIĆ and M. TEOFILOVIĆ, [1979, *a, b*]. In the first phase of the granitization of gabbros granitoids were formed and the dominant conversion of the ilmenite took place within this process.

The newly formed granitoids show increased concentrations of the "basic" elements like *vanadium* (up to 1000 ppm), *nickel* (up to 190), *cobalt* (up to 320) and chromium (up to 105 ppm), as well as the micro-residues of the altered primary gabbro. The main titanium deposit of this type was detected in the Leska Mahala village, where the leucoxene ore body is exposed in a lenght of about 270 m, is 80 m large and sinks more than 40 m. In no direction the ore body is thinning out so far.

The ore body shows average TiO_2 contents of about 6% and averages of vanadium of 500 ppm. However, the leucoxene concentrations may reach up to 30% or more in the specimen. The groundmass of the leucoxene is represented by sphene or by rutile, or by both, containing numerous inclusions and residues of the ilmenite. In some cases inclusions and minute grains of rutile and ilmenite have also been seen in the sphene matrix. Although the sphene is as a rule grey-white (!), the examinations of the mineral show its normal chemical composition as well as the X-ray diagrams. Leucoxene is usually coarse (up to 2 mm in size). Its grains are often rounded as a result of resorption of the primary ilmenite during the granitization of the gabbro. Contrary to the titanium minerals of the metasomatic type (see below), the leucoxene does not contain traces of columbium, lanthanium, tin or other "acid" elements, except for the increased contents of zirconium (0—250 ppm), and the traces of lead (up to 14 ppm). Both of the latter elements were introduced under the influence of the granitization processes. The manganese contents in the leucoxene reach up to 500 ppm, those of chromium up to 40 ppm, including the traces of nickel and cobalt. These elements are genetically related to the primary gabbroic rock and the ilmenite.

In the leucoxene ore body also sparce chrom-spinel has been observed. This mineral has been the accessory constituent in the primary gabbro, partly resorbed later during granitization processes and in a considerable part also magnetitized.

The sulphide assemblage has also been detected in the leucoxene ore body, and is hydrothermal in origin. The predominant sulphide minerals are pyrrhotite and pyrite and the associates are scarce sphalerite and chalcopyrite. This paragenesis is very young and genetically related to the latest granitization processes, which also attacted the described gabbro massif (granitization II). This conclusion may also be supported by the fact that the mentioned sphalerite contains a number of the "acid" elements such as *cadmium* (up to 4500 ppm), *silver* (up to 150 ppm) and *bismuth* (up to 70 ppm).

The increased contents of *titanium* in the sphalerite (up to 150 ppm) may be explained by remobilizing the said element from the primary gabbro or the ilmenite.

4. The titanium mineralizations which are the products of the Ti-metasomatic front are genetically connected with the young granitoids. The case is of the rocks of the Tertiary/Quaternary age which metasomatically intruded in the crystalline rocks introducing titanium minerals in many places in the mentioned rocks. This type of titanium mineralizations is usually disseminated showing high concentrations in many places (up to 8% TiO_2). However, the bulk of these mineralizations is usually small with variable contents of titanium. The disseminated titanium mineralizations may appear within a large area with numerous "points" of the increased concentrations of the metal (the mountains of Juhor, Crni Vrh, Jastrebac, Pasjača, Vidojevica, Lebane, Crna Trava; further on the areas of the towns of Bosiljgrad and Vranje etc.). The only minerals are ilmenite and sphene, with rutile sporadically. Minerals are relativelly fine-grained or crystalline. In many cases the sphene is almost exclusively in form of elongated crystals (up to 0.2 mm in size) which often are double-twinned. The twin lamellations in the ilemnite and the rutile could be only rarely seen.

Although veinlets of titanium minerals have been observed, metasomatic replacement structures are dominating. Namely, the titanium minerals penetrated along the rock-forming grain contacts, or along the cleavages in them, as well as along the schistosity of the rock. The enclosures of the rock forming minerals in the newly formed titanium minerals have usually been seen in the localities in which the titanium concentrations are high. Thus, in some areas in the Rhodope mass (Juhor, Crni Vrh, Vidojevica, Pasjača, Lebane, Surdulica area etc.) a strong sphenization of the crystalline schists took place (up to 40% of sphene in the specimen), namely along their schistosity and newly formed sphene encloses numerous rock grains. However, strong ilmenitization of the crystalline rocks has only rarely been seen. Intense ilmenitization and sphenization are best expressed in amphibolites and amphibol migmatite gneisses, i.e. in the lower levels of the stratigraphical column.

The paragenetical relationships between the titanium minerals are very simple. The oldest is ilmenite, the youngest is sphene. However, rutile also often appears as sparse transformation product of ilmenite and in such cases it is the latest titanium mineral.

The high concentrations of the ilmenite as a rule caused the retreating of the sphene and vice versa; this fact may support the conclusion that both ilmenitization and sphenization have been separate processes caused by identical granitoids.

The way of occurrence of titanium minerals of the discussed type is uniform along the whole Rhodope mass in Serbia, i.e. not depending on the area or on the host rock.

During the titanium metasomatism some associates were also introduced, thus ilmenite, rutile and sphene often contain the increased concentrations of such elements as *lanthanium* (up to 2000 ppm), *tin* (up to 316 ppm), *columbium* (up to 2000 ppm) and *zirconium* (up to more than 1%), with some *tantalum, hafnium* and *vanadium,* as well as the increased contents of *nickel, cobalt* and *chromium.* However,

the latter elements are probably partly remobilized from the surrounding crystalline and gabbroic rocks.

During the sphenization processes beside the influx of calcium also its remobilization is supposed, namely from the limestones, marbles and cipolines which are included in the metamorphic complex. In connection to this conclusion we would point out the fact that young calcite is very widespread within the Rhodope mass, forming in some cases carbonatite-sövite masses (Jastrebac mountain). After the titanium metasomatism also an intense alkaline one took place developing throughout the whole Rhodope mass in Serbia. This process which also developed within the Tertiary/Quaternary period was observed within the formation of the crystalline schists sometimes also in the granitoids and the gabbros. This metasomatism introduced a number of felspars such as orthoclase, anorthoclase, microcline, albite, oligoclase, oligoclase-andesine, andesine and rarely andesine-labradorite, with the frequent and strong silification and biotitization of the schists including also an usually moderate muscovitization. All of the minerals described are younger than those of the Ti-metasomatic front (ilmenite, sphene and the associates) and the latter are often replaced by the former. The felspars and the biotite are preserved as a rule.

The alkali-metasomatism is varying in chemistry throughout the Rhodope mass in Serbia. In northern portions potassium metasomatism is dominating and in the central and the southern part the soda and calcium metasomatism. In the latter part of the Rhodope mass the potassium metasomatism is prevailing only is some areas notably in the Mačkatica molybdenum district (Surdulica), where considerable parts of dacites are totally granitized by the influx of orthoclase, anorthoclase and the associates.

The latest mineral assemblages in the region are sulphidic, which are hydrothermal and also genetically related to the late granitoids [V. VUJANOVIĆ, 1978]. The case is of the disseminated copper occurrences which are widespread within the whole Rhodope mass in Serbia, notably in the crystalline schits, sometimes also in the granitoids and the gabbros. These mineralizations are, as a rule, scarce and include pyrite, pyrrhotite and chalcopyrite which may be associated with some sphalerite, bornite, valleriitie, pentlandite, chalcocite, covellite and marcasite. The non metallic minerals are quartz and calcite sometimes also barite and fluorite.

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