GEOLOGICA BALCANICA, 33. 1-2, Sofia, Jun. 2003, p. 103-109

Minerals in the coal from the Oranovo-Simitli Basin, Bulgaria

Anton Sotirov[1], *Jordan Kortenski*[2]

[1]*Institut für Geowissenschaften, Montanuniversität Leoben, A-8700 Leoben, Austria*
[2]*University of Mining and Geology "Sv. Ivan Rilski", 1700 Sofia, Bulgaria*

(submitted: 17.01.2002; accepted for publication 10.06.2002)

А. Сотиров, Й. Кортенски. Минералы в углях Ораново-Симитлийского бассейна, Болгария. В углях Ораново-Симитлийского бассейна установлено 25 минералов. Большинство из них принадлежит ко классу силикатов. В подчиненном количестве представлены сульфидные минералы. Кроме того в незначительных количествах присутствуют окислы, сульфаты и фосфаты. С генетической точки зрения выделено три группы минералов. В первую группу входят минералы, образованые "in situ" в самом торфняке. Это: пирит, марказит, медный колчедан, галенит, кальцит, сидерит, арагонит, виерит, доломит, гематит, браунит и апатит. Вторая группа представлена минералами, входящими в состав пород, которые обнажены около угольного бассейна и которые поступали в торфяное болото при помощи водяного транспорта. Это: кварц, альбит, анортит, серицит, кеммererит, анальцим, эпидот, титанит и рутил. Минералы поступали в торфяной бассейн главным образом с севера, северо-запада и северо-востока. Третья группа объединяет глинистые минералы (каолинит, иллит и монтмориллонит), т.е. минералы, образованные или в торфняке, или в породах около при химическом изменении уже существующих минералов. По сравнению с подстилающими и перекрывающими глинами угольный пласт обогащен минералами. В подстилающих глинах выявлено большее разнообразие минералов, чем в глинах размещенных в верхних отделах угольного пласта. Кеммererит, анальцим и браунит являются новыми минерлами для угольных месторождений.

Abstract. Twenty-five minerals were established in the coal from the Oranovo-Simitli Basin. More of them were silicates. The sulfide minerals were less than the silicates. All other minerals were oxides, sulphates and phosphates, which were presented, in small amount. Three groups of the minerals were separated according to their genesis. First group includes minerals, formed mainly "in situ" in the peat bog: pyrite, marcazite, chalcopyrite, galena, calcite, siderite, aragonite, witherite, dolomite, hematite, braunite, and apatite. The minerals from the second group were formed mainly "in situ" in the rocks around the basin. They were transported in the peat bog by water streams: quartz, albite, anorthite, sericite, kämmererite, analcime, epidote, titanite, and rutile. The minerals from the third group were the clay minerals. They were separated in an extra group, because they had formed in the peat bog or in the rocks around the basin and they were products of chemical decomposition of already existed minerals. The minerals from the third group were kaolinite, illite and monmorillonite. The main supplying provinces with minerals were the rocks around the basin from North, Northwest and Northeast mainly. The coal seam was most rich of minerals than the shales from the upper and the bottom of the seam. The shale from the bottom has more variety of minerals than the shale from the upper of the seam. The kämmererite, analcime and braunite are new established minerals for the coals.

Sotirov, A., Kortenski, J. 2003. Minerals in the coal from the Oranovo-Simitli Basin, Bulgaria. – *Geologica Balc.*, 33, 1-2; 103-109.

Key words: minerals, mineral genesis, supplying areas, subbituminous coal.

Introduction

The Oranovo-Simitli basin is situated in South-west Bulgaria (Fig. 1). It belongs to the Struma-Mesta coal province (Siskov, 1997). Precambrian amphibolites and gneisses build the area around the basin in association with Paleozoic granites, Eocene and Oligocene sandstones and conglomerates (Fig. 1). The sediments of the Oranovo Formation are coal bearing and they are 150-200 m thick (Маринова, Загорчев, 1993). They include 16 coal layers, but only one of them, which is the matter of the present study, is suitable for exploiting. It is thick up to 53 meters. (Каменов et al., 1965). The age of the Oranovo Formation is Middle Miocene and its sediments are composed from alternation of sand, sandstone, and siltstone and sand clays, enriched with bitumen and plant debris (Вацев, 1991). Божков (1970) published data for some accessory minerals in this coal.

