

## GENETIC MODEL OF LJUBIJA BRANDS DEPOSITS – RAW MATERIALS FOR PRODUCTION OF MINERAL PIGMENTS

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**Abstract:** Specific characteristics of iron ore deposits in Ljubija ore region are given by pelitoid iron ores („brand“) which occupy a substantial part of iron mineral resources, on which industrial production of natural iron oxide – pigments depends. This particular technology type of iron ore deposits, until recently was waste from mining production, and now when it is possible to implement new technological processes, that waste became an important commercial product. This paper presents the results of detailed geological research which lasted for a few years, as well as laboratory and technological tests. It presents the new data on the metallogenetic characteristics of the environment where iron oxides originate as a raw material for mineral pigments. In this paper, we answered and resolved dilemma about brand identity in adequate genetic iron types in Ljubija mining regions, about their specificity as well as the ore formations and geohistorical development. Through the technological characterization of the ore and its domain of application, we provide the basis for economic evaluation of the deposits of this very important mineral resource.

**Keywords:** Ljubija mining area, mineral pigments, ore formations, geological research, laboratory tests.

### 1. INTRODUCTION

The Ljubija ore region is one of the most important regional units of the Dinaric metallogenic province [1], because it contains the largest concentrations of iron ore on the Balkan peninsula. Besides economically less significant mineral raw materials such as barite, fluorite, there is important goethite – pelitoid ores – „brand“. This last one was named „brant“ by I. Jurković, and later was given the name the „brand“ in the literature, and is exploited as a raw material for high furnaces and raw materials for mineral pigments [2].

Pelitoid Fe ores („brand“) as a special technological type of mineral raw material represents the concentration of pulverized particles of goethite/limonite, yellow, ocher and brown color, mixed with clay. The iron content in this mass is usually 40 – 55%. According to the conditions of the genesis occurrence, they are secondary allochthonous, rarely autochthonous masses.

The brand's ore bodies are mainly related to the Tomašica ore field, they are significant in size and economically significant. The deposits are facial

identical and have developed a series of lithofacial different types of ores with variable content of iron and clay components.

A favorable granulometric composition (80% of particles below 25 microns), intense color palette, atmospheric resistance, adsorption properties, etc., are reason that brands can be treated as raw materials for natural mineral pigments. In this sense, the brands are Fe – Oxide and Mn – Fe oxide pigments, where in the first case chromophores represent oxides and hydroxides of iron, and in the second case oxides and hydroxides of iron and manganese, where the participation of manganese gives the tones of brown color. The tests carried out in terms of pigmentation–technical characteristics found that the results far exceed the requirements of the international standards for natural iron oxide pigments.

The results of the formation analysis of brands with the emphasis on the Neogene – Quaternary lake formation, which contain the economically important deposits of brands that enable the separation of a wide spectrum of mineral pigments, are presented in the paper on the basis of many years of research and rich fund material.

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## 2. ANALYSIS OF ORE BEARING AND ORE FORMATION OF BRANDS

The geological column of the Ljubija ore region has been composed: Carboniferous Javorik flysch, Permo – Triassic clastite, Triassic terigenous – carbonate formation, Volcano – clastic terigenous and carbonate formation, and Neogene – Quaternary lakes formations. In the Javorik flysch there are next members: Lower flysch, Olistostrome member and the Upper flysch. Magmatic rocks in the region are important, but only Triassic riolites and lesser trachites, then granitoids (Figure 1 and Figure 2).

Taking into account the tectonic characteristics of the Ljubija ore region, the criteria and characteristics used to separate a geological body under the name „formation”, we need to know that they are larger rock complexes, connected by the unity of the place, time and conditions of creation, geological formation which does not contain ore minerals is identified in the treated area as well as two ore – bearing formations of the brands – mineral pigments. Thereby, there are clearly defined rocks that form part of the formation, its lower and upper bounds and the position towards the surrounding formations. The rocks that form one of this

formation make a genetic complex according to the physical–geographical conditions in which it is created [3].

