

Siderite-barite-polysulfide deposits and early continental rifting in Dinarides

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Key words: Siderite-barite-sulfide deposits, Dinarides, Early continental rifting, Alpine metallogeny.

Extensive geochemical, isotopic and microthermometric investigations have been undertaken in order to elucidate the dilemma: Hercynian or Alpine metallogeny in formation of siderite-barite-polysulfide deposits in Inner Dinarides. On grounds of research results of his own and other investigators, the author is inclined to accept early continental rifting in Permian time, the first phase of Alpine Wilson cycle, as a global tectonic process responsible for their formation.

Ključne riječi: Sideritno-baritno-sulfidna ležišta, Dinaridi, rano intrakontinentalno riftovanje, Alpska metalogenija.

Sideritno-baritno-polisulfidna rudna ležišta u Fočanskom paleozoiku, Srednjobosanskom rudogorju, Sansko-unskom paleozoiku (Ljubija), Trgovskoj gori, Petrovoj gori, Samoborskoj gori i Bistranjskoj gori (Medvednica) smještena su u dinarskom eugeo-sinklinalnom pojasu, neposredno uz vanjski rub mezozojske karbonatne platforme. Usprkos mnogobrojnim sličnostima u geološkom, mineraloškom i geokemijskom pogledu, geneza ležišta je i danas predmet kontroverznih stavova, a dilema: hercinska ili alpska metalogeneza, privlači i nadalje pažnju istraživača. Koristeći rezultate raznih istraživačkih metodologija; sedimentne facijelne analize, geokemije sumpornih izotopa i elemenata u tragovima, plumbologije i paleogeotermije, autor se priklanja alpskoj metalogenezi, tj. rudnim procesima vezanim za rano intrakontinentalno riftovanje u permu.

Introduction

There is a long lasting dispute on time and way of formation of siderite-barite-polysulfide (\pm Cu, Pb, Zn, F) deposits on Mid-Bosnian ore mountains, Ljubija, Trgovska gora, Petrova gora, Samoborska gora, Lika and Gorski Kotar. In principle, there have been two distinguished hypothesis offering solution of that problem, Hercynian and Alpine metallogeny, and both of them have been postulated after numerous field observation, detailed microscopy and laboratory investigation.

Mid-Bosnian ore mountains, Trgovska gora, Petrova gora and Samoborska gora ore deposits were elaborated by Jurković (1958, 1959, 1960, 1961, 1962, 1962 a), Jeremić (1958, 1959), Šinkovec (1971) and others, and all of them have been considered to be hydrothermal and Permian in age, with exception of Ljubija siderite deposit, which was also regarded as to be volcano-sedimentary or pure sedimentary, formed in Middle or Upper Carboniferous time (Jurković, 1961, Jurić, 1971). They were related to Hercynian metallogeny in terms of geosynclinal concept.

Introduction of global-tectonics and applying of Mesozoic Wilson cycle into Dinaric orogeny evolution put forward a logical explanation for much of regional geological and petrological phenomena.

Janković studying Triassic mineral deposits in Central Bosnia and NW Montenegro (1974, 1977, 1982, 1987), and Kubat (1982), arrived at a conclusion that the mineralization in Foča Paleozoic, Mid-Bosnian ore mountains, Sana-Una Paleozoic, Trgovska gora and Petrova gora, what is basically eugeosynclinal belt of Dinarides, must be affiliated

to the Triassic metallogeny and accompanying magmatism.

Jurković (Jurković and Durn, 1988, Jurković, 1989) revised his former hypothesis on time and way of formation of Trgovska gora and Petrova gora deposits, linking them all to Middle Carboniferous igneous activity and therefor to Hercynian metallogeny. They are »distal volcano-exhalative« by origin.

Extensive geological, geochemical, isotopic and microthermometric investigation have been undertaken in order to elucidate this dilemma (Palinkaš, 1988, 1988a). The aim of the article is to present in a short way basic achievements and ideas which come out from field observation and laboratory measurements.

Short review of recent investigation results

Recent developments attained by sedimentological facies analysis, geochemistry of sulfur isotopes and trace elements in ore and rocks, principles of plumbology and paleogeothermometry are briefly outlined.

During some earlier regional geochemical explorations Palinkaš and Šinkovec (1987), using a large number (a few thousand) of geochemical stream sediment data (Cu, Zn, Pb, Co, Ni, U), collected all over the Paleozoic regions and applying standard statistical procedure, observed a significant distinction in »stream sediment« geochemistry of each particular region.