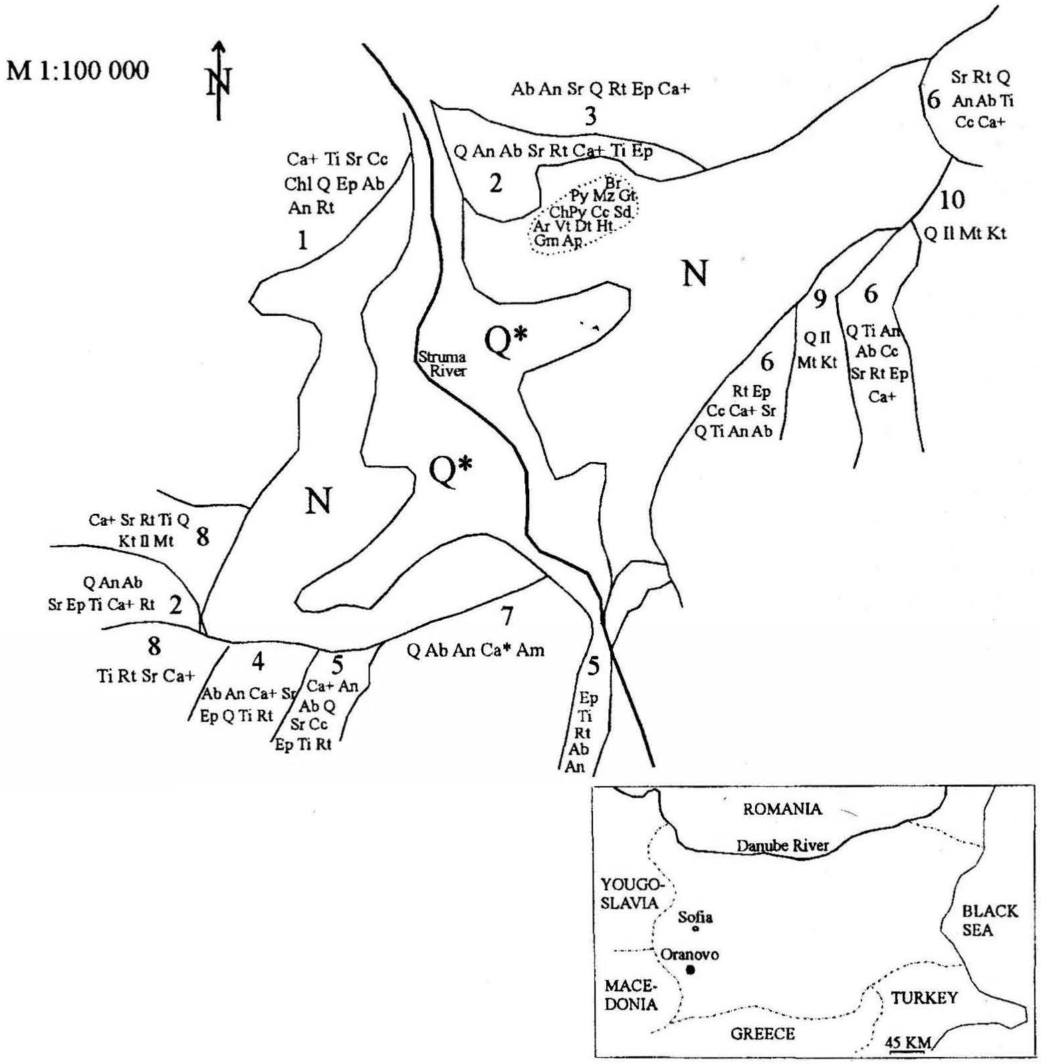

Fig. 1. Scheme of mineral supplying of the peat bog and location of the Oranovo-Simitli basin.

