

PROSPECTS OF DISCOVERY OF NEW DEPOSITS OF LEAD AND ZINC IN THE REPUBLIC OF MACEDONIA

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A b s t r a c t: Deposits of SEDEX and MVT types in the territory of Macedonia have not been identified yet, although they are known in neighboring Serbia (Bobija, Lece, Kišnica and Blagodat). Since they are of major industrial importance in other regions of the world, an attempt has been made to study and summarize the available information on the discovery possibility of such deposits in the territory of the Republic of Macedonia, as well as to show their significance in the future. One of the tasks of this paper is to adapt the known forecasting and prospecting model of deposits of these types to the territory of the Republic of Macedonia. The information given in the article is of great importance for predictive-metallogenic constructions, prospecting and evaluation of deposits of these types not only in the territory of Macedonia, but also globally.

Key words: Macedonia; metallogeny; zinc; lead; ore deposit; exhalative; Mississippi type; prospecting model

INTRODUCTION

The mineral resources of Macedonia is currently determined mainly by the reserves of deposits: iron-nickel ores (Ržanovo), lead-zinc skarn (Sasa-Toranitca), gold-copper porphyry (Bučim, Borov Dol, Ilovica, Kadiica, Plavica), vein and brecciated Pb-Zn-Cu-Ag + Au (Lece, Zletovo, Rudnik), (sediment-hosted) Au-As-Sb-Tl deposits of the Carlin type (Alshar, Dudica and others). Lead-zinc deposits and their flanks, except for skarn ores, are represented mainly by quartz-vein formation in metamorphosed rocks spatially confined to discontinuous zones with cataclase features in marbles (Munkov, 2006). Less abundant pyritic volcanogenic-sedimentary occurrences of the Cyprian type associated with ultrabasic-basite complexes.

The development of lead-zinc deposits plays an important role in the economy of the Republic of Macedonia. The main reserves of these metals are concentrated in the skarns of the Sasa deposit. The ore deposits of this formation, in addition to the main commodity of Ag-Pb-Zn, contain Cd, In, Sb, As, Bi, Te and Au. More than 40,000 tons of lead and 30,000 tons of zinc in concentrate are annually extracted from this deposit (Xun, 2013).

Lead-zinc deposits of SEDEX and MVT types in Macedonia are unknown, although they are in neighboring Serbia (Bobija, Lece, Kišnica and Blagodat). The Blagodat deposit is located within the Serbo-Macedonian massif zone and located in the Lower Paleozoic metamorphosed carbonate complexes of the back-arc basin. With these complexes, the Sasa deposit is also associated, but the proximity of the granitoid Serbo-Macedonian massif have determined the skarn and vein composition of its ores.

Other Serbian deposits of SEDEX type occur in the limestones of the northern extension of the West-Macedonian zone, composed of Paleozoic metamorphosed terrigenous, volcanogenic and carbonate rocks. According to studies (Robertson, Shallo, 2000), the development of the zone is due to the closure and partial subduction of the oceanic crust in the early Tertiary period. In the modern structure, the rocks of this zone wrap Precambrian metamorphic complexes of the Pelagonian massif (craton terrane), which is bounded from the east by the rift of Vardar zone, that being composed of island-arc ophiolite complexes, divides the geological structure of Macedonia into two parts: the

West Macedonian zone and the zone of the Serbo-Macedonian massif (Figure 1), which rock complexes were formed, most likely, in the conditions of the back-arc basin. The latter is the most potential for discovery of new lead-zinc deposits.

The West-Macedonian zone complexes are the part of the Hellenides (External Dinarides) and are characterized by features of a passive margins and subplatforms. It is this that determines the possibility of identifying ores of the MVT and SEDEX types.

The lead-zinc deposits are the one of the most important sources of Zn and Pb. In the total world balance, their reserves and resources are about 27%, and the share of all deposits of this type in the world extraction of lead and zinc is about 30% (Tikkanen, 1986). The largest and most explored deposits are located in North America (the basin of the Mississippi river). The major share of global reserves was provided by the largest deposits: Viburnum, Brashi Creek, Fletcher (USA); Pine Point, Polaris (Canada); Tara, Navan (Ireland); Asnacallar, Reosin, Rubiales (Spain), Anguran (Iran), Tunsit (Morocco).

