

The Alpine manganese ores in Bulgaria — paleogeodynamic control

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Резюме. Мангановите руди са разновъзрастни, разнотипни и имат различен произход. Окисните руди са жили в туфи или конкреции, лещи и тела в сантонски и кампански варовици. Те са вулканогенно-хидротермални или вулканогенно-седиментни. Образувани са в междудъговия Средногорски трог с интензивен субаквален островнодъгов вулканизъм. Желязо-мангановите кори в кампанските скали са хидрогенно-хемогенни и са свързани с подморска ерозия. В олигоценските скали окисните манганови руди, конкреционните и слоевите ясписи са вулканогенно-седиментни. Възникват след колизия в колапсови морски депресии в Източните Родопи с интензивен среден до кисел субаерален вулканизъм. Манган-хидросиликат-карбонатните (родохрозитовите) руди в олигоцена от Варненската депресия са нормално седиментогенни. Образувани са при седиментация на глини, мергели и пясъчници в причерноморско епиконтинентално море (шелф). Рудопроявленията върху мангансъдържащи скали при Кремиковци, Чипровци и Еньовче са обусловени от изветрителни процеси.

Key words: Alpine, manganese ores, paleogeodynamic, environment, manganite, rodocrosite, pyrolusite

Introduction

Bulgarian manganese ore-mineralisations have been studied in single deposits and outcrops or as separate genetic types. A systematic study of manganese minerals was performed recently. However, reviews on them are still not available.

The IGCP Project 226 "Correlation of Manganese Sedimentation and Paleoenvironments" initiated detailed studies of minerals and ore types, as well as synthesis of the manganese sedimentation in paleogeodynamic environments of different age and type during the Proterozoic in Bulgaria.

Paleogeodynamic reconstructions and maps are based mainly on geologic, paleoclimatic and partly paleomagnetic data for Bulgaria. This data, in lateral direction, indicates the spatial changes in paleogeodynamic environments while vertically it is indicative of paleogeodynamic environment temporal changes. The main concepts, on which the interpretation of the Alpine evolution of Bulgaria is based are: (1) horizontal drift of the area from 40° southern latitude (Ordovician) across the equator or 0° (Carboniferous) and 20° (Permian) up to 40° northern latitude (Jurassic); (2) polycyclic change of various paleogeodynamic environments in Bulgaria.

This paper is trying to relate the manganese ores to the sedimentation, diagenetic origin of minerals and the paleodynamic environments in Bulgaria.

Alpine paleogeodynamics and manganese ores

The Alpine orogen has a complex geologic structure

consisting of numerous folds, nappes, sutures and crystalline massifs. The sutures are considered as relics of paleooceans with ophyolites, glaucophane schists, flysch and pelagic rocks. The crystalline massifs are fragments of likely microcontinents or island-arcs, located predominantly along the Tethys northern margin. The continent drift, the Tethys northward subduction and repeated collisional events led to the collage the Alpine orogen.

During the Triassic and Jurassic, the evolution of the Tethys was related to fragmentation of Pangea and formation of a southern (Africa) and a northern (Eurasia) supercontinent, as well to the origin of some microcontinents - Apulian, Pelagonian, Balkan microcontinents, etc. Mesozoic divergence and spreading created microoceans with oceanic crust — Ionian-Levantine, Othris-Pindos, Vardar, Dobrogea-Crimea-Caucasus, etc. The convergence and subduction controlled the origin of amagmatic to mature island-arcs, inter-arc troughs and back-arc marginal seas with flysch deposition and submarine volcanism. The closure of the oceans and the collisions (continent-continent or arc-continent), occurring at different times, resulted in folding, obduction, thrusting and collages: Dobrudgea-Crimea-Caucasus microocean - Middle Jurassic (Cimmerides); Vardar microocean — Early Cretaceous (Austrides); Othris-Pindos and Tauride microocean — Late Cretaceous (Subhercynides and Laramides); Cenozoic troughs and marginal seas — during the Eocene (Illyrides) or Miocene (Styrides). Individual zones in the Alpine orogen (the Alpides in Bulgaria) have a polycyclic development (Начев, 1969;1976a, б; 1980 a, б; 1985, 1986; Nachev, 1989a, b, c; Hsu et al.,1977; Начев,

Янев, 1980).