1 – Dokatitchevska Formation – amphibolites and marbles; 2 – Stariretchka Formation – gneisses and amphibolites; 3 – Tchetirska Formation – amphibolites and gneisses; 4 – Gneiss Migmatic Complex – gneisses and amphibolites; 5 – Tchepelarska Formation – Proterozoic gneisses, marbles and amphibolites; 6 – Vatchanska Formation – Proterozoic gneisses and marbles; 7 – Krupnik Pluton-Paleozoic granite; 8 – Logodashka Formation-Eocene conglomerates and sandstones; 9–Katchovska Formation-Oligocene sandstones and conglomerates; 10–Goreshtishka Formation – Oligocene argillites; N-Neogene – sandstones and conglomerates; Q* – Quaternary – sands and gravels.

Q* – Contour of the coal seam

Py – pyrite, Mz – marcazite, ChPy – chalcopyrite, Gt – Galena, Q – quartz, Ab – albite, An – anorthite, Am – analcime, Kt – kaolinite, Sr – sericite, Il – illite, Chl – kämmererite, Mt – montmorilonite, Ep – epidote, Ti – titanite, Cc – calcite, Sd – siderite, Ar-aragonite, Wt – witherite, Dt – dolomite, Ht – hematite, Br – braunite, Rt – rutile, Gm – gypsum, Ap – apatite, Ca+ – calcium.

Methods

One hundred and thirty-seven channel samples from coal and shale were studied. They shale from the upper and the bottom of the seam at the contact with the coal were sampled. The coal and shale samples and their heavy fractions were studied with X-ray diffractometry, X-ray (Debye-Scherer method), electron microprobe (EMP) and differential-thermal analysis (DTA). The optic microscope with reflective light, binocular microscope and scanning electron microscope (SEM) were used.

Minerals

Twenty-five minerals are found: pyrite, marcazite, chalcopyrite, galena, quartz, albite, anorthite, analcime, kaolinite, sericite, illite, kämmererite, montmorilonite, epidote, titanite, calcite, siderite, aragonite, whitherite, dolomite, hematite, braunite, rutile, gypsum and apatite. The most of the minerals are silicates. The sulphide minerals are less than the silicates. All other minerals are oxides, sulphates or phosphates and they are presented in small amount.

Sulphides

Pyrite. Macroscopically it is observed as very small grains. Pyrite is established in the heavy fraction from the coal and the shale from the upper and the bottom of the coal seam. Pyrite is about 50% from the heavy fraction. The pyrite content is up to 7.5% in the coal. The four morphological types of pyrite (Kortenski, Kostova, 1996) are observed: framboidal, euhedral, massive and infiltration pyrite.

Framboidal pyrite. This is the prevailing morphological type (Fig. 2a). It forms globule aggregates from cubic crystals with octahedron and pentagon dodecahedron shape. The inorganic framboidal pyrite (with uniform size of the grains and well-shaped crystals) and bacterial framboidal pyrite, which has crystals with various size and shape are observed. The framboidal pyrite usually occurs between the macerals from the Huminite group and the clay minerals (Fig. 2a). The electron microprobe shows presence of Ni and Au (0.02%) in the bacterial framboidal pyrite. The framboidal pyrite had been formed at the time of the peat genesis of the peat bog.

Euhedral pyrite. It is well shaped crystals, raised in small holes of the organic matter and around the framboidal pyrite. Aggregates of euhedral crystals are observed but sometimes single crystals are established – isolated euhedral pyrite. The euhedral pyrite had been formed in the time of peat genesis of the peat bog.

Massive pyrite. The homogeneous massive pyrite is prevailing. It is in little grains with irregular shape (Fig. 2c). Usually the massive pyrite forms the cement between the framboidal globules. Sometimes it associates with the clay minerals (Fig. 2c). Ni is established as trace element in this type of pyrite. The massive pyrite had been formed at the time of peat genesis.

Infiltration pyrite. It is represented by vein type, which fills small fractures (Fig. 2b). Usually it is homogeneous, but sometimes it has well shaped crystals. The electron microprobe shows high Ni content. The infiltration pyrite in this coal had been formed at the time of late diagenesis.