The study of these deposits has been going on for about 100 years and their results are widely covered in general publications (Leach et al., 2010;

Paradise et al., 2007; Sangster, 2009). According to the classification developed by V. Smirnov, they are divided into geological-industrial types – pyritic in volcanic complexes (VMS), pyritic in terrigenous and terrigenous-carbonate complexes (SEDEX) and lead-zinc in carbonate complexes (MVT – Mississippi Valley type). The most famous among them are: Red Dog, Selvin Basin (Howard Pass), Pine Point and Pavlovskoe (Novaya Zemlya, Russia). In addition, about 120 small deposits and occurrences exist in Urals (Saurey), Yakutia (Sardana, Mengeriller, Agakukan, etc.), Scandinavia (Mofjellet, Bleikvassli), Greenland (Citronen), Canada (Macmillan Pass, Prairie Creek, Bear-Twit, etc.) and United States. The largest number of known objects is located on the North American continent,

The study the SEDEX-MVT type ore deposits is particularly relevant, because of Morgan Stanley's forecasts, that in the near future the cost of Zn and Pb may be the most significant among other non-ferrous and rare metals.

The purpose of this paper is to attempt to study and summarize the available information and draw conclusions about the possibility of discovery of SEDEX-MVT type ore deposits in Macedonia, and to show their significance in the future.

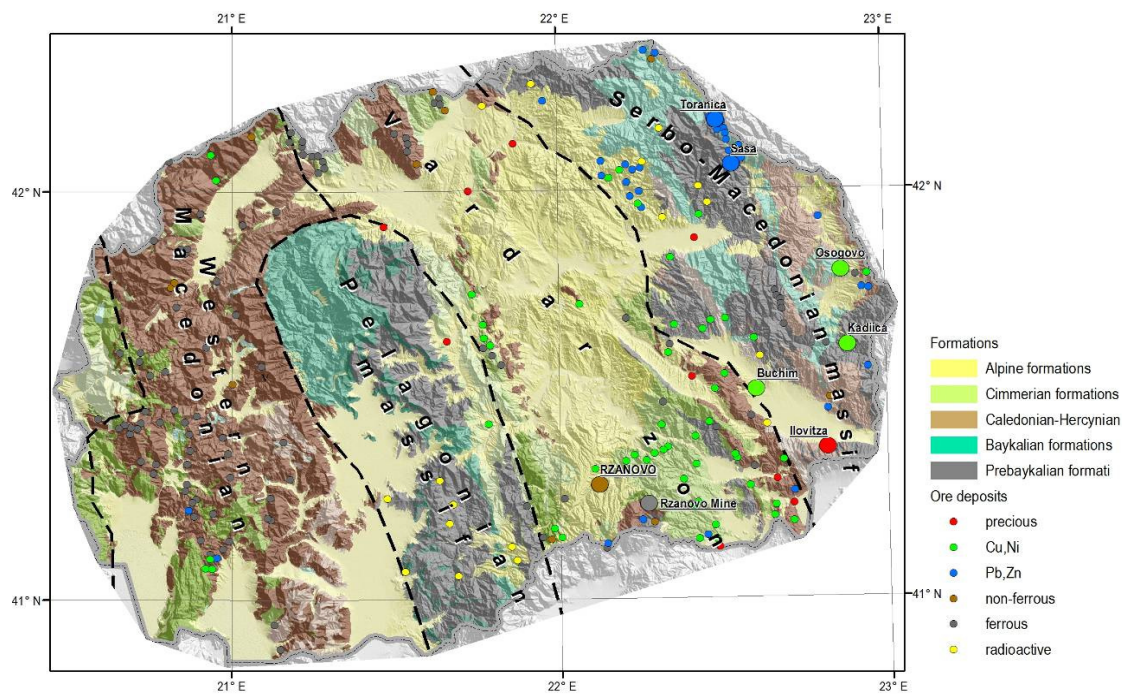


Fig. 1. Position of ore deposits within different aged rock series of Macedonia (by Dumurđžanov et al., 2004)

