CONTROL FACTORS OF IRON MINERALIZATION IN THE METALLOGENY OF THE LJUBIJA ORE REGION

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ABSTRACT

The control factors of mineralization in the Ljubija ore region are stratigraphic, lithological, magmatogenic, structural-tectonic and hypergenic. The distribution of iron ores in the Ljubija ore region is primarily controlled by the spread of the Olistostrome member of the Carboniferous Javorik flysch formation. Only that member, whether uncovered on the surface or overlain by an Upper flysch member, contains primary siderite-ankerite iron ores. In addition, the distribution of ore bodies is significantly affected by the concentration and location of mineralized limestone and limestone-dolomite olistoliths. The seating of carbonate olistolithic bodies in the member is irregular, that is, chaotic. The size, shape, and morphology of these bodies and their boundaries are extremely uneven and diverse, in both primary and tectonic occurrences. Not all olistolithic bodies are mineralized. Those that are can be completely, partially or minimally mineralized. Due to all this, ore bodies and deposits “have no continuity and appear in isolation”. Therefore, there is a high exploration risk. These major irregularities are not characteristic of redeposited powdered limonite ores in Plio-Quaternary lacustrine sediments. Cimmerian lateral ruptures were important for the distribution of hydrothermal solutions and today’s distribution of ore deposits and occurrences within ore fields and ore nodes. The hypergenic control factor significantly influenced the forming of iron oxide ores. In the Alpine tectogenesis, old systems of faults and joints were renewed and new created. In this respect, the most significant were transverse, open, steep SW-NE ruptures.

Keywords: Ljubija ore region, metallogenic map, ore formation, control factors, prospecting indications.

INTRODUCTION

The Ljubija ore region is located in the internal metallogenic zone of the Middle Dinarides of Triassic age. It strikes from the Tara-Lim segment, through the Central Dinarides, Vareš and Ljubija-Samobor segments, and all the way to Bistrinskijska Gora on Mt. Medvednica. There are deposits of polysulphides, iron and barite [1] in this more than 300 km long intermittent zone, which is followed from the south by the Dinaride Ophiolite Belt. The zonal regularity is related to the geodynamic development of that Dinaridic segment of the Earth’s crust.

In regional metallogenic analysis, one of the most important tasks is to identify the factors that control the distribution of mineral deposits. This task is creative as it does not conform to established procedures. Each ore region has its own factors and their priorities. The main purpose of this review...
paper is to identify the control factors of iron mineralization in the Ljubija ore region and analyse their impact on the occurrence of iron ore. The control factors of mineralization have been determined based on many years of field research by the authors and examination of all previous reports on Ljubija ores. They will be used for further regional and detailed geological research of iron ores in this region.

The collected results of all types of previous research were then studied and critically reviewed. In the extensive published materials, two sources of information were of great importance: a three-volume study by M. Jurčić that comprises all mineralization occurrences in the Sana Paleozoic, Figure 1, [2], and nineteen reports on geological research in the area of Ljubija, sixteen of which were conducted from 1987 to 1991 as part of the project “Metallogeny of the Ljubija ore region” [3].

![Figure 1. Location of the Sana Paleozoic complex (gray) [4]](image)

In the Ljubija ore region there are primary carbonate iron ores (siderite and ankerite) and secondary oxidised iron ores (limonites). Siderite and ankerite inherently imply a hydrothermal-metasomatic genesis of iron.

Some researchers have left the question about the genesis of stratiform deposits open [5,6]. This paper includes an unpublished REE diagram showing a pronounced Eu and a weak Ce anomaly from the “stratiform siderites of Adamuša”. The REE diagram illustrates that some of them have been formed by hydrothermal metasomatosis of stratiform and lenticular limestone bodies in the olistostrome.

GEOLOGIC SETTING

All the studied materials reliably indicated that Carboniferous, Permian and Triassic evolution of the Ljubija ore region was rather complex. It left clear traces in the geological column. The Carboniferous is represented by three main members of the Javorik flysch formation: the Pre-flysch and Lower flysch member, the Olistostrome member and the Upper flysch member, Figure 2.