Marcazite. It is established in the coal with the reflective light. Its chemical compound is similar to the massive pyrite.

Chalcopyrite is determined with electron microprobe in the coal. Ni is established in the chalcopyrite.

Galena. It is recognized with X-ray diffractometry in the coal. It associates with the other sulphide minerals (mainly with the chalcopyrite). The presence of galena is a sign for high alkaline environment in some stages of the peat genesis.

Oxides

Hematite occurs mainly in the heavy fraction of the coal and it is recognized with X-ray analysis and binocular microscope.

Braunite is found with X-ray analysis in the coal. It is very fine mixed with the organic matter.

Rutile is found with binocular microscope and X-ray analysis of the heavy fraction of the coal shale.

Silicates

Quartz. It is established in the coal and coal shale. Sometime it may be seen with reflective light as small grains with high relief and dark halo around them. With binocular microscope the quartz of the shale is seen as spherical or sharp-edged grains with gray colour. The quartz is recognized with X-ray analysis and electron microprobe also.

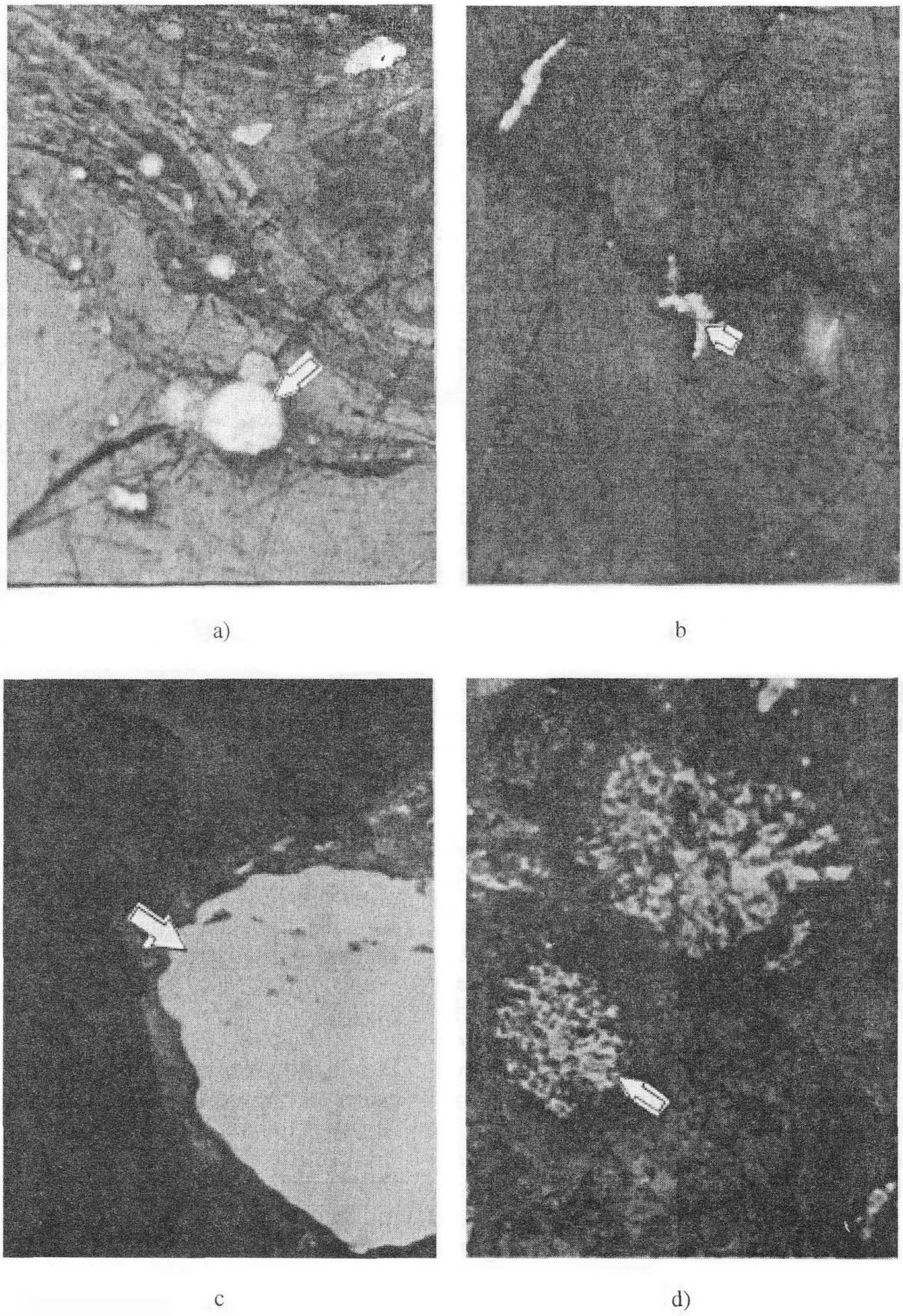

Fig. 2. Some minerals in the coal from the Oranovo-Simitli basin.
a) Framboidal pyrite in association with humodetrinite and clay minerals, reflective light, oil immersion, magnification ×1500.
b) Infiltration pyrite in small fractures, reflective light, oil immersion, magnification×1500.
c) Massive pyrite in association with humodetrinite and clay minerals, reflective light, oil immersion, magnification ×2500.
d) Siderite in association with humodetrinite and clay minerals, reflective light, oil immersion, magnification×1500.

Albite is found in the coal and rocks from the bottom of the coal seam with X-ray analysis. Feldspar is established with electron microprobe also.

Anorthite is recognized with X-ray analysis in the coal and shale from the bottom of the seam.

Analcime. That zeolite is established in the coal with X-ray analysis.

Kaolinite. Macroscopically it fills very thin fractures and it gives white color of the coal surface. The kaolinite occurs in the coal and shale from the bottom of the seam. It is diagnosed with X-ray and differential-thermal analysis. It is product of replacement of the potassium feldspar.

Sericite occurs in the shale from the bottom of the seam. It is established with X-ray analysis, electron microprobe and binocular microscope.

Illite is recognized with X-ray and differential-thermal analysis. It occurs in the shales from the upper and the bottom of the seam.