In the area of the Ljubija ore region, the brands belong to two–time and spatially separated ore formations, Middle Carboniferous olistostrome formation and Neogene – Quaternary lake formation. Each of them has one ore formation, the first one – formation of the Secondary autochthonous brands of the Ljubija, and the second one – Secondary alochthonous brands of the Tomašica, and several formational types of brand deposits (ore subformations).

### 2.1. Olistostrome formation of the Ljubija as a brands ore formation

For the genesis of the Ljubija iron ores (brands belong there), an Olistostromic formation is particularly important as the bearing of numerous primary and secondary autochthonous deposits and the occurrence of limonite and brands. In this formation, the material is also formed for the creation of deposits of secondary alochthonous redeposited brands from Neogene – Quaternary lake formation.

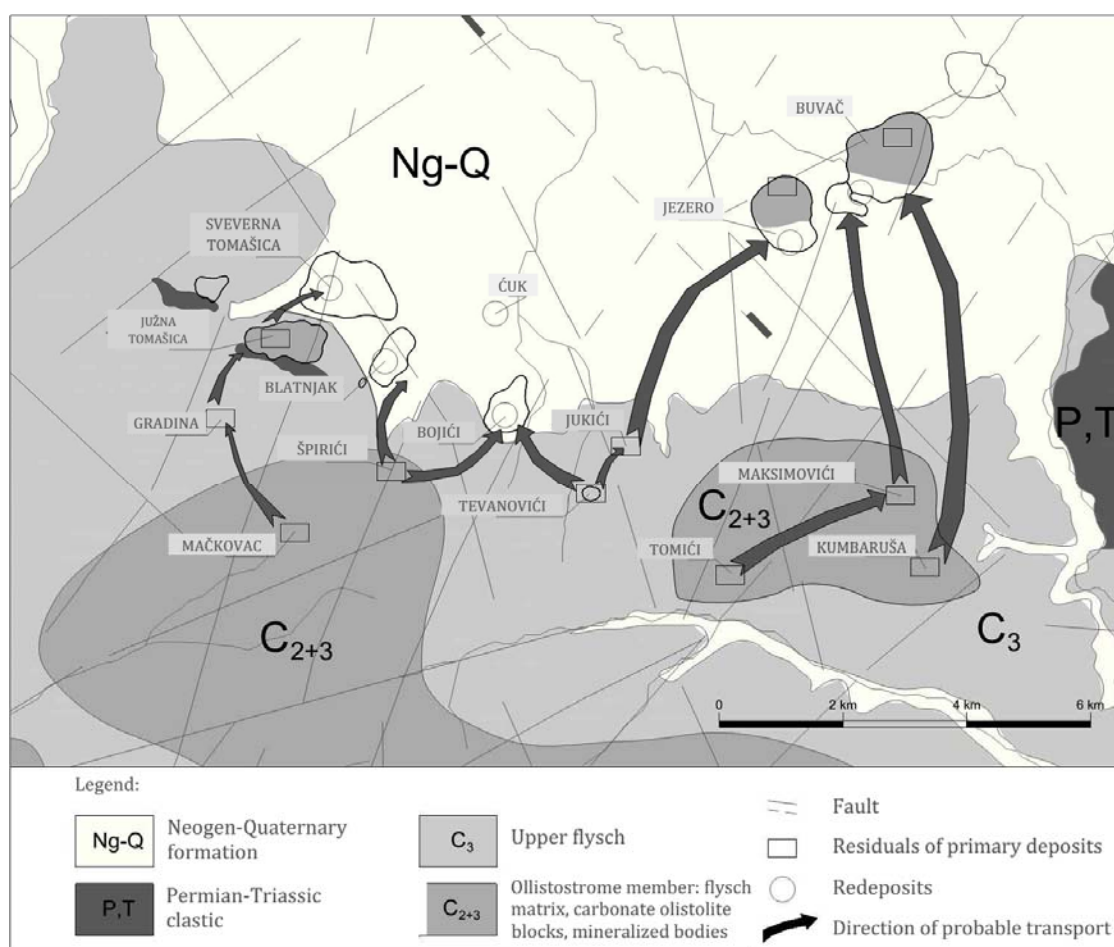


Figure 1. Geological sketch of the Ljubija ore region with possible directions of transport of limonite material