There was a basic presumption that the rock chemistry in all regions should be fairly similar and the

main differences would appear because of different metal content in the ore deposits. Ore deposits in Croatia, associated with Paleozoic terrains, which are built up mostly of Permo-Carboniferous clastic sediments, are arranged approximately along a line which goes over the Mesozoic carbonate platform (miogeosyncline, Outer Dinarides), passing through the eugeosynclinal region (Inner Dinarides) and terminating in still undefined Pannonian horst-mountains (Papuk, Psunj). The examined regions are Lika, Gorski Kotar, Petrova gora, Trgovska gora, and Samoborska gora.

The following peculiarity has been observed. The ratio of mean values for particular elements or their sums, like $Cu+Ni+Co/Zn+Pb+U$, $Cu+Ni+Co/Zn+Pb$, $Cu/Zn+Pb$, $Ni+Co/U$, Cu/Zn and Mn/Fe shows persistently increasing tendency toward the center of the eugeosyncline. This conspicuous feature might be logically related to initial rifting magmatism, i.e. oceanization and influence of the upper mantle as well.

Lead isotopes in galenas sampled in Lika, Trgovska gora, Ljubija, Samoborska gora and Bistranjska gora (Medvednica), along a similar traverse, show another kind of regularity, which fits into global tectonic model as well.

Isotopic analyses, using Doe-Stacey, Stacey-Kramer and Doe-Zartman models of lead growth curve, have given ages appropriating to Permo-Triassic (Palinkaš, 1985, 1988). On the other hand, increase of μ -values from the inner margin of the carbonate platform were Lika undoubtedly belongs, toward Bistra, which is the nearest to the ensialic Pannonian mass, is another confirmation. It means that material from the African promontory had much lower U/Pb ratio, i.e. originates from the lower part of the crust. Further consideration should be directed toward origin of clastic material, or contribution of African Precambrian and younger structures in the Hercynian Europe. There is also significant difference of μ -values in galenas between Dinaric siderite-barite-polysulfide deposits and Pb-Zn ore deposits affiliated to terrains of Hercynian tectonogenesis and Carboniferous granitic magmatism in Hungary (Kiss, 1982), increased in favor of the latter.

Paleogeothermal conditions have been examined by extensive microthermometric measurements on minerals (barite, fluorite, quartz) from the ore deposits in Ljubija, Trgovska gora and Petrova gora (Palinkaš, 1988).

The corner-stone in solving the problem was Ljubija siderite mine and deposits in its close vicinity (Žune, barite-fluorite deposit), which appeared to be hydrothermal-metasomatic and Permian in age.

The deposit was formed during early intracontinental rifting, followed by bimodal magmatism. Increased thermal gradient, deep open fractures and emplacement of volcanics generated thermal plums. The width of the thermal cell has been approximated at 20 km, gradually passing into domains of Trgovska gora hydrothermal activity. Chemical character of circulating hydrothermal water was mostly NaCl, less frequently KCl, $CaCl_2$, $FeCl_2$ and was formed by,

- intake of hypersaline water from the Permian evaporitic basins and lagoons,
- influence of terrestrial waters, recognized by presence of SO_4^{2-} , HCO_3^- , CO_3^{2-} , CO_2 (chlatrates) in higher parts of the thermal cell,
- boiling phenomena (inclusions of high salinity and (L+V+S/halite/inclusions),
- interaction of brines with volcanics and graywackes.

Ore body in Žune originates from a two phase region of the hydrothermal convective cell, and Ljubija from its lower margin. The depth of formation determined on a basis of PTX parameters of boiling fluids is between 200 m and 500 m depending on whether lithostatic or hydrostatic pressure was encountered.

Fluid inclusions in Trgovska gora and Petrova gora display similar thermal characteristics and composition.