Kämmererite. It is established with X-ray analysis in the shales from the upper and the bottom of the seam.

Montmorilonite presents in the coal and in the shale from the bottom. It is found with X-ray and differential-thermal analysis.

Epidote is established in the heavy fraction of the coal and shales from the bottom with X-ray analysis.

Titanite occurs in the shales from the upper and the bottom of the seam. It is recognized with X-ray analysis and binocular microscope study of the heavy fraction from shales.

Phosphates

Chlorapatite, mainly with Cl content is established, when small bones were studied with X-ray analysis. The bones are not recognized, but they are probably relicts from small reptiles. The bones are empty with thin walls.

Sulphates

Gypsum is fine mixed with the clay minerals in the shale from the bottom of the seam. It is recognized with X-ray analysis.

Carbonates

Calcite presents in the coal and the shales from the upper and the bottom of the seam. It is diagnosed with X-ray, differential-thermal analysis and binocular microscope.

Siderite is established in the coal and the shale from the upper of the seam with reflective light and X-ray analysis. It has radial concretion shape and light brown color, and associate with humodetrinite (Fig. 2d). Probably one part of the siderite is a product of metamorphism of the pyrite. Trace elements, found in siderite are S, Co and Mn.

Aragonite and witherite are established only with differential-thermal analysis in the coal.

Dolomite is found in the coal with X-ray and differential-thermal analysis.

Mineral supplying of the peat bog

The minerals established in the coal and shales might be separated into three groups, according to their places of genesis (Kortenski, Sotirov, 2000). The first group of minerals includes minerals, formed manly "in situ" in the peat bog: pyrite, marcazite, chalcopyrite, galena, calcite, siderite, aragonite, witherite, dolomite, hematite, braunite and apatite. The second group of minerals includes minerals, formed mainly "in situ" in the rocks, which build the area around the basin. They are transported at the peat bog by slides and rivers: quartz, albite, anorthite, sericite, kämmererite, analcime, epidote, titanite and rutile. The minerals from the third group are products of chemical decomposition of already existed minerals and they had probably been formed in both places – the rocks around the basin and "in situ" in the peat bog or the coal bed: kaolinite, illite, monmorillonite, gypsum and epigenetic (infiltrational) pyrite.