The Olistostromic formation is important for primary siderite – ankerite – limonite mineralized. It has been discovered in the middle parts of the Sana Paleozoic, exactly at the core of the Sana anticline. Below, there is the Lower flysch member and over it there is a member of the Upper flysch. It has been formed in the deep waters of the sea, as well as other Ljubija creations flysch members of the Ljubija [4,5].

The Olistostromic formation has an extremely complexed composition dominated by four groups of rocks: flysch matrix, carbonate olistolitic blocks, autoclastic mélange and partially or completely mineralized ore bodies. Flysch matrix occurs in two ways: either in the form of more or less continuous packages of several tens of meters thick or as thinner packets of sequences between olistolytic bodies. In the first case, it is described in Southern Tomašica as the „Middle flysch” [6]. It alternates: mostly argillaceous schist (subflysch), sandstone (argillaceous euflysch) and sandstone (coarse flysch).

Another case of flysch matrix, which is very widespread, is also described from Southern Tomašica [6]. It is mostly about two–interval sequences, type Ta–b in which the lower part has been composed of gray and dark gray middle grain size sandstone and the upper part of the black parallel laminated metasiltstone.

Carbonate rocks in the section appear in the form of fragments and blocks, boulders, and which belong in olistoplaque which are hectometers dimensions. Their larger forms were found especially in the wide area of the „Southern mines”. These carbonates are made of black micrites and gray biomicrites and dark grey organogenic sparites (rich in fossils). There are also dolomitic limestone and dolomite. Carbonate bodies are often with traces of metasomatic changes, so it is then iron ferruginous and sideritic or ankeritic limestones and dolomites.

## 2.2. Neogene – Quaternary lake formation of the Prijedor basin – ore bearing formation on the brand

Neogen – Quaternary creations are represented in the Prijedor basin in the north and in the Kamengrad basin in the south. They are different by many characteristics, from age to lithological content. Metalogenetically, the characteristic of the Kamengrad basin is that there are no redeposited iron ore in it.

Prijedor neogene basin was created as a consequence of the uplifting of Mesozoic sediments and the creation of the formation of deep depression in that area after the Pyrenees orogenic phase, in which Neogene sediments are sedimented. The basin

as a separate tectonic unit is located between two significant geotectonic units, between the horst of the Kozara in the north, according to which it has a stepping downlifting along several faults and a Paleozoic block in the south, where is the shallow decline of the underlying sediments.

In the Prijedor – Omarska basin, the oldest sediments are marine Miocene limestones with cardiac, located in a small area near Kozarac. The younger of these creations are: (1) pliocene clay with lignite, (2) yellow and brown sands with clay and (3) iron sandstones developed on the northern part of the basin. However, the pliocene–quaternary clastics has the largest distribution in the basin, described in the literature as „valleous – basin material” [7]. This is a chaotic mixture of poorly rounded fragments of all rocks from the paleozoic column, then clay and redeposited iron ores (piece and pulverized limonite). The thickness of these interesting sediments is up to 200 m, due to the fact that it is actually unevenness in paleorelief filled with sediments. The concentration of limonite ores and "brand" in these creations is so significant that they have been successfully exploited.