GEODYNAMIC ENVIRONMENT OF DEPOSIT LOCALIZATION AND CHARACTERISTICS

The SEDEX and MVT types deposits were formed in different geodynamic settings. SEDEX deposits were formed under conditions of reducing hydrothermal processes in intracratonic and epicraton rift troughs, often adjacent to rift troughs, with high rates of deflection and sedimentation [Goodfellow, 2007; Mac Intyre, 1991]. The SEDEX type includes three subtypes [Goodfellow, 2007]: sedimentation-exhalative deposits, deposits formed at marine bottom (Irish subtype – Irish) and deposits similar to Broken Hill (BHT). The first two occur in carbonate rocks and can have features of both syngenetic and epigenetic ore depositions. The Irish subtype is similar to the MVT, but because of the high degree of solubility of the carbonate silts that are lithiated in the diagenesis stage in moderately acidic ore-bearing solutions, the ores were deposited here in the considimental karst volumes. Deposits of BHT are metamorphosed, spatially related to Fe-Si-Mn oxide exhalites, and host rocks are the contrasting series of volcanic-sedimentary rocks.

MVT deposits are located in platform and subplatform carbonate strata, usually associated with barite or fluorite, and, in contrast to the SEDEX type, have a epigenetic appearance.

The main differences in the geological position of the SEDEX and MVT deposits are in the proximity of the former to the rifts, and the latter to the platform carbonate sedimentation basins. This difference determines the different sources, com-

position and mechanisms of migration of ore-forming fluids. The question of the mechanism of migration of solutions is very controversial the relief features of conducting regions and gravity play the important role in the migration of fluids. The favorable paleoclimatic conditions of the basins are important for the existence of evaporite layers and large mineralized volumes to form regional fluid systems. An outstanding role was played by the marine biosphere. Biogerm buildings were formed in sections above the more porous and permeable carbonate, mainly dolomitic, strata.

Most researchers recognize the existence of a series between deposits of types SEDEX and VMS, on the one hand, and SEDEX and MVT on the other [Goodfellow, 2007; Mac Intyre, 1991, Sangster, 1996]. Although the SEDEX and MVT deposits were formed in different geodynamic settings, the numerous early stage occurrences of MVT ores are known, with the signs of landslide processes. When comparing deposits, the common features are often identified, which are the basis for combining part of the distal SEDEX facies and peripheral MVT facies. At the same time, the average and maximum reserves and resources of MVT deposits are significantly smaller (Figure 2). For example, the resources of the largest MVT-deposit Pine Point in Canada are inferior to SEDEX-deposits: Broken Hill, MacArthur, Red Dog, and others.