The first group of minerals is formed mainly "in situ" in the peat bog as a result of the condi-tions, had existed there at the time of the peat genesis. The presence of the pyrite in coal is a sign for neutral and low-acid environment and reduction conditions of the peat bog. The shapes of the crystals (octahedron and pentagon dodecahedron) are characters for low-temperature pyrite, formed in high and middle mineralised zones (Костов, 1993). The small amount of marcazite supports the hypo-thesis for low-acidity of the environment, but with existing of small changes at single stages of the peat genesis. In these periods the acidity had increased or decreased and the enviro-nment had become alkaline. The small amount of galena and its association with chalcopyrite is an evidence for that. Calcite is formed mainly as a result of migration of Ca^{+} from the enriched of plagioclases and calcite rocks around the peat bog. These rocks are the amphibolites, gneisses and marmors of the Dokatitchevska Formation (1) from the West (Fig. 1), Vatchanska Formation (6) from the East and Southwest and the Tchepelarska Formation (5) from the South (Fig. 1). The gra-nite from the Krupnik Pluton (7) and the am-phibole from the Gneiss-Migmatic Complex (4) from the South are probably the source of Ca^+ for the waters in the area. The cold water from the rivers, which had been reached of CO_2, probably easy had taken out the Ca^+ from the rocks. When the rivers had flown into the peat bog, good condition for accumulation of Ca^+ had existed. In this case aragonite and witherite were formed at the beginning, had been followed by calcite and dolomite. The hydrogeological investigations of the basin support, this hypothesis. There are established mainly hydrocarbonate-sodium waters in the basin and the determined zones of mixing of waters with different genesis: thermal alkaline water and sulphate-hydrocarbonate-sodium water (Тодоров et al., 1985). One part of the element had probably been composed with the humic acids at the time of increasing of the acidity of the environment. Other part of Ca^+ probably is terrigenous, which is result of destroying of the marbles from the Dokatichevska (1), Vatchanska (6) and Tchepelarska (5) formations (Fig. 1). The spreading of these marbles is limited and they probably had not been the main source of clastic calcite. The observed spherical calcite grains in the shale from the upper of the seam might be a result of re-sedimentation of calcite, formed "in situ" in the peat bog. The calcite has low hardness and the shape of the grains is not evidence for long transportation. The plant relicts are source of Ca^+ also. Because of all of these facts the calcite is included into the first group of minerals, which are formed "in situ" in the peat bog. The siderite has concretion shape, therefore it is sediment mineral. It occurs mainly in the samples with high content of clay minerals and frequently it may be seen in zones around fractures. The siderite is established in many coal deposits (Костов, 1993). Hematite frequently forms as a result of sediment processes and it is typical low-temperature mineral in reach of Fe zones (Костов, 1993). Braunite is hydrothermal product of manganese sediments. The chemical studies show that the coal is reach of Mn (Кортенски, Сотиров, 2000). Apatite has biogenetic genesis.

Second group of minerals. These are the minerals, which are formed mainly in the rocks, which build the area around the basin: quartz, albite and anorthite had probably been transported from all rock formations around the basin and especially the rocks, which are close to the peat bog. These are the amphibolites from the Dokatitchevska (1) and Tchetirska formations (3) and the gneisses from the Stariretchka (2) and Vatchanska formations (6) (Fig. 1). The sericite is a result of chemical decomposition of the gneisses from the Stariretchka (2), Tchetirska (3), Tchepelarska formations (5) and the Gneiss-migmatic complex (4). Kämmererite is transported probably from the amphibole of the Dokatichevska formation (1) (Fig. 1). A source of epidote had been the amphibolites from the Dokatichevska (1), Tchepelarska (1) and Stariretchka (2) formations (Fig. 1). The rutile and titanite are accessory minerals and they were introduced into the peat bog from the rocks, built the area around the basin. Last mineral from this group is analcime. It forms at 525°C, but with presence of quartz at 280°C and pressure 1000 bars (Костов, 1993). Such conditions in the peat bog had not existed and therefore it is formed in the rocks around the basin and it had transported to the peat bog.