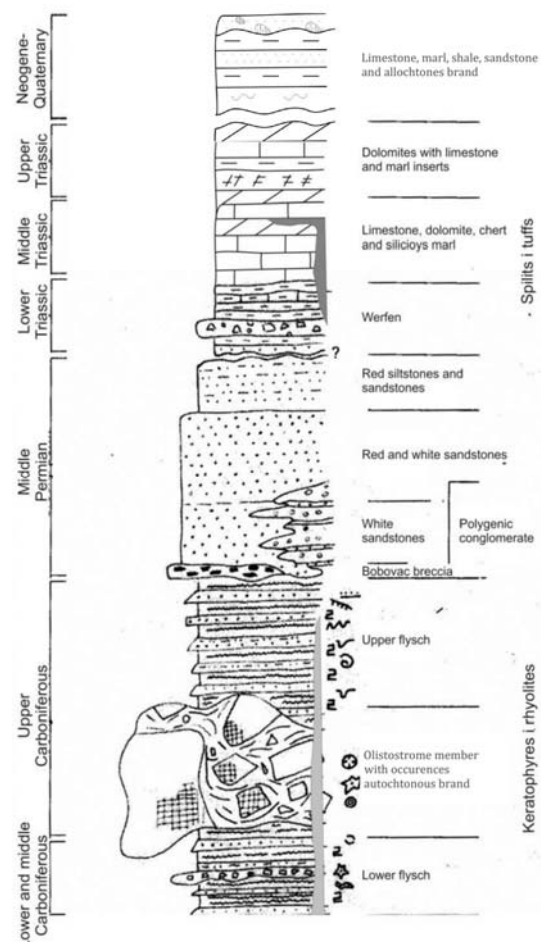


Figure. 2. The geological column of the Ljubija ore region with the brand zones

### 3. ORE FORMATIONS OF THE BRANDS

Brands deposits are integral parts of two ore formations: Secondary autochthonous brands of the Ljubija and Secondary allochthonous brands of the Tomašica. The first ones, autochthonous, were created by the surface decomposition of primary siderite – ankerite ores in the continental phase after the Middle – Triassic intracontinental Tethyan rifting processes. These concentrations of pelitoid ores are represented through the entire area of the Ljubija ore region. They do not form homogeneous bodies with continuous distribution, carbonate olistolitic blocks are most partially and locally transformed into brands. Thus, these bodies are not economically interesting, and they are not given greater attention here.

The redeposited allochthonous concentrations of pelitoid limonite and clay in the Pliocene – Quarternary lake sediments of the Omarska – Prijedor field are economically significant. The largest deposits were registered in the Tomašica ore field: North Tomašica, South Tomašica, Šiljezi – Stankovići, Jukići, Ristin gaj, Stevanovići, Dabića Brdo, Blatnjak, Bojići and Čuk, but also on the smaller part of the mining bodies Jezero, Mamuze and Buvač in Omarska ore field. Here is also given a description of the North Tomašica deposit which is characteristic of this ore formation (formational type) [3,4].

*Northern Tomašica* has redeposited a brand deposit that covers an area of about 1,7 km<sup>2</sup>, with dimensions of 2.0 x 1.2 km. The general direction of providing the ore body is east – west. In the northeast, it almost goes to the surface, and in the central part it goes deep to 260 m. The ore mass is mostly represented by a tiny pulverized ore – „brand”, rarely small – sized limonite. The brand is made of pizoliths (size of 30 – 300 microns) and 70 % of the grain size is below 100 microns. Pizolites are densely packed and poorly cemented, they are made

of cryptocrystalline goethite and hidromica hydrolysis. The color of the brands varies from light yellow to dark brown depending on the content of manganese. The brightest shades most often contain less than 1 % of manganese [3].

The shape of the ore body converges with the morphology of the paleorelief, and it is incorrectly stratified to the lens – cone. There were frequent occurrences of thickening and exclusion, conditioned primarily by the paleomorphological conditions of sedimentation and subsequent tectonic events. Besides, the continuity of the ore body is disturbed by the frequent presence of clay–alevrolitic sediments or less mineralized accompanying rocks within the ore mass. Alternations of clayey and iron sediments are mostly expressed in the vertical direction, and there are accentuated forging, lateral displacement and passing one through the other. This complexity in structural characteristics is the result of very variable conditions when the deposits were formed.