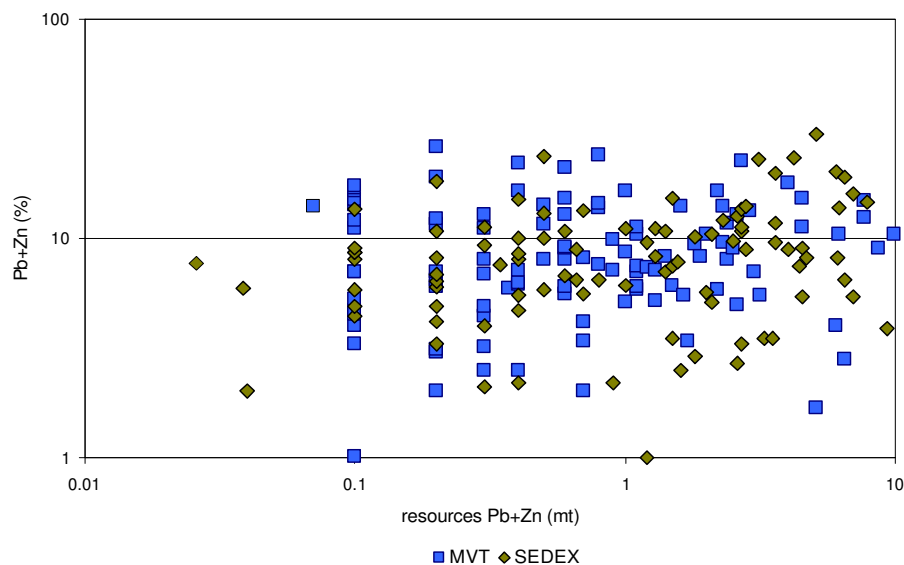


Fig. 2. Grade-tonnage of total Pb+Zn amount for worldwide MVT and SEDEX deposits

The SEDEX ores contain predominant sphalerite, galena, barite and quite often pyrite. Usually pyrite, galena and sphalerite prevail near the exhalation channels, the barite bodies are found at the top of the ore column or on the periphery of the ore deposition area. Zinc is more widespread than lead, which explains the decrease in the ratio of lead to the sum of metals in the direction from the centers of exhalation. Copper everywhere, especially in volcanic sections, is present in the ore in a diffuse form, sometimes forms stockwork bodies (Mount Isa) or stratabound massive deposits (Rammelsberg).

Stratiform MVT deposits, being closely associated with carbonate formations, are represented by substrata and veins. Wallrock transformations are relatively weak, that is expressed in dolomitization, baritization and silicification. MVT deposits are also combined into a family that includes subtypes [Donets, 2003]: Mississippi, Sardinian (with germanium), Silesian – Krakow (pyrite) and Mirgalimsai (barite). In ores, in addition to basic metals, there may be associated silver, antimony, arsenic, barium, bismuth, cadmium, cobalt, gallium, indium, mercury, molybdenum, nickel, thallium.

The resources of deposits are usually less than 2 million tons of total metal, and the contents rarely exceed 10% (by the amount of metals), with the predominance of zinc (Paradis et al, 2007). The area of deposits usually occupy significant areas. The basin of the Mississippi river has up to 400 different-scale deposits, and this is most likely due

to more or less the same geodynamic conditions of sedimentary accumulation and their subsequent transformations during diagenesis, catagenesis and epigenesis.

The ratio of lead and zinc in the MVT deposits is relatively stable, the amount of zinc in the ores is usually larger than that of lead, averaging 2–3 : 1, and this is one of the few differences from objects of the SEDEX type in which the Zn : Pb ratio varies in a much wider range (Figure 3). Numerous studies show that in addition to the different composition of host rocks, which is due to the geodynamic position of sedimentary basins, and some ore structure differences and productive stage ore bodies morphology, these deposits have many common features. These include the general mineralogy and texture of the ores of the early stages, the complex of trace elements in the ores, the isotope composition of lead and sulfur, reflecting the diversity of their sources, the structural factors controlling the mineralization of the late stages.

Isotope systems in Pb-Zn deposits characterize the different interaction of solutions and host rocks (Maynard, 2001). Lead isotopes indicate the same source of MVT and SEDEX ores, with radiogenic sources that are more characteristic of thick sedimentary complexes. Ancient deposits are divided into two groups by Sr isotope content. Radiogenic Sr is present in the deposits of Meggen, Rammelsberg and Jason, while it is poorly represented in Red Dog and Western Cuba. The latter can determine the more open ore-forming system.