The Alpine evolution of Bulgaria is closely related to the Balkan microcontinent, situated between the Dobrudgea-Crimea-Caucasus microocean to the north, the Vardar microocean to the south and the suboceanic crust of the Black Sea to the east (Fig. 1). The basement of the microcontinent consists of Archean-Proterozoic metamorphic rocks and granitoids, Vendian-Cambrian ophyolites and metamorphic rocks (Baykalides), Ordovician phyllites, Silurian shales, Devonian graywacke-siltstone flysch or dolomites with limestones, Carboniferous-Permian sandstones and shales with coal, and Permian red conglomerates, sandstones, siltstones and shales (Caledono-Hercynides).

Several stages may be distinguished in the Alpine evolution of Bulgaria (the Balkan microcontinent) (Начев & Янев, 1980; Nachev, 1989 a, b, c).

Continental stage (Triassic – Kimmeridgian, 248-150 Ma)

It is characterized by Early Triassic continental clastic accumulation, Spathian-Norian evaporite dolomitelimestone and Norian variegated regressive clasticclayey sedimentation in an epicontinental Triassic sea. Locally (Chiren, Knezha, Pelovo), basalts were related to volcanism in an embryonal rift (Hayes, Shes, 1980) or a transform fault. During the Hettangian-Bathonian cycle, Hettangian-Pliensbachian sandstones, sandy limestones and clayey limestones, Aalenian-Bajocian black shales and siltstones and Upper Bajocian-Bathonian sandstones and sandy polydetritic limestones, correspondlingy in transgressive, stable or regressive epicontinental sea, were formed. During the Middle Jurassic, the northern microocean was closed and, as a result of collision, the Dobrogea-Crimea-Caucausus Cimmerian orogen was created (Начев, 1976а,б; 1985). The Balkan microcontinent was accreted to the Eurasian plate through the Dobrogea Cimmerian orogen. Shallow-water bedded biogenic to micritic limestones were deposited during the Callovian to the Late Kimmeridgian in a transgressive-stable epicontinental sea. Oolitic iron ores, void of manganese, were formed in the Jurassic epicontinental seas (Начев, 1976a, б; 1985).

Early Alpine stage (Late Kimmeridgian – Middle Albian, 150-105 Ma)

Intracontinental faulting and extension in the southern part of the Balkan microcontinent resulted in the formation of an extensional basin — the Nish-Troyan trough. As a result of later extension, the epicontinental sea with limestone sedimentation (Kimmeridgian-Albian) was formed upon the northern paleo-Moesian relic of the microcontinent. The southern part of the microcontinent was transformed into an Early Alpine island arc system (Late Kimmeridgian-Valanginian). It included the trench of the Vardar Ocean, accretional prism (Circum-Rhodope zone?), the Serbian-Macedonian-Rhodope arc and the Nish-Troyan back-arc trough or marginal sea with a graywacke-siltstone flysch. Compressional events folded the flysch sediments and the zone

(Cimmerides) was elevated. A collision between the island-arc and the paleo-Moesian relic of the microcontinent occurred. The collision determined the northern migration of the basin and its transformation into a Pirot-Tarnovo fore-deep with clastic, calcareous and clayey sedimentation. The Albian compression led to a new folding (Austrides), elevation and draining with a new collision. The southern active margin of the Balkan microcontinent was transformed into a passive one. During this stage manganese ores were not formed (Haueb, 1969; 1980a,6, 1985; Nachev, 1986b).