Third group of minerals. They had been formed "in situ" in the peat bog or they had been formed in the rocks around the basin also. They were transported mainly from the surface streams and rivers. These minerals are products of chemical destroying of the rocks, mainly decomposition of the feldspar of alumo-silicate rocks. These are the minerals kaolinite, illite, and montmorilonite. The source rocks of clay minerals had been the sandstones, mudstones and conglomerates from the Logodashka (8), Katchovska (9) and Goreshtishka (10) formations and the sediments of the Neogene (Fig. 1). The epigenetic pyrite fills small fractures, cleavages and cracks and had been formed at the time of late diagenesis. Gypsum in this group is formed probably as a result of chemical destroying of the sulphide minerals. More acid environment, which had not existed in the peat bog, is necessary for accumulation of gypsum.

Conclusions

The main supplying provinces with minerals are the rocks around the basin from North, Northwest and Northeast. These are the rocks from the Dokatitchevska (1), Stariretchka (2), Tchetirska (3) and Vatchanska (6) formations. Most of the minerals are established in the coal. Occurrence of the albite, anorthite, and sericite in the shale from the bottom is a result of quick transgression and accumulation and quick covering of the existed minerals with terrigenous material. By this way further destroying of these minerals had been escaped. The coal seam is rich of minerals, because of the enriching of the peat bog with them, result of many geological, biological and chemical processes. The rocks from the upper of the seam are pouring of minerals, because the peat bog had become dry and strong destroying of the minerals had begun at last stage of the swamp development. The pyrite is about 50% from the heavy fraction in the coal and most of the pyrite is framboidal. A significant part from this amount is bacterial framboidal pyrite, which consist 0.02% Au. The kämmererite, analcime and braunite are new established minerals for the coals.

References

Kortenski, J., I. Kostova. 1996. Occurrence and morphology of pyrite in Bulgarian coals. – *Int. J. Coal Geol.*, 29; 273–290.

Kortenski, J., A. Sotirov. 2000. Mineral content, feeding provinces and genesis of the minerals in the coal from the Oranovo-Simitli Basin, Bulgaria. – *Comp. Rendus Acad. Bulg. Sci.*, *53*, 11; 37–40.

Siskov, G. 1997. Bulgarian low rank coals: geology and petrology. – *European Geology and Technology, Geol. Soc. Spec. Publication*, 125; 141–148.

Божков, Й. 1970. Някои акцесорни минерали във въглищата от Ораново-Симитлийския въглищен басейн. – *Год. МГУ*, 14, 2; 115–121.

Вацев, М. 1991. Литостратиграфия на неогена от Симитлийския и Брежанския Грабен. – *Год. МГУ*, 37, 1; 23–38.

Каменов, Бл., В. Константинова, Б. Йорданов. 1965. Геология и въгленосност на Ораново-Симитлийския терциерен басейн. – *Сп. Бълг. геол. д-во, 26* 1; 1–19.

Кортенски, Й., А. Сотиров. 2000. Геохимични особености на въглищата от Ораново-Симитлийския басейн. – *Сп. Бълг. геол. д-во,* (под печат).

Костов, Ив. 1993. *Минералогия.* С., Наука и изкуство, 734 с.

Маринова, Р., И. Загорчев. 1993. *Обяснителна записка към геоложката карта на България М 1:100 000, картен лист Разлог.* 62 с.

Тодоров, А., Б. Маринов, Л. Кузманов, Е. Колев, В. Чачев, П. Недялков. 1985. Ролята на тектонските фактори за формирането на хидрогеоложките условия в Симитлийския артезиански басейн. – *Сп. Бълг. геол. д-во, 56*, 3; 346–360.