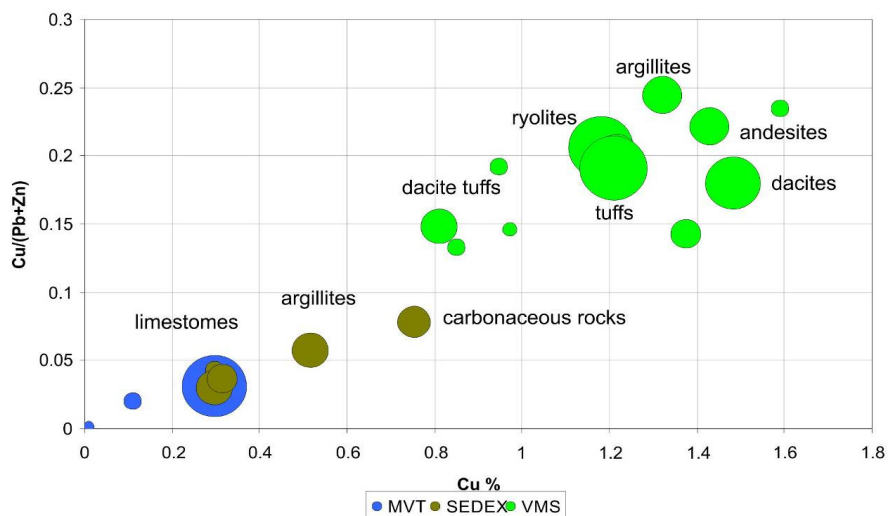


Fig. 3. Ratio of Cu/Pb+Zn and Cu in the MVT, SEDEX and VMS ores (by open source).

Average metal contents are shown for different types of host rock – volcanic lavas and their tuffs, clastic, clay and carbonate rocks

PROSPECTING MODELS OF SEDEX-MVT ORE DEPOSITS

The existing geological prospecting models aimed at the immediate search for a deposit of these types are based on a set of direct and indirect features observed on the surface and a shallow depth that is achievable during drilling operations. At the same time, in order to identify promising areas for prospecting, it is usually necessary to analyze global and regional signs of possible large deposits. These signs, in their own right, stem from the notions of the genesis of deposits of this type.

There are several hypotheses. The first involves the participation of deep-seated basin brines descending from the uplifting areas of foredeep (Garven, 1985). The second hypothesis examines the participation of solutions generated under conditions of carbonate sediments diagenesis and catagenesis and their respective compaction (Beales, 1966). According to the third hypothesis, the mineralization is associated with the circulation of brines in huge volumes of rocks, due to the difference in pressure, temperature, and salinity (Morrow, 1998). These conditions ensure the functioning of the system for a long time and explain the possibility of processing, including dolomitization, of large volumes of enclosing rocks.

All these hypotheses presuppose the existence of strata formed in certain geodynamic conditions. The main regional prospecting feature for the SEDEX and MVT types is their position in the intracratonic and epicraton sedimentary basins of various orders. The location of the basins was controlled by faults, which also contain mafic intrusions (sills and subvolcanic bodies), which, according to most researchers, are in paragenetic connection with polymetallic mineralization. The mobile geodynamic conditions of sedimentation in intracratonic and epicraton rifts and in platform and subplatform conditions determine the corresponding formation shape of the strata that contain the SEDEX and MVT deposits.

The sedimentary rocks of the SEDEX type are represented by hemipelagic marine fine-grained sedimentary rocks – clays, carbonaceous-argillaceous, black shale, and limestone and dolomite. The morphology and structure of lenticular stratiform deposits with a thickness of tens of meters and a length, more than a kilometer, depends on the distance from the brine outlet to the seabed and the morphology of the basin bottom. The predominant sulfide mineral is pyrite, sometimes pyrrhotite. The main commercial minerals are

sphalerite and galena, less often chalcopyrite. Barite can occupy more than 25% of the volume of hydrothermal formations. In this case, according to Emsbo (2009), the depth to the surface of the crystalline basement should exceed 3 km, which, as empirically proven, allows to lower the temperature of fluids to 100°C. In this case, the neighborhood with the occurrences of Ba, Mn, Fe and PO₄ is especially important.

For deposits of the MVT type, the clay-dolomite-limestone formation is considered as ore-bearing, the sediments were deposited in the shallow marine conditions of continental margin basins and are characterized by complex facies composition, including barrier reefs, terrigenous-carbonate and chemogenic-carbonate rocks. In the ore district of Pine Point (Canada), the ore-bearing barrier reefs divide the evaporite sediments and limestone-shale sediments of the marginal sea. The silica-limestone-dolomite rock series hosts the ore deposits of the Mississippi type (Lamog, Cocker, Joplin, Tri-State, Led-Hill, USA). The decrease in the siliceous component is typical for ore-bearing subformation. It should be taken into account (Leach et al., 2010) that although slightly deformed subplatform carbonate strata of passive margins usually do not have a high potential, there are, however, exceptions (Lennard Shelf model).