The basal unit of the Javorik flysch formation is the Pre-flysch and Lower flysch member consisting of dark argillaceous schists with alternations of medium-grain sandstone. The Pre-flysch and Lower flysch member is overlain by the deposits of the Olistostrome member [4]. The thickness of this member varies between 100 and 300 m. It consists of a flysch matrix with embedded carbonate olistoliths-boulders and blocks, and their mineralized parts. The mineralized bodies are represented by siderite and ankerite. Carbonate fragments and blocks or boulders of the Olistostrome member include black micrite, dark grey organogenic sparite (rich in fossils), dolomitic limestone and dolostone, ankeritic limestone and ankerite. The Olistostrome member was formed under deep-water conditions found in the core of the Sana antiform [7].
The youngest member of the Javorik flysch formation is the Upper Flysch unit that is also the most widespread in the Sana-Una Paleozoic complex. It is mainly composed of sandstone-siltstone flysch. Due to Mn oxides and particularly hydroxides, its lower part is black [5].

The Permian-Triassic clastic formation appears in discontinuously exposed zones in the north and south limbs of the Sana antiform, and south of the Sana Nappe. Two Permian series have been preserved: cavernous dolomitic limestones and multicoloured clastics with white quartz conglomerates. The maximum thickness of this formation is estimated at 150 m [2].

The colourful Werfen strata are overlain by limestone and dolomite, covered by a Ladinian volcanogenic-sedimentary porphyrite-chert formation. The younger sediments are exclusively represented by Neogene-Quaternary lacustrine formations, Figure 2 and 3.

The geological evolution of the studied terrain was reconstructed on the basis of such a geological column and the environments in which its parts were formed [5,7]. In the Carboniferous, this area was an integral part of an ocean basin, at the bottom of which deep-water flysch sedimentation took place. The basin turned into land during intensive Hercynian folding. In the Middle and Upper Permian, the study area was covered by a shallow sea with carbonate, clastic and evaporite sedimentation. Early intracontinental riftogenesis also began at that time [7]. Deposition of clastites and carbonates continued into the Triassic.

In the Middle Triassic, however, the study area underwent well-defined (internal) Dinaridic riftogenesis with transtensional faulting, which was accompanied by volcanism and hydrothermal
processes. This led to mineralization processes in several phases, which primarily affected the lower, Paleozoic parts of the geological column because they were at appropriate depths and impacted by tectonics as late the Hercynian time. In part, however, hydrothermal vents reached dislocated Permian and even Triassic formations, especially those Werfenian. Vein iron ores (Volar, Tomašica) were also formed in them.

Figure 3. Simplified metallogenetic map of the Ljubija ore region [7]

The study area was also affected by old and young Alpine tectonics that occurred between the Alb and Oligocene times. That was when nappes, folds, faults and new joint systems were created. All this enabled intensive circulation of descending waters rich in oxygen, through the uppermost parts of the lithosphere, and the formation of "iron hats" on carbonate iron ores. The area was exposed to long-term erosion and hypergenic influences in the continental phases. Lakes were formed solely in the Late Neogene and Quaternary, during which clastic sediments eroded from the neighbouring ore-bearing terrains were accumulated. The redeposited iron ore bodies were formed in continental lake conditions [5,8].

GENESIS OF THE LJUBIJA MINERALIZATION

The first scientific researcher of iron ore in the Ljubija ore region, F. Katzer, argued that the iron ore was mostly of hydrothermal-metasomatic origin and suggested the possibility that some occurrences were of synsedimentary origin [9]. Thereafter, all researchers supported the hydrothermal-metasomatic genesis of this deposit. In the early sixties, M. Jurković suggested that all the iron ore in this region was exclusively of synsedimentary origin [10]. This opinion was shared by M. Jurić and M. Šarac [2,11]. During the nineties, after detailed studies of the Adamuša and South Tomašica mines, A. Grubić and Lj. Protić assumed that there had been two metallogenic events in the region. The older was deemed Carboniferous hydrothermal-sedimentary and sideritic, and the younger Triassic hydrothermal-metasomatic, ankeritic and polymetallic accompanied by sulphides [5].
S. Strmić-Palinkaš et al. analysed sixty samples from Adamuša, South Tomašica and other mines for major and trace elements, including rare earth elements (REEs), isotopes of oxygen, sulphur and carbon, and hydrocarbons. All results, in particular REE concentrations, suggested a hydrothermal metasomatic genesis of iron. In this regard, particularly indicative were cerium (Ce) negative and europium (Eu) positive anomalies, which indicated that the ore could not be of sedimentary origin [12]. These findings were confirmed by V. Garasić and I. Jurković, but they left an open question about the genesis of stratiform deposits [6].