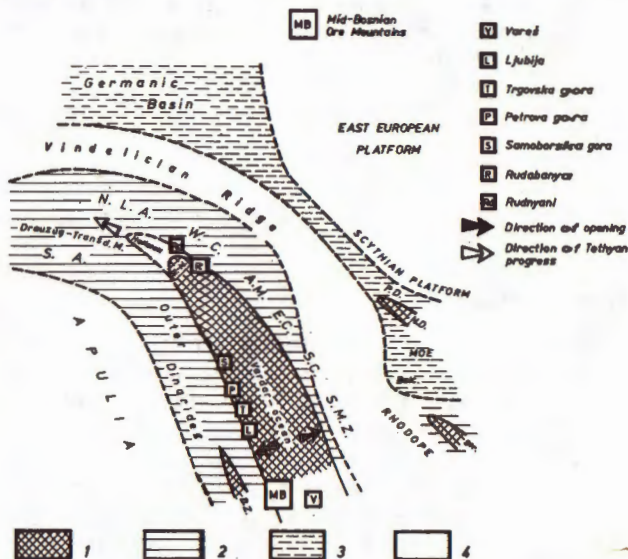


Fig. 1. Palinspastic sketch showing Ladinian paleogeography (not to scale!, after Kovacs, 1984) accomplished by approximate position of siderite-barite-polysulfide deposits discussed in the paper. Abbreviations: R.-M. Rudabanya-Meliata Triassic, S. Silica nappe, Transd. M. Transdanubian Midmountains, S.A. Southern Alps, B.Z. Budva zone, N.L.A. Northern Limestone Alps, W.C. West Carpathian, M. Mecsek, A.M. Apuseni Mountains, E.C. East Carpathian, P. Pienniny Exotic Cordillera, Transylv. Transylvanides, S.C. South Carpathians, S.M.Z. Serbo-Macedonian zone, P.D. Pre-Dobrogea, N.D. North Dobrogea (Tulcea zone), MOE Moesian-platform, Balc. Balkanides+Kraistides, Str. Stranda Mts., 1. open sea (in part with ocean basement) 2. shelf 3. epicontinental sea 4. dryland.

Sl. 1. Palinspastička rekonstrukcija ladinjske paleogeografije (nije u mjerilu, prema Kovacsu, 1984) s naknadno unesenim, približnim položajem sideritno-baritno-polisulfidnih ležišta, diskutiranim u članku. Kratice: R.-M. Rudabanya-Meliata trijas, S. Silica navlaka, Transd. M.T. transdanubijsko sredogorje, S.A. Južne Alpe, B.Z. Budva zona, N.L.A. Sjeverne vapnenjačke Alpe, W.C. Zapadni Karpati, M. Mecsek, A.M. Apuseni planine, E.C. Istočni Karpati, P. Pienniny egzotični kordiljeri, Transylv. Transylvanidi, S.C. Južni Karpati, S.M.Z. Srpsko-Makedonska zona, P.D. Pred-dobruđa, N.D. Sjeverna Dobruđa (Tulcea zona), MOE Mezijska platforma, Balc. Balkanidi+Krajistidi, Str. Stranda pl., 1. otvoreno more (djelomično s oceanskom korom), 2. šelf, 3. epikontinentalno more, 4. kopno.

Sulfur isotope data in barite from Rude (Samoborska gora), Ljubija ore district and Mid-Bosnian ore mountains (Kreševo region) are also indicative (Šiftar, 1988, 1989, 1990), and $\delta^{34}\text{S}$ values between 8–12‰ points out on influence of Permian sea water in ore-forming processes.

Geological evidences in all three ore districts and Samoborska gora speak greatly in favor of the Permian formation time (especially absence of the mineralization in the overlying Lower Triassic rocks).

The deposits are confined to early intracontinental rifting and accompanying bimodal magmatism. They were implaced along the passive continental margin, demarcating future opening of the Tethys. Early rifting structure, caused by thermal dome, were thereafter covered by shallow water platform and shelf sediments and preserved during oncoming global tectonic events. Placing the deposits on the palinspastic sketch of Ladinian paleogeography (Kovács, 1984, Fig. 1), the idea got its full illustration.

It should be stressed, however, that numbered deposits are strictly related to the Permian and should be distinguished from the Middle Triassic ones. The main distinction is in the style of mineralization. While the former ones are subterrestrial, siderite-barite (+ sulfides and fluorites), occasionally exhalative, the latter are pronounced exhalative (Vareš, Borovica, Brskovo, Bužim, Čevljanovići) usually with increasing quantity of manganese. This is a sign of advanced rifting phase (Read sea stage) and influence of basic volcanism. Mn-occurrences may be found around all investigated regions but always in younger sediments (Fig. 2).

Conclusion

While the siderite-barite-polysulfide deposits on the outer margin of the carbonate platform (eugeosyncline) were formed by activity of hydrothermal convective cells in subterrestrial level, showing only locally exhalative phenomena (volcano-sedimentary), the deposits on the inner margin (probably failed rift) are detached of any pronounced thermal events at that time (Lika and Gorski Kotar), but not necessarily in Middle Triassic (Tršće, mercury).