The Middle Alpine stage (Middle Albian — Palaeocene, 105-64 Ma)

This stage started in the Balkan microcontinent with local limnic (sandstones, shales, coal) and Kotelgraben (breccia, conglomerates, sandstones and shales) accumulation (Cenomanian?). A transgression followed and in the epicontinental sea sandstones, limestones and shales (Cenomanian, Turonian) were deposited. After a new faulting, the southern part of the microcontinent was fragmented and as a result of extension, it was transformed into a Middle Alpine island-arc system: Vardar trench accretional prism with flysch, Serbian-Macedonian-Rhodope frontal arc, extensional Sredna Gora intra-arc trough, third Balkanide arc and extensional back-arc Kula and Emine troughs or marginal seas.

Limestones and argillaceous limestones (Coniacian-Campanian), graywacke-siltstone flysch (Coniacian, Santonian; Campanian), tephraturbidite flysch (Coniacian-Campanian), volcanic tuffs (Coniacian-Campanian) and clastic-limestone flysch (Conjugation and Campanian) were deposited in the Sredna Gora trough (Coniacian-Campanian, 88.5-73 Ma). The perivolcano facies zonality was as follows: effusive rocks - tuffs - tephraturbidite flysch - limestones with argillaceous limestones - packets (deep sea fans) of a graywacke-siltstone flysch and packets of a clastic-limestone flysch. The volcanism (about 50 volcanoes) was predominantly sub-marine and explosive, Ca-alkaline, subalkaline to K-alkaline with basalts, basaltic andesites, andesites, dacites, latites, trachybasalts and trachytes. The intrusive magmatism (50 plutons) and dykes have the same petrochemical characteristics. The submarine volcanoes at the bottom of the trough were positive structures, local volcanic islands. Their zone was characterized as an active volcanic arc. Sedimentation in the trough was normal hemipelagic with superimposed resedimentation of tephra, extraclastics and intraclastics. The sedimentary environments were shelves, trough slopes, depressions and bottom axial parts or submarine volcano slopes, rise and depressions between volcanoes. The trough was highly seismic and hydrodynamically active as well being subparallel, deep (4 km) and symmetric. The pre-Maesrtichtian compression lead to folding (Late Subhercynian orogeny), elevation and transformation of the trough into a paleovolcanic zone. During the Maestrichtian (73-65 Ma) the paleovolcanic zone in Western and Eastern Sredna Gora was flooded by a superimposed sea with shallow-water clastic and calcareous sedimentation. In Panagiurishte district, there was an alluvial environment with conglomerates up to 200 m thick (Начев, 19766; Начев et al., 1980; Начев, Начев, 1986a, б).

Normal pelagic sedimentation and superimposed extraclastic resedimentation dominated in Kula backarc trough (Turonian-Maestrichtian, 91-65 Ma). Flysch, consisting of shales, siltstones and graywackes, up to 1000 m thick, was formed. The sedimentary environments were a southern shelf, trough slopes, rises and bottom axial part. It was submeridional, narrow, deep and asymmetric, joining an epicontinental sea in the east. It was extensional by nature. The flysch was folded, while the trough was eliminated after the Maestrichtian (Laramide orogeny) (Начев, 19766; Начев, Янев, 1980).

Flysch of shales, siltstones and graywackes, argilla-

ceous limestones, micritic limestones and clastic limestones or locally argillaceous limestones and tephraturbidites was formed in the Emine trough (Turonian-Paleocene, 91-64 Ma). The Emine flysch is 2000 m thick. The proximal flysch (facies C) was developed to the south, while the distal one (facies O) — to the north. The sedimentation was normal hemipelagic. while the superimposed resedimentation was epiclastic, intraclastic (with benthic fossils) and tephraturbiditic. The trough was a back-arc basin, subparallel, narrow, deep and asymmetric, with a southern shelf, trough slopes, rises and bottom axial part. To the north it was connected with the epicontinental sea. It was formed during the Turonian and eliminated by compression, folding and uplift during the Paleocene (Late Laramides) (Начев, 1976б; 1986; Начев, Янев, 1980). North of the marginal seas,