The overall structural control in the deposits at the stages of basin development is manifested in the accumulation of the ore-bearing formations at paleodepressions on the uplifts slopes with barrier reefs adjacent to sedimentary (including oil and gas bearing) basins with sedimentogenic and catagenic waters. The areas of unloading of metalliferous brines and, probably, oil waters are confined to the large faults that bound rifts and have controlled the volcanic activity.

Carbonate formations of Macedonia include the Riphean-Cambrian marbles of the Pelagonian massif and the Upper Paleozoic-Mesozoic limestones (Figure 4). In the West-Macedonian zone, they underlie the Mesozoic evaporite formations, with wide haloes of lead, zinc and copper. Substantially terrigenous-carbonate formations in the zone of the Serbo-Macedonian massif form part of the Upper Paleozoic-Mesozoic island-arc complexes marked with multiple anomalies of copper, lead and zinc. Later in the Cenozoic, such formations were formed in the Vardar zone in back-arc basins.

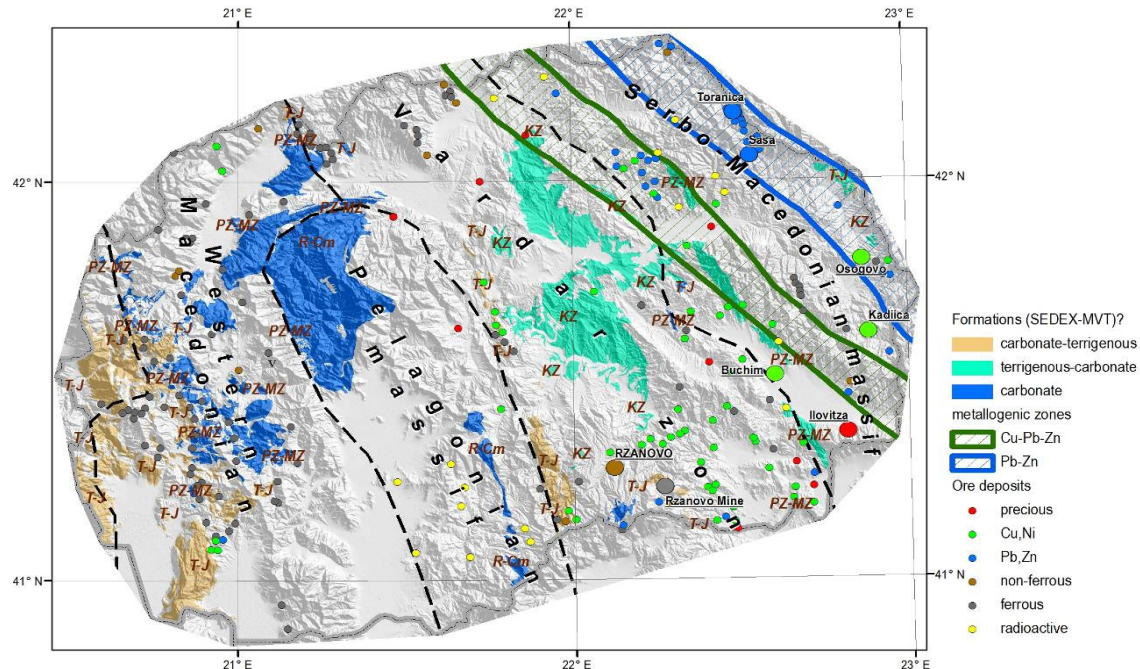


Fig. 4. Spreading of potential ore-bearing carbonate, carbonate-terrigenous rocks and metallogenetic zoning for lead, zinc and copper (by Volkov et al, 2010).

The metallogenetic zoning of Macedonia, conducted earlier for lead and zinc (Volkov et al, 2010), is specialized in the identification of skarn and vein deposits associated with granitoid intrusions. At the same time, the wide distribution of carbonate and terrigenous-carbonate rocks may be the basis for increasing the lead-zinc potential of the country due to the possible detection of SEDEX and MVT type ores.