The contact of the ore body with underlying rocks is mostly sharp, while the transition to the overlying one is mostly gradual, characterized by an increased share of poor ore and mineralized clay – alevrolites layers. The upper level of the deposit, in which relatively small ore masses are located, was formed in the Pliocene – Quaternary. The ore substance is located within a series of clay sediments. It occurs in the form of smaller, mutually separated and elongated lenses, within which the diversity in structural characteristics is very expressed. The transition to underlying and overlying layers is also generally gradual and marked by increased participation of branded clay and clayed brands.

On all the deposits of the brand, three basic types of pelitoid ore – brands are distinguished: mining subformations and formation deposit types (Figure 3).

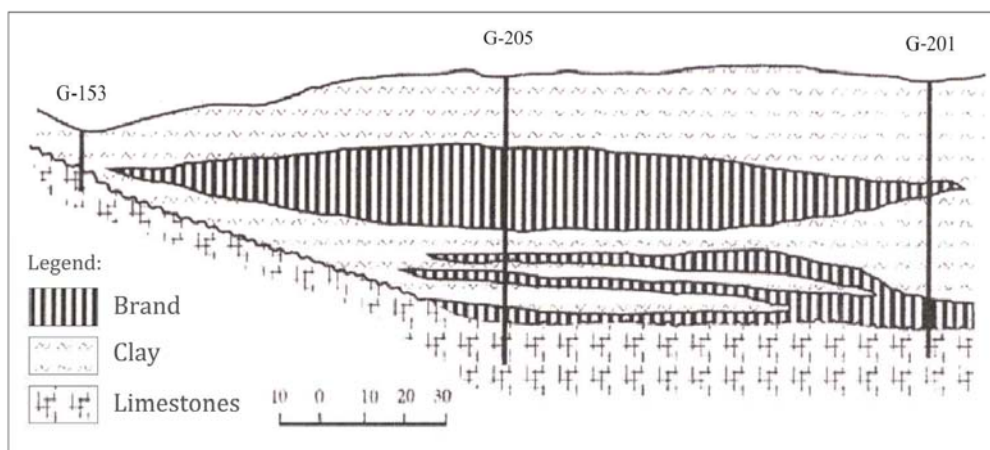


Figure 3. Detail of a part of the Pliocene – Quaternary deposit of iron ore in Tomašica

1. Brand (Fe content over 40 %) is actually a pulverized limonite in the mixture with allophanoid clay. The intermediate spaces are usually replaced by clay or iron hydroxide. It is different from pulverized limonite to which it visually resembles by granulometric composition and increased content of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ .

2. The branded clay represents a transitional type of ore in which iron content ranges between 30 and 40 %.

3. Branded clay represents the transition between the clay and the brand. It represents the highest and lowest parts of the ore body, as well as their peripheral parts. The content of iron decreases in them. The clay that cements the microliths and disperses the iron hydroxides in them, is also in the form of alternations. It is represented in all deposits.

#### 4. THE GENESIS OF BRAND'S DEPOSIT IN THE LJUBIJA ORE REGION

The genesis of pulverized limonite („brand“) was interpreted in various ways [6,7]. However, special geochemical studies of this problem have shown that these ores could be produced alternatively: either from „carbonate shale“ or from the primary „fine-grained ankerite“ if it was contaminated by other substances during transportation in the lake environment [8].