Fig. 1. Paleogeodynamic environments and manganese ores in Bulgaria

(A) Geographic sketch; (B) Morphotectonic sketch: I — relicts of Early Ordovician (?) epicontinental sea; 2 — Coniacian-Campanian intra-arc Sredna Gora trough; 3 — Oligocene intramountain depressions in the Eastern Rhodopes; 4 — Oligocene epicontinental sea around the Black sea; 5 — gondites; 6 — Santonian and Campanian oxide manganese mineralisations; 7 — Oligocene oxide manganese mineralisations; 8 — Oligocene manganite-hydrosilicate-carbonate manganese deposits and mineralisations; 9 — hypergene manganese deposits and mineralisations

Numbers: (1) Bilo Mountain; (2) Pozharevo; (3) Chelopech; (4) Goliama Rakovitza; (5) Dalgi rat; (6) Milkova cheshma; (7) Toplika; (8) Svoboda; (9) Kermen; (10) Kabile (Izvor); (11) Glushnik; (12) Gorno Aleksandrovo; (13) Skalishte; (14) Zjinzifovo; (15) Kochash; (16) Biala; (17) Goritsa; (18) Rudnik; (19) Beloslav-Asparuhovo; (20) Pripek-Kalimantsi; (21) Ignatievo; (22) Obrochishte; (23) Kranevo; (24) Tulenovo; (25) Shabla; (26) Blateshnitsa, (27) Kremikovtsi; (28) Chiprovci; (29) Eniovche

Фиг. 1. Палеогеографски обстановки и манганови орудявания в България

(A) Географска схема; (B) Морфо-тектонска схема: 1 — реликти от ранноордовишкото (?) епиконтинентално море; 2 — кониас-кампански вътрешно дъгов Средногорски трог; 3 — олигоценски вътрешнопланински депресии в Източните Родопи; 4 — олигоценско епиконтинентално море около Черно море; 5 — гондити; 6 — сантонски и кампански манганово-окисни минерализации; 7 — олигоценски манганово-окисни минерализации; 8 — олигоценски манганит-хидросиликат-карбонат манганови находища и минерализации; 9 — хипергенни манганови находища и минерализации

Цифри: (1) Било Планина; (2) Пожарево; (3) Челопеч; (4) Голяма Раковица; (5) Дълги ръг; (6) Милкова чешма; (7) Топлика; (8) Свобода; (9) Кермен; (10) Кабиле (Извор); (11) Глушник; (12) Горно Александрово; (13) Скалище; (14) Жинзифово; (15) Кочаш; (16) Бяла; (17) Голица; (18) Рудник; (19) Белослав-Аспарухово; (20) Припек-Калиманци; (21) Игнатиево; (22) Оброчище; (23) Кранево; (24) Тюленово; (25) Шабла; (26) Блатешница; (27) Кремиковци; (28) Чипровци; (29) Еньовче

there was an epicontinental sea over the paleo-Moesian relic of the Balkan microcontinent.

There is a great number of manganese deposits and mineralisations, associated with the Upper Cretaceous rocks in the Sredna Gora zone (Fig. 1). Depending on the type of the host rocks, the manganese ore-formations are divided in two groups.

The effusive rocks and tuffs (Santonian) contain quartz-pyrolusite (Gorno Alexandrovo, Panagiurishte region) or psilomelane-manganite-pyrolusite (Pozjarevo) nodules and veins (up to 5 cm). The content of manganese is from 20 to 30 % (Велчев, 1973; Начев, Начев, 1986а, б).

A packet (up to 50 m) of gray to red micritic and clayey limestones (Campanian) with nodules, lenses and irregular bodies of manganese mineralisations is typical. The nodules reaching up to 1 m are ironjasper or manganese-jasper (up to 9% Mn). The lenses and bodies are up to 100 m long and up to 8 m thick. They consist of pyrolusite, braunite, manganite, vad and psilomelane in association with chalcedony, opal, quartz, calcite and barite, and contain up to 29 % Mn. The mineralisations are located in the lower, middle or upper part of the limestone packet (Panagiurishte area) or at the contact between tuffs and tephraturbidite rocks with limestones. In the sections, there is a vertical alternation of tuffs, tephraturbidites, limestones and tephraturbidite flysch (Pozjarevo, Panagjurishte district, Glushnik). The manganese mineralisations are located in the lateral transition of the packet from limestones to bentonites, tephraturbitites or tephraturbidite flysch, i.e. in proximity of the volcanoes. There are neither siliceous rocks, nor manganese mineralisations in the limestones far from the volcanoes (Haves, Haves, 1986a, 6).