In addition, a set of elements of the prospecting model may also include features relating to the deep geodynamic conditions for the paleobasin formation and resulting from the regional studies on the ancient stages of the development of the earth's crust and mantle. The use of geophysical methods, among which a seismic and gravity prospecting, the method of nuclear magnetic resonance are outlined, could contribute to contouring of regions with potential environments.

CONCLUSIONS

Though, SEDEX and MVT deposits in Macedonia are unknown, the information given is of importance for predictive-metallogenetic constructions, prospecting and evaluation of deposits of these types not only in the territory of Macedonia. Revision-search and prospecting-appraisal works taking into account the numerous criteria and signs will allow to assess the prospects for the development of the mineral base of lead and zinc in the Republic of Macedonia. The problem of studying

the SEDEX-MVT type deposits is particularly relevant, because, according to Morgan Stanley's forecasts, in the near future the cost of Zn and Pb may be the most significant among other non-ferrous and rare metals.

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REFERENCES

- Bau, M. (1991): Rare-earth element mobility during hydrothermal and metamorphic fluid-rock interaction and the significance of the oxidation state of europium. *Chem. Geol.*, V. **93**, pp. 219–230.
- Beales, F. W., Jackson, S. A. (1966): Precipitation of lead-zinc ores in carbonate reservoirs as illustrated by Pine Point ore field. – *Canada: Institution of Mining and Metallurgy Transactions, section B*, 1966. pp. B8278–8285.