In order to solve the issue of brand genesis, it is important to determine the origin – the source of the material for their formation. The material comes from an olistostromic member of the Javorik flysch formation, that is, of the mineralized carbonate blocks. They are mineralized hydrothermally – metasomatic, and represent the primary siderite – ankerite ore bodies or their parts, as evidenced by detailed geochemical tests [9,10,11,12]. The main elements, rare elements, isotopes C, O and S, and organic matter are studied. The most important results were achieved by analyses of rare elements. Thus, it was established, by examining magmatic rocks, that the metallogeny of the region was associated with the early stages of intra – continental rifting and that it was subcontinental origin [11,12]. In addition, the total content of rare elements and light lanthanides, and in particular the anomalous content of Ce and Eu, eliminated the long-standing working hypothesis about the sedimentary origin of stratiform deposits of iron. In this regard, a particularly decisive fact is the positive anomaly of Eu (2.24 – 3.40 ppm), because hydrotherms in the middle – ocean ridges have such qualities [8,12]. In the arrangement of mineralized bodies of the olistostromic member, two regularities were empirically determined. First, these bodies

are located in the deeper parts of the member article, the more fully they are primarily mineralized. Secondly, these bodies are at lower depths and they are more fully limonitised [4,5].

In contrast to primary siderite and ankerite ores, oxide iron ores are secondary and have been formed by subsequent changes of siderites and ankerites in epigenetic conditions. Therefore, these ore formations carry the main characteristics of siderite – limonite and ankerite – limonite paragenesis. This fact agrees with all recent researchers [3,5,7,13,14]. Quaternary continental mineralized deposits belong to occurrences in the Dabića Brdo, Šiljeg, Blatnjak and Bojić, and the belt of the Quaternary sediments of the northern part of the Tomašica ore field (Figure 1), and in the Omarska area they belong to the parts of the deposits Jezero and Mamuze.

Large fault zones and intense rocks cracks, occurring in Alpine tectonic phases, enabled the descendent penetration meteoric water into the underground throughout the entire Cenozoic (about 65 Ma). This long influence led to the gradual oxidation of carbonate iron ores. The upper half of the lenses of primary siderites, which were mined and discovered in the southern part of the surface mine Southern Tomašica, and they are completely limonitised. Similarly, only to a greater extent, it happened also with ankerite from olistostrome member. Here, they were converted into limonite (brand) entire blocks of imposing dimensions in the middle parts of the northern half of the surface mine. Sometimes, however, in the middle parts of the surface mine, there are preserved relics of the ankeritic limestone in the form of irregularly rounded bodies with a diameter of up to 4 m.

The oxidation processes in the epigenetic underground region flowed in siderites by the following reaction:  $2\text{FeCO}_3 + \text{O} \rightarrow \text{Fe}_2\text{O}_3 + 2\text{CO}_2$ , where the iron oxide also received a considerable amount of water, which allowed this chemical transformation from siderites into limonite. One part of the limonite was infiltrated for the duration of the formation process in the surrounding cracks or empty karst areas in the form of rich concentrations a „kidney“ goethite.

Depending on the depth of the terrain, which was penetrated by oxygen – rich water through the system of cracks, the extent of the primary carbonate iron ore (siderites and ankerites) was translated into oxide ores (compact and pulverized limonite, autochthonous brand). It is closely related to the discovery of Carboniferous creations, then to the intensity of their tectonic damage and, finally, to the length of this process. According to some researchers, the processes of limonization reach to a depth of about



40 m. In the M-1 drillholle (Mačkovac), however, limonitisation was found at a depth of 300 m, which means that the epigenetic changes were not affected only near the surface.

Through these exogenous processes, autochthonous limonite parts of the ore bodies were formed in the siderite-limonite, or ankerite – limonite formations, but also the specific ore formation „Secondary autochthonous brands of the Ljubija”, whose ore occurrences can be traced through the ore deposits of the Ljubija ore region.