The manganese mineralisations are a result of early diagenetic silicification (replacement) of the limestones with formation of iron jaspers, manganese-jaspers or siliceous-manganese ores. The source of Mn, Fe and SiO₂ is volcanic. The deposition was deriving of hydrothermal solutions or exhalations for the veins or of laterally migrating pore waters into the marine limestone packet. Probably part of the manganese was a result of leaching and alteration of the volcanic glass or of sub-marine weathering (halmirolisis) at the bottom of the sea basin (Hauer, Hauer, 1986a, 6).

In the section at Chelopech (Fig. 1), over a thickrhythmic mixed graywacke and tephraturbidite flysch (deep-sea fan), follows a packet of marine red micritic limestones with planktonic foraminifers, 40 m thick and of Lower Campanian age. The contact is a parallel unconformity. There is a basal bed in the base of the limestone packet, and above — individual lenses consisting of lithoclasts of effusive rocks with manganese-iron crusts. The crusts contain 10,1 % Mn and 10.2% Fe. The origin of these hydrogenous manganese-iron crusts is related to the processes of submarine erosion and is analogous to the origin of the manganese crusts at the bottom of recent oceans (Nachev, 1989b).

Hence, the vein manganese mineralisations are of volcano-hydrothermal origin. The nodules, lenses and the irregular manganese ore bodies in the marine limestones are of volcanogenic-sedimentary type.

Manganese-iron crusts are a result of a hydrogeneoushemogeneous deposition during the Pre-Campanian local submarine erosion. These manganese mineralisations are specific only of the Coniacian-Campanian intra-arc Sredna Gora trough with intensive subaqual andesitic to basaltic volcanism.

Late Alpine or collisional stage (Paleocene-Late Eocene, 64-48 Ma)

North of the folded Sredna gora, Kula and Emine zones, the Kula-Obzor foredeep was formed. Conglomerates, sandstones and clays, up to 2000 m thick, were deposited. This stage was characterized by a complete closure of the Vardar ocean and by intensive collisions. A collision between the Pelagonian microcontinent and the Balkan arc occurred. The collision between the Balkan arc and the paleo-Moesian relic of the Balkan microcontinent determined the intensive deformation of the Emine Flysch and the elimination of the Emine back-arc trough (Late Laramides). Synsedimentary horizontal movements towards the north resulted in a reverse fault to thrust along the northern boundary of the Sredna Gora zone (Botev-vrah thrust, Sliven region), along the dislocations of Chudni skali, etc. The Kula-Obzor trough was folded very slightly mainly in its southern parts and was eliminated prior to the Late Eocene (Illyrides). During this stage, manganese ores were not formed (Начев, 1976 б; 1980а, б; Начев, Янев, 1980).

Final or postcollisional stage (Late Eocene to present, 42-0 Ma)

During this stage, almost in all southern structural elements and zones, Late Eocene-Oligocene intramountain collapse basins and depressions, as well as a Peri-Black Sea epicontinental sea were formed (Bourgas and Varna Depressions). Continental to shallow-water clastic rocks, clays and limestones were deposited. In the Serbian-Macedonian-Rhodope zone, an intensive intermediate and acid, predominantly explosive volcanism (latites, andesites, rhyolites), as well as weak intrusive magmatism were manifested.

The magmatism is believed to be of Andean type at a lithospheric boundary or of collisional origin (Янев, Бахнева, 1980). During the Neogene, intramountain grabens and valleys (gravels and sandstones) in South Bulgaria or in the Getian and Crimea-Caucasus epicontinental seas in North Bulgaria (sandstones, clays, limestones) were formed.