The geochemical properties of real stratiform bodies of siderites were checked in order to answer the open question: do real stratiform bodies of siderites and ankerite have the same geochemical characteristics as other undoubtedly hydrothermal-metasomatic ores? Spectrochemical analyses of specimens of the representative, certainly stratiform body at Adamuša, Figure 4 and 5, showed identical compositions of rare earth elements and all hydrothermal metasomatic deposits, Figure 6. In this regard, the positive Eu anomaly (2.24-3.40 ppm) in siderite was the overriding fact. This was decisive evidence hydrothermal-metasomatic origin of the siderites and ankerite in the stratiform bodies.

In the Ljubija ore region, there are primary carbonate iron ores (siderite and ankerite) and a secondary oxidised ore (limonite) [2]. Limonite ores were formed first by long-term oxidation under hypergenic conditions to a depth of about 300 m. Apart from iron ore, there are sulphides of Pb, Zn, Cu, Hg, Ag and Au, as well as fluorite and a considerable amount of barite. It is a unique "siderite-polysulfide-barite ore formation", which consists of three subformations: a) siderite - ankeritic, partly limonitised; b) polysulfidic, and c) barite-fluoritic. Based on the mutual relations of the members of the subformations in the ore field, they were likely fashioned in three phases. In the first phase, siderite and ankerite were formed by hydrothermal metasomatism of carbonate olistolitic blocks at moderate
depths and temperatures around 246 °C [12]. In the second phase, sulphides in the form of veins were generated in almost all parts of the geologic column. It appears that siderite veins were created in parallel (at temperatures around 186 °C) [12]. Finally, in the third phase, barite was created in several places in the region, in all formations except for Neogene.

Based on the regional geological fact that the veins with limonite, polysulphides and barite are found in Permian and Lower and Middle Triassic rocks, the conclusion is that all mineralization phases took place in the Triassic, possibly beginning at the end of the Permian. However, Strmić-Palinkaš et al. believe that this happened in the Permian, mainly because the composition of the fluids in the inclusions is consistent with Permian mineralized seawater [12]. That is the reason why this question remains open.

Alpine tectogenesis, when wide tension ruptures were opened under brittle deformation conditions, was followed by the final metallogenetic phase in which descending atmospheric waters enabled the conversion of siderites and ankerites into iron oxide ores.

The redeposited pieces and powdered limonites in the Plio-Quaternary lacustrine formations originated independently of the above events, with a time distance of several million years. “Iron limonite hats”, developed on primary siderite-ankerite ores, were affected by surface degradation. Eroded material was partly in the form of dry foothill deltas or alluvially transported to neighbouring lake basins.

**CONTROL FACTORS OF IRON MINERALIZATION**

The geologic framework of the study area, its formation and all the collected mineralization data showed that the main drivers of mineralization in the Ljubija ore region were stratigraphic, lithological, magmatogenic, structural-tectonic and hypergenic factors.

**Stratigraphic factor**

From the stratigraphic point of view, the main concentration of the Ljubija ores and the occurrences of iron are found almost exclusively in Carboniferous formations, especially in the Olistostrome member. [7]. Occurrences of iron in Permian sandstones, Werfen clastites and the porphyrite-chert formation, although frequent, are insignificant in terms of both iron concentration and ore quality. However, they are a very important indicator of the time of mineralization.

Blocks and large olistolitic bodies of limestone, dolomitic limestone and dolomite in the Olistostrome member are carriers of the main bodies of commercial iron ores that have been exploited so far. Mineralizations in Carboniferous flysch silicate clastites are local, minimal and of no practical importance.

Another stratigraphic position is occupied by locally redeposited iron ores in the lower parts of the Neogene-Quaternary column of the Prijedor basin. These are iron ores between North Tomašica and the redeposited parts of Omarska. They belong to the Plio-Quaternary continental formations with redeposited ore material from older, primary iron deposits [13].

**Lithological control factor**

The lithological control factor was reflected in the types of mineralization. Siderites were predominantly formed in olistolitic bodies built of limestones, as well as those composed of dolomite limestones in dolomite-ankerites (Fig. 5). Where there were both siderite and ankerite in a carbonate body, that meant that its composition was partly limestone and partly dolomite. There were also siderites and ankerite in clastites, mostly as veins but also as impregnations in the rock matrix. The latter is an interesting phenomenon, but rarely investigated [14]. The genesis of powdered limonites (“brands”) has been interpreted in different ways [5, 10]. However, special geochemical studies of this problem have shown that these ores could have been formed from either “carbonate shale” or primary
"fine-grained ankerite" if contaminated with other substances during transport to the lake environment [6].