Allochthonous redeposited branded ores were created at the end of Tertiary and at the beginning of the Quarternary. The material for their formation was obtained from the mentioned autochthonous secondary iron ore deposits. Water and other forms of transport, the ore material is carried in the basins and it is deposited there (Figure 1). A lot of waste has been accumulated, and some continental deposits of the brand and limonite have poor quality. In the new space, the ore was deposited in the form of fine sludge and in the form of pieces of fractions mixed with clastic rocks. In the first case, in addition to the physical ones, certain chemical changes were made in the case of deposited ones. In the other case, the transported material is embedded in the paleorelief without signs of chemical changes. It is assumed that the ore of the first group is deposited in the lake phase. The redistribution of the second group's ore material was carried out outside the water space.

Quaternary iron concentrations are represented by various lithofacial ore types, which are different distinguished by the variable Fe content. The reason for this is that the conditions for the formation of deposits were very variable and that the inflow of iron in the water environment was not carried out consistently. The fact is that more qualitatively different levels of mineralization of limited sludge sorting can be distinguished in the deposits, which are mutually alternating. The transitions of one lithofacial species to others are not sharp but rather gradual (Figure 3). The highest concentrations of iron have been developed in depression of the paleorelief, or fossil valleys. In these positions, usually the best quality ores are found, while on other, qualities decreases. The content of iron has been reduced due to the increased content of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

## 5. CHARACTERISTICS AND POSSIBILITIES OF THE APPLICATION OF THE LJUBIJA PIGMENTS

Fe – oxide and Mn – Fe oxide pigments, then manganese and clay pigments are distinguished in the Ljubija ore region.

Fe oxide and Mn – Fe oxide pigments have the highest distribution and significance. Chromofores represent oxides and hydroxides of iron (30 – 60%) and manganese, where the hematite gives the tones of red and dark – red color. The presence of manganese minerals gives the tones of brown to dark brown. Especially high content of chromofores, as well as color intensity, have many hematite, goethite hydrothermal iron ores.

In this group of pigments, the water content is up to 20 %, indicating intensive hydration. These are formatione types of brands, clay brands and brand clays.

Manganese pigments are rare. Chromofore manganese is associated with iron oxides, but locally there are such pigments that are mainly made of oxide and hydroxide of manganese. Thus, a pyrolysite black pigment that contains over 90% Mn<sub>2</sub>O<sub>3</sub> occurs.

Clay pigments belong to differently colored clays and clay rocks in which chromofores represent iron hydroxides, iron oxides and manganese and carbon. They are mostly widespread in Tomašica and Omarska fields. Clay matter is most often represented by kaolinite in association with a variable amount of montmorillonite and other clay minerals. In clay minerals, hydroxides of iron and oxides and hydroxides iron and manganese are isomorphically replaced by Al<sub>2</sub>O<sub>3</sub>. In relation to Fe oxides and Mn pigments, clay pigments is characterized by low chromofores content, which usually ranges from 5 to 12 %, and only sometimes reaches 20 to 30 %. Clay pigments can be yellow, red, brown, purple, gray and black color.

The pigmental technical properties of brands as natural iron oxides were examined at the Boris Kidrič Chemical Institute in Ljubljana [16]. Through these studies, it was found that all types of natural pigments, which can be obtained from two basic types of raw materials – ocher and brown brand – far exceed the requirements of the standard ASTM specification for natural iron oxide pigments, Table 1.

Table 1. Quality of Ljubija Fe – oxide pigments according to the standard ASTM

Characteristics	ASTM requirements for Fe oxide pigments	Results of testing of Ljubija Fe oxide pigments
Fe oxide (min.), %	37 – 55	72 – 94
Calcium compounds (max), %	5	0,1
Lead chromate, %	not determined	0,0

Characteristics	ASTM requirements for Fe oxide pigments	Results of testing of Ljubija Fe oxide pigments
Organic pigments, %	not determined	0,0
Moisture and other volatile substances (max), %	1 – 5	1
The rest on the sieve 44 microns (max), %	1 – 2	1
Water soluble fraction(max), %	1	1
ph	5,5 – 7,5	6,5 – 7,2