The Neogene ultrabasic to basic volcanic rocks (basalts) are related to an intraplate post-collisional volcanism in the Eastern Rhodopes, Sarnena Gora, Gabrovo district and from Suhindol up to the town of Svishtov (Янев, Бахнева, 1980; Начев, 1980а,б; Начев, Янев, 1980). Probably this volcanism was related to transcurrent faults, transversal with respect to the Alpine Orogen in Bulgaria (Nachev, 1989b). The Upper Eocene-Oligocene and Neogene rocks are very slightly folded, mostly close to faults. They are considered to be post-collisional, post-tectonic rocks or elements of the cover (Nachev, 1989b). During the post-collisional stage (Late Eocene-Oligocene), man-

ganese ores were formed in two different paleogeodynamic environments (Fig.1).

In the intramountain collapse marine depressions (Late Eocene-Oligocene) of the Serbian-Macedonian-Rhodope zone with intensive manifestations of andesite and rhyolite subaerial volcanism, there are rare and small manganese mineralisations (Kochash, Skalishte, Zhinzifovo, etc.). Manganese-jaspers consist of pyrolusite, ramsdelite, chalcedony, calcite, barite and other minerals. The manganese minerals were formed after the chalcedony. They are nodules, lenses or thin (to 20 cm) beds in association with red micritic or coral limestones. Evidently, the manganese had a volcanic source. The role of volcanic exhalations, underwater weathering (chalmirolisis) or leaching of manganese during the alteration of volcanic glass and formation of deposits of bentonites, zeolites rocks or nodular or bedded cherts, is not clear yet. The manganese mineralisations are likely to have formed by an early diagenetic substitution of limestones and therefore should be considered to be of volcanogenenic-sedimentary type (Начев, Начев, 1989).

Nodular and bedded manganite-hydrosilicatecarbonate manganese ores were deposited in Varna depression (1500 km²) of the Peri-Black Sea epicontinental sea (shelf). The ore body (layer or horizon) is thick from 2 to 24 m. It is localized at the base of the Oligocene. In the section there are quartz-glauconite sandstones, manganese ores, smectite (montmorillonite) clays, diatomites, marls, volcaniclastic rocks tuffs, tuffites, etc. (Алексиев, 1959, 1960; Василев et а1., 1959; Алексиев, Начева, 1968, 1969; Богданова, 1968; Алексиев, Богданова, 1974). The ores show mainly pisolitic and partially nodular structure. Manganite, hydrosilicate (neotokite-saponite), carbonate and mixed types of manganese ores are distinguished (Василев et al., Aleksiev, 1960; Алексиев, Начева, 1968, 1969; Богданова, 1968; Начева, 1973, 1974, 1976). The ores consist mainly of manganite (Василев, 1969), manganese hydrosilicates from the sequence neotokite-saponite (Алексиев, 1960) and manganese carbonates-rhodochrosite, manganese-calcite (Василев и др., 1959; Алексиев, 1960; Алексиев & Начева, 1968, 1969; Начева, 1969, 1975, 1976; Начева и др., 1974). They contain also alabandine (Василев, 1969), chauerite, pyrolusite, psylomelane, vad and other secondary manganese minerals. The host minerals are calcite, opal, chalcedony, smectite (montmorilonite), klinoptylolite (Алексиев, Киров, 1967), glauconite, pyrite, barite (Алексиев, 1967), etc. The manganese ores contain in average 28.0% Mn, 1.5% Fe and up to 0.19 % P (Василев et al., 1959; Aleksiev, 1960; Алексиев, Начева, 1968, 1969; Начева, 1973, 1974, 1976). The manganese module is constant and high: Mn/Fe — 6.6—29.2, on the average 17.3 (Начева, Начев, 1976). The ores do not contain higher concentration of copper, molybdenum, germanium and other microelements. The Upper Eocene and Oligocene host rocks (clays, marls, sandstones) have increased contents of manganese - from 0.24 up to 1.78 % Мп (Начева, Начев, 1976). The organic substance (C_{org}) varies from 0.27 up to 0,96 %. The sequence of deposition of the manganese minerals is as follows: manganese hydroxides - manganite - neotokite - rhodochrosite - Ca-rhodochrosite - manganese-calcite - alabandine. The geochemical environment has changed from an oxidising one into a neutral and reductional one. According to K-Ar dating for the glauconite, the manganese ores were formed between 42 and 32 Ma (Nachev, Lilov, 1975).