**Magmatogenic control factor**

The accompanying magmatogenic control factor is very important because mineralization is its consequence. There are few igneous rocks in the Ljubija ore region, as they are widespread in other parts of the main metallogenetic zone of the Middle Dinarides. Spilites, diabases, keratophyres and rhyolites were found. The rhyolites from the area around Trnava have been studied most extensively. It is significant that the best match of their geochemical characteristics is with early magmatism in continental rift zones and subcrustal magma origin.

The keratophyric, quartz keratophyric, spilitic and porphyritic volcanism of the Porphyry-chert formation in the Dinarides is well developed and expressed in the Middle Triassic epoch, especially in the Ladinian stage. It usually follows rift extension dislocations of NW-SE direction. Magmatic rocks have been registered in the Ljubija ore region (for example, in the wider area of Volar west of Prijedor and to the south near Trnava). This magmatism was accompanied by multiphase hydrothermal processes that were the main carrier of polymetallic mineralization with specializations in polynmetallic sulphides and barite. Among other things, they led to metasomatic iron substitutions in carbonate olistoliths.

This important conclusion is based on Stefanovska's interpretations of the olistostromic nature of limestone and the "invasion of hydrothermal solutions with iron" [14], and those of S. Karamata that the Middle Cretaceous isotopic age of Trnava magmatic rocks is a consequence of subsequent thermal influences above 350 °C [15], as well as the opinion of L. Palinkaš that siderite-barite-polysulfide deposits of the (internal) Dinarides were formed "by the action of hydrothermal convective cells at the subterrestrial level" during "early intracontinental rifting in the Permian" [16] and of S. Strmić-Palinkaš et al. about the Permian-Triassic "underground hydrothermal convective cell of the intracontinental rift process" and the "hydrothermal-metasomatic origin of Fe mineralization in Ljubija" [12].

**Structural - tectonic factor**

As a phenomenon, metallogenetic linear zonation is genetically related to extension Cimmerian dislocation tectonics. A system of large dislocations in the NW-SE direction was formed due to rift ruptures of the lithosphere in the northern periphery of the Adria microcontinent. The group of these dislocations on the southern fringe of the rift included the Sana dislocation zone, which is today the southern border of the Ljubija ore region. Like most of these ruptures, it cut the entire continental lithosphere and became the supply channel for magmatic movement and circulation of hydrothermal solutions at shallower levels. Ore occurrences mainly follow the strike of the Sana dislocation and are located near it.

The trending of the accompanying systems of Cimmerian lateral ruptures was mostly NE−SW. They are well expressed in the ore field. In metallogeny, they were important for the distribution of hydrothermal solutions and today's distribution of ore deposits and occurrences within ore fields and ore nodes.

The above Cimmerian regional mega-frame also left its mark in the metric area. Transcurrent shear along longitudinal rift dislocations was accompanied by intense fracturing and crushing of all rocks between them. D. Stefanovska states that all Carboniferous rocks are "extremely brecciated", which led to an "invasion of hydrothermal solutions". Siderite and ankerite are unevenly distributed in clastites, in which they are found in the form of grains, aggregates and concentrations in the matrix [14].

Mineralization in Carboniferous rocks was most directly influenced by their tectonic cracking. This is especially true of limestone olistolitic blocks. The dense chain of ruptures in them, which occurred in the process of riftogenesis, opened the way to later hydrothermal solutions. They were circulating in...
large quantities through the joint systems and caused metasomatic processes and mineralization. At Adamuša, the orientation of decimetre-sized paleojoints, filled with siderite and siderite with silica, was identical to that of the regional ruptured mega-assembly, Figure 7. Two conjugate systems, NW-SE and NE-SW, have been determined [5].

Alpine tectogenic formatting have led to intense post-ore tectonics, which included folding of the Cimmerian geological bodies, followed by re-folding and tectonic leafing of the Carboniferous geological column due to expansion in the zones of thrust. All ore bodies were affected by these processes, so many of them were torn out and dismembered, thereby acquiring a completely new morphology.

This was effectively determined by N. Vasković who studied the petrographic composition of rocks and ores from the Javorik formation. She noted that after all mineralizations, "subsequent tectonics" defined the general schistosity of clastites and led to the formation of neominerals (chlorite, sericite, muscovite and epidote) and recrystallization of siderites, all indicating metamorphic changes in the greenschist facies [17]. Metamorphic changes in the greenschist facies were confirmed by recent research [12]. At the same time, the Sana dislocation was transformed into a Sana nappe, which physically limiting the ore region from the south.