Lika barite deposits is implaced in Carboniferous sediments, probably early-late diagenetic, connected with dolomitization processes, while Gorski Kotar barite mineralization is early diagenetic formed in a tidal flat evaporitic facies (Sabkha, Palinkaš and Šinkovec, 1986, Palinkaš and Sremac, 1987). Distribution of $\delta^{34}\text{S}$ values in pyrite, along a vertical profile in the footwall rocks, bears characteristic of microbiological fractionation in muddy environment.

The Permian siderite-barite deposits along the margin of the Mesozoic carbonate platform demarcate opening of the Tethys. Demarcation line may be followed to Rudabanya (NW Hungary), siderite-barite-polysulfide deposits in Gemericides (Slovakia) and Eastern Alps siderite-barite deposits and occur-

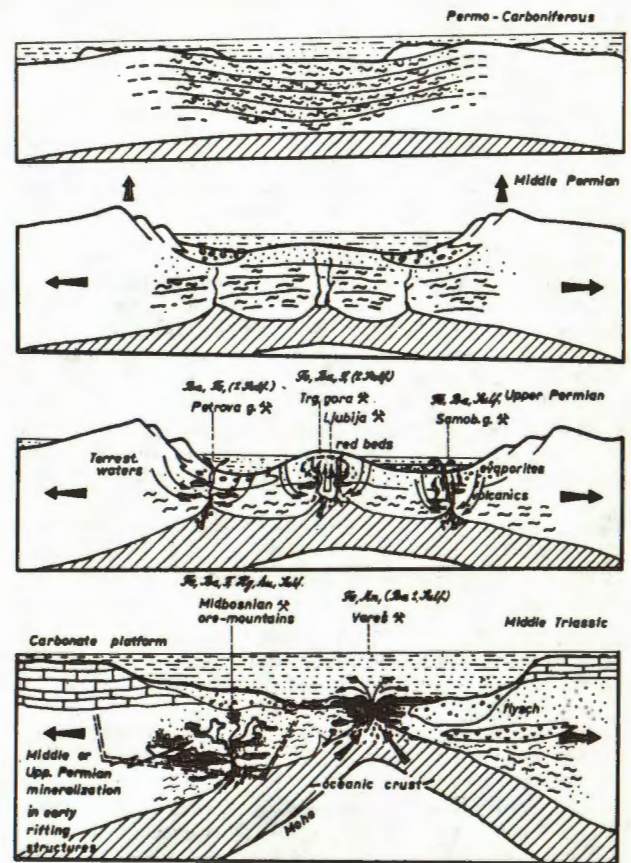


Fig. 2. Simplified chart of ore forming processes in Permian time. Thermal doming, extension tectonics, bimodal magmatism are evidences of early intracontinental rifting, the first phase of the Alpine Wilson cycle. The deposits were formed by subterrestrial hydrothermal convective cells predominantly. Volcano-exhalative phenomena are less frequent (Rude, Samoborska gora, Bukovica, Petrova gora). Early rifting structures were then covered by sediments along the passive continental margin and preserved from destruction during oncoming global-tectonic events of Tethyan opening and closure. Volcano-exhalative deposits in Middle Triassic, like Vareš, Borovica, Čevljanovići etc., were formed in rifting deep-water basins (Read sea type).

Sl. 2. Pojednostavljeni niz geoloških događaja i rudotvornih procesa u permsko vrijeme. Termalna doma, ekstenziona tektonika i bimodalni magmatizam su manifestacije ranog intrakontinentalnog riftinga, prve faze alpskog Wilsonovog ciklusa. Rudna ležišta se pretežno formiraju u subterestričkom nivou, hidrotermalnom aktivnošću konvektivnih ćelija. vulkanogeno-ekshalativni fenomeni su rjeđi (Rude, Šamoborska gora, Bukovica, Petrova gora). Rane riftne strukture bile su prekrivene sedimentima uzduž pasivnog kontinentalnog ruba i sačuvane od razaranja u toku nadolezećih globalno-tektonskih događaja. Vulkanogeno-sedimentna ležišta u srednjem trijasu, kao na pr. Vareš, Borovica, Čevljanovići itd., stvarana su u riftingnim bazenima s već uspostavljenom dubokomorskom sedimentacijom (tip Crvenog mora).

rences. There is a certain shift in formation time from the Dinarides to the Carpathians and the Alps in concordance with delay in opening (Channel, et al., 1979).