- Donets, A. I. (2003): *Stratiform lead-zinc deposits in carbonate rocks: classification and prospecting principals*, Doctoral thesis, Moscow.
- Dumurdžanov, N., Serafimovski, T., Burchfiel, B. C. (2004): Evolution of the Neogene-Pleistocene basins of Macedonia: *Geological Society of America Digital Map and Chart, Series 1* (accompanying notes), 20 p., <http://gsamaps.gsjournals.org/gsamaps/toc>.
- Emsbo, P. (2000): Gold in SEDEX deposits, *SEG Reviews*, Vol. 13, pp. 427–437.
- Garven, G. (1985): The role of regional fluid flow in the genesis of the Pine Point deposit, Western Canada sedimentary basin, *Econ. Geol.* 80, pp. 307–324.
- Goodfellow, W. D., Lydon, J. W. (2007): Sedimentary exhalative (SEDEX) deposits, In: *Mineral Deposits of Canada: A Synthesis of Major Deposit Types, District Metallogeny, the Evolution of Geological Provinces, and Exploration Methods*. Geological Association of Canada, Mineral Deposits Division. [S. l.] (Special Publication No. 5), pp. 163–183.
- Kun, L., Ruidong, Y., Wenyong, Ch. et al. (2014): Trace element and REE geochemistry of the Zhewang gold deposit, southeastern Guizhou Province, China, *Chin. J. Geochem.*, 33, pp. 109–118.
- Leach, D., Taylor, R. D., Fey, D. L., Diehl, S. F., Saltus, R. W. (2010): *A Deposit Model for Mississippi Valley-Type Lead-Zinc Ores*, Scientific Investigations Report 5070–A, U.S. Geological Survey, Reston, Virginia.
- Mac Intyre, D. G. (1991): SEDEX — Sedimentary-Exhalative Deposits, In: *Ore Deposits, Tectonics and Metallogeny in the Canadian Cordillera*, McMillan, W. J., Coordinator; B. C. Ministry of Energy, Mines and Petroleum Resources. [S. l.], (Paper 1991–4), pp. 25–69.
- Maynard, J. B. (2001): Pb, Sr, and S isotopic data from SEDEX sulfide deposits: separating the effects of host rock and seawater composition, In: *Sediment-Hosted Lead-Zinc Deposits: Roles of Basin Evolution, Tectonics, and Geochemistry in Ore Genesis, I*, GSA Annual Meeting, November 7, 2001.
- Morrow D. (1998): Regional subsurface dolomitization; Models and constraints, *Geoscience Canada*, 25, pp. 57–70.
- Munkov, S. (2006): The ore belt “Osogovo-Besna Kobila” (Ore formations, morphogenetic types of deposits and physicochemical conditions of forming). In: *Ann. of the University of Mining and Geology “St. Ivan Rilski”*, 49, I – *Geol. and Geophys.*, 119–130.
- Paradis S., Hannigan P., Dewing K. (2007): Mississippi Valley-Type lead-zinc deposits, In: *Mineral Deposits of Canada: A Synthesis of Major Deposit-types, District Metallogeny. The Evolution of Geological Provinces and Exploration Methods*. Geological Association of Canada, Mineral Deposits Division, Special Publication, no. 5, pp. 185–203.
- Robertson, A., Shallo, M. (2000): Mesozoic-Tertiary tectonic evolution of Albania in its regional Eastern Mediterranean context, *Tectonophysics*, 316, pp. 197–254.
- Sangster, D. F. (1996): Mississippi Valley-type and SEDEX lead-zinc. In: Eckstrand, O. R., Sinclair, W. D. & Thorpe, R. I. (eds.), *Geology of Canadian Mineral Deposit Types*. Geological Survey of Canada, *Geology of Canada*, Vol. 8, pp 253–261.
- Sangster, D. F. (2009): Geology of base metal deposits, *Encyclopedia of life support systems*, Vol. 6 (Geology), UNESCO, pp. 91–116.
- Sangster, D. F. (ed.) (1996): *Carbonate-hosted lead-zinc deposits*; Society of Economic Geologists. [S. l.] (Special paper 4).
- Sediment-Hosted Zinc Potential in Greenland*. Reporting the Mineral Resource Assessment Workshop, 29 November – 1 December 2011.
- Taylor, S. R., McLennan, S. M. (1985): *The Continental Crust: Its Composition and Evolution*. Oxford, London, Edinburgh, Boston, Palo Alto, Melbourne: Blackwell Scientific, 312 p.
- Tikkanen, G. D. (1986): World resources and supply of lead and zinc, In: Bush, W. R. (ed.), *Economics of Internationally Traded Minerals*: Society of Mining Engineers, Inc., p. 242–250.
- Verplanck, P. L., Murray W. Hitzman (2016): *Introduction: Rare Earth and Critical Elements in Ore Deposits*: Society of Economic Geologists, Inc., 18.
- Volkov, A. V., Serafimovski T., Alekseev V. Yu., Tasev G. (2010): The structural-metallogenic maps of ore districts of F.Y.R. of Macedonia // *Scientific Annals, School of Geology, Aristotle University of Thessaloniki, Proceedings of the XIX CBGA Congress, Thessaloniki, Greece*, Special volume 100, pp. 359–367.
- Xun, S. (2013): The mineral industry of Macedonia, *Minerals Yearbook 2013*. U. S. Geological Survey, 2013.

Резиме

**ПЕРСПЕКТИВИ ЗА ОТКРИВАЊЕ НОВИ НАОГАЛИШТА НА ОЛОВО И ЦИНК
ВО РЕПУБЛИКА МАКЕДОНИЈА**

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Клучни зборови: Македонија; металогенија; цинк; олово; рудни наоѓалишта; ексхалација; Мисисипи-тип;
проспектиски модел

На територијата на Република Македонија досега не биле определувани седиментно-есхалациони наоѓалишта

од типот SEDEX и Mississippi Valley (MVT) иако тие се познати во соседната Србија (Бобија, Леце, Кишница и

Благодат). Бидејќи во други региони во светот тие се од големо индустриско значење, направен е обид да се прочат и сумираат достапните информации за можноста да се откријат такви наоѓалишта и на територијата на Република Македонија, како и да се укаже на нивното идно значење. Една од задачите во овој труд е да го приспособи познатиот модел за предвидување и проспекција на овие

типови наоѓалишта на територијата на Република Македонија.

Информациите дадени во овој труд се од големо значење за прогнозирање металогени конструкции, како и за проспекција и оценка на овие типови наоѓалишта не само на територијата на Република Македонија, туку и глобално.