The younger generation of systems of Alpine joints, Figure 8 and faults, among which transverse systems the strike of NE-SW were wide open, enabled descending atmospheric water circulations and hypergenic oxidation processes, and thereby the conversion of primary siderites and ankerites into limonites.

**Hypergenic control factor**

The hypergenic control factor significantly influenced the forming of iron oxide ores. In the Alpine tectogenesis, old systems of faults and joints were renewed and new created. In this respect, the most significant were transverse, open, steep SW-NE ruptures [11]. They opened pathways for atmospheric waters rich in oxygen, so their long-term action in the underground transformed oxidite and ankerite into oxide ores of iron, mostly limonite but also hydrohematite. The extent to which surface water rich in oxygen penetrated the system of young joints depended on how far the primary carbonate iron ores (siderites and ankerites) had been converted into oxide ores (compact and powdered limonite). This is closely related to outcropping of Carboniferous formations, the intensity of their syn-riftogenic rupture damage and the duration of the process. According to some researchers, limonitization processes reached depths of about 40 m. In borehole M-1 (Mačkovac), limonitization was detected at a depth of 300 m, which means that hypergenic changes did not affect only the near-surface parts of the terrain [13].
ORE-BEARING IRREGULARITY OF THE OLISTOSTROME MEMBER

There are several ore-bearing irregularities of the Olistostrome member, which are significant for the metallogeny of the region.

- First, the seating of carbonate olistolitic bodies is irregular, or chaotic, which is very important due to the special importance of their commercial ores. Laterally, ore bodies gradually pass into the surrounding rocks or they are abruptly interrupted.

- Second, the size, shape, and morphology of these bodies and their boundaries are extremely uneven and diverse, both where they are primary and tectonic. Changes in ore body thickness range from a few tens to 100 m and are mostly sudden, in the form of thickening or thinning. Only in extreme cases the ore bodies featured a stratiform morphology and internal texture.

- Third, not all olistolitic bodies are mineralized. In cases where they are, two adjacent bodies can be mineralized, but also one can be mineralized and the other entirely mineralization-free.

- Fourth, olistolitic bodies can be completely, only partially or even minimally mineralized (to the level of ferrous limestone or dolomite). Due to all this, ore bodies and deposits "have no continuity but appear in isolation”. In addition to all the above, "The content of metals in carbonate iron ores and their by-products varies widely” [18].

These irregularities in the ore-bearing capacity of the Olistostrome member place Ljubija iron ores in deposits of, for example, bauxite and antimony, where the exploration risk associated with covered ore bodies is relatively high. These major irregularities, however, are not characteristic of redeposited powdered limonite ores in Plio-Quaternary lacustrine sediments. Such ores appear in the form of more or less regular lenses of various dimensions, in which the quality of the ore is slightly poorer but stable. The amount of iron is smaller (40 to 50%) and the concentrations of SiO₂ (16-17%) and Al₂O₃ (6-8%) higher [7,18].

CONCLUSION

The Ljubija ore region is part of the Triassic, regional, internal metallogenic zone of the Middle Dinarides. It is located approximately in the middle of this large metallogenic unit and has many features in common with its other parts. The entire ore-bearing territory has an area of about 1500 km², which is characterized by identical geological conditions and the development of ore formations and types of commercial deposits of iron and other mineral resources. The evident zonal regularity is apparently not accidental, but related to the geodynamic development and accompanying structures formed in that Dinaridic segment of the Earth's crust.

The geologic composition of the ore field, its origin and all collected mineralization data show that the main control factors of mineralization in the Ljubija ore region were stratigraphic, structural-tectonic, lithological, magmatogenic and hypergenic. Among these factors, the region stands out stratigraphically because the main concentration of the Ljubija ores and the occurrences of iron are found almost exclusively in Carboniferous formations, especially the Olistostrome member. It is very important in further research to keep in mind the irregularity of the distribution of carbonate olistolitic bodies (chaotic and difficult to predict), which is why the risks of finding and exploring ore bodies are quite pronounced.

The main prospecting indications that were identified include the location of the ore deposits and occurrences, peri-ore changes, geochemical analyses, indicator elements, mineral indicators, dislocations, ring structures, geophysical anomalies and all forms of old mining and smelting, suggesting the possibility that there are deposits of minerals and raw materials.
In order to minimize the risk, further research into primary iron ores should focus exclusively on the search for carbonate olistolitic bodies in the Carboniferous Olistostrome member of the Javorik formation, whether found on the surface or located underground. Redeposited iron ores should be sought only in Neogene-Quaternary sediments of the Prijedor-Omarska Basin, mostly in its southern half.

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