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Sideritno-baritno-polisulfidna rudna ležišta i rano intrakontinentalno riftovanje u Dinaridima

L. A. Palinkaš

Sideritno-baritno-polisulfidna rudna ležišta u Fočanskom paleozoiku, Srednjobosanskom rudogorju, Sansko-unskom paleozoiku (Ljubija), Trgovskoj gori, Petrovoj gori, Samoborskoj gori i Bistranjskoj gori (Medvednica) smještena su u paleozojskim klastičnim sedimentima i karbonatima. Njihov položaj je striktno vezan za dinarski eugeosinklinalni pojas, uz neposredni rub mezozojske karbonatne platforme.

Uprkos mnogobrojnim sličnostima u geološkom, mineraloškom i geokemijskom pogledu, geneza ležišta je i danas predmet kontroverznih sitavova, a dilema: hercinska ili alpska metalogeneza privlači i nadalje pažnju istraživača.

Koristeći razne istraživačke metodologije; sedimentnu facijelnu analizu, geokemiju sumpornih izotopa i elemenata u tragovima, plumbologiju i paleogeotermiju, autor se priklanja alpskoj metalogenezi, ali u smislu razvoja tektonike ploča. Na osnovi vlastitih istraživanja, kao i nekih novijih literaturnih podataka, postanak navedenih ležišta bi mogao prikazati u vidu sljedećeg sažetka.

Sideritno-baritno-polisulfidna ležišta u eugeosinklinalnom prostoru Dinarida, na vanjskom rubu mezozojske karbonatne platforme, nastala su djelovanjem hidrotermalnih konvektivnih ćelija u subterestričkom nivou. Vulkanogeno-ekshalativni fenomeni su lokalnog značaja, ali jasno određuju permsko vrijeme postanka (Rude, Samoborska gora i Bukovica, Petrova gora). Rudna ležišta markiraju mjesto otvaranja budućeg Vardarskog oceana (Tetisa), koje je započelo s dugotrajnim intrakontinentalnim riftovanjem već u permu, bez značajnijeg morfološkog diferenciranja sedimentnih prostora na karbonatne platforme ili riftne bazene. Ova pojava se jasno raspoznaje tek u srednjem trijasu (stadij Crvenog mora) s razvojem dubokomorskih facijesa.

Hidrotermalna aktivnost je posljedica poremećaja termalnog gradijenta, ekstenzione tektonike i bimodalnog magmatizma. Rane riftne strukture i rudna ležišta bili su prekriveni sedimentima karbonatne platforme i šelfa na pasivnom kontinentalnom rubu Jadranske ploče, s velikim prezervacionim potencijalom u nadolazećim globalno-tektonskim procesima alpskog Wilsonovog ciklusa (Sl. 2). Prateći liniju otvaranja Tetisa, rudna ležišta siderita slijedimo u sjevernu Mađarsku (Rudabanya) i Gemeride (Slovačka sideritno-baritno-polisulfidna ležišta, Sl. 1). Izvjesna razlika u njihovoj starosti može se objasniti napredovanjem riftnog procesa u vremenu i prostoru prema alpskom domenu.

Treba naglasiti da su opisana ležišta u Dinaridima striktno permske starosti i moraju se razlikovati od srednjotrijaskih po stilu mineralizacije. Dok u prvima prevladavaju subterestrički hidrotermalni procesi, a vulkanogeno-ekshalativni su sporadični, u srednjotrijaskim, naprotiv, vulkanogeno-sedimentne tvorevine dominiraju (Vareš, Borovica, Bužim, Čevljanovići, tip Crvenog mora).

Nadalje, sideritno-baritno-polisulfidna permska ležišta na vanjskom rubu karbonatne platforme nastala su hidrotermalnim putem kao posljedica magmatskih termalnih poremećaja. Ležišta na njezinom unutrašnjem rubu (abortirani rift) su pak bez znakova termalne aktivnosti u to vrijeme. Lička ležišta barita su vjerojatno rano-kasno dijagenska (ne isključuje se Mississippi tip) a goranska permotrijaska ležišta barita su rano-dijagenetska, vezana za facijes plimskih zaravni (Sabkha), što dokazuje sedimentna facijelna analiza i geokemija sumpornih izotopa. Živina mineralizacija u Tršću je već znak srednjotrijaskih hidrotermalnih riftnih procesa i u ovom prostoru.