The original (sedimentary) manganese-ore marine sediments were likely to have manganese-hydrooxide (psylomelane) composition. During the early diagenesis manganite, neotocite, rhodochrosite, Ca-rhodochrosite, manganese-calcite and alabandite were formed. The nodules and pisoliths are early diagenetic. According to the processes of mineralisation, the manganese ores are marine sedimentary — earlydiagenetic. The veinlets of rhodochrosite and alabandite probably belong to the formations of the late diagenesis (Алексиев, Начева, 1968, 1969; Начев, Начев, 1986a, б). From this point of view, the manganese ores are normally of sedimentary type (Начева,, Haves, 1974), while the source of manganese is exogenic. Yet the source of manganese is hypothetical and is widely debated. The volcanogenic-sedimentary genesis is determined on the basis of endogenic (volcanic) sources of hydrotherms, rich in manganese and SiO₂, into a water basin (the Black Sea) (Aleksiev, 1960; Василев et al., 1959; Алексиев, Начева, 1960, 1969; Алексиев, Богданова, 1974). А serious counter point to the volcanic source of manganese is the circumstance that in the Serbian-Macedonian-Rhodopes zone, with intensive volcanism, there are extremely rare and small manganese mineralisations.

The following assumptions on manganese as a hypothetical source for the formation of ores in the Peri-Black Sea epicontinental sea may be made as well: 1 — hydrothermal source of fluids at the bottom of the Black Sea and transfer by upwelling into the shelf; 2 — chalmirolisis at the Black Sea bottom; 3 — leaching of manganese during the alteration of volcanic glass related to the Oligocene acid volcanism and the ash-falls in the Black Sea area.

Weathering manganese deposits and outcrops were formed during Eocene-Quaternary over rock rich in manganese (Fig. 1).

Varied manganese weathering minerals — psylomelane, pyrolusite, vad, rancieite, manganite, vernadite, etc. — were formed in the barite-polymetal-manganese-iron-ore deposit of Kremikovtsi.

Similar weathering manganese mineralisations are also found in the West Balkan Mountains.

There is an original skarn mineralisation of johannsenite, rhodonite and bustamite (overlain by a weathering crust with pyrolusite, psilomelane and other oxide and hydrooxide manganese minerals) in the lead-zinc deposit of Eniovche hosted by Precambrian gneisses, schists, marbles and other metamorphic rocks.

The hydrosilicate-carbonate manganese ores are oxidized in part of their outcrops (Rudnik, Beloslav, Pripek, Ignatievo). Secondary oxide manganese ores with psilomelane, vad, pyrolusite, etc. were formed. Another part of these deposits are partially exploited (Ignatievo, Beloslav, etc.).

Conclusions

The above review on the paleogeodynamic and manganese ores in Bulgaria leads to the following conclusions:

- 1. The oxide manganese ore-formations in Santonian and Campanian rocks of Sredna Gora zone are mainly volcanogenic sedimentary and were formed in the intra-arc Sredna Gora trough with subaqual island-arc volcanism. They are economic.
- 2. The oxide manganese (pyrolusite) ores in Oligocene nodules and layered jaspers and limestones are volcanogenic-sedimentary and were formed in post-collisional collapse marine depressions (basins) in the Eastern Rhodopes with subareal intermediateacid volcanism. They are not of economic importance.
 - 3. Manganite-hydrosilicate-carbonate manganese

ores in the Oligocene rocks of Varna depression are normal sedimentary and were formed in the Peri-Black Sea epicontinental sea. They are a part of the Oligocene Peri-Black Sea manganese-ore province and are economically very important.

4. The weathering manganese mineralisations related to rocks rich in manganese in Kremikovtsi, Chiprovtsi, Eniovche, etc. are not economic.

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