Comparison of the characteristics of different types of Ljubija Fe – oxide pigments ( $Fe_2O_3$  content, water –soluble salts content, residue on sieve 63 microns) with corresponding German and Spanish pigments, it results have yielded satisfactory results. The analysis included red, yellow and brown pigments, and the tests were performed according to the BSI 3981 standard. Ljubija Fe–oxide pigments, as well as natural Spanish, belong to the B category, with the Ljubija purple red Fe – oxide pigments having a significantly higher content of  $Fe_2O_3$  (80 – 94%). Bayer oxides are classified in category A with a  $Fe_2O_3$  content of 85 to 97%. When it comes to water – soluble salts, the most favorable are Ljubija ocher and brown Fe – oxide pigments with a content ranging from 0,08 to 0,16%, and in comparison the red pigments, the best effects are shown by Spanish (0,13%). All the above pigments have satisfactory results by the BSI standard (residue on sieve 63 micron).

Comparative reviews of Ljubija and Bayer Fe – oxide pigments, according to tests at the „Boris Kidrič Chemical Institute” in Ljubljana and Bayer Uerdingen, are given in Table 2.

These testing of Fe – oxide, pigments, made by Bayer, indicate that they are quality pigments, whose applicability should not be compromised when it comes to paints for coatings, construction, etc.

The granulometric composition of Ljubija’s natural Fe – oxide pigments was examined on a sedimentograph at the Boris Kidrič Institute of Chemistry in Ljubljana [16] and is shown in the following table. The results of the granulometric analysis show that 62% of the particles have a size below two microns.

The application characteristics of Ljubija pigments were also made in ocher, brown, red and black pigments. Resistance to acids, alkalies, as well as cement and lime resistance, is rated as very good. Resistance to light, solvents and distilled water was rated as excellent [16,17].

Table 2. Comparative overview of Ljubija’s and Bayer’s pigments

Characteristics	Ocher – Ljubija		Bayer		Red – Ljubija		Bayer
	KIBK	Bayer	415	910	KIBK	Bayer	222
Fe, %	84	81	82–84	85–87	90	88	92–95
$Al_2O_3 + SiO_2$	3–6	4,8	4,2	0,2	3–6	5,2	3,0
Oil number, %	35–38	27	40	52	45,48	35	15
The rest on the sieve 45 $\mu$ , %	0,0	0,0	0,5	0,03	0,0	0,0	0,05
Watersoluble salts, %	0,08	0,12	0,4	0,4	0,18	0,15	0,5
Loss by ignition, %	12,0	10,5	12,0	13,0	0,5	3,5	0,7
ph	7,0	6,2	5,5	5,5	7,5	6,9	6,0
Spec. mass (g/cm <sup>3</sup> )	4,5	3,9	4,0	4,1	5,2	5,1	5,0
Dispergid.	–	30/40/70	25/40/70	–	–	20/30/70	20/20/40
Spec. surface (m <sup>2</sup> /g)	19,6	25	20	–	22,7	28	26

Table 3. Granulometric analysis

Fraction (micron)	Ljubija oxide		Spain oxide	
	ocher	red	Prominca	Malaga
10	100,00	100,00	100,00	0,3 (%) above 53 micron
8	96,70	98,00	94,43	
6	94,00	94,10	90,24	
4	88,60	89,70	75,95	
2	75,10	77,90	42,81	
1	47,25	48,50	10,19	

Table 4. Technical characteristics of Ljubija pigments

Characteristics	Ocher	Brown	Red	Brown	Black
	150	550	350	750	850
Oil number (g/100g)	27–30	28–30	30–38	30–38	30–35
Fe <sub>2</sub> O <sub>3</sub> (%)	72–80	70–78	80–88	82–90	80–85
Al <sub>2</sub> O <sub>3</sub> + SiO <sub>2</sub>	5–9	6–10	5–9	5–9	5–9
Bulk density (g/cm <sup>3</sup> )	0,75	0,90	0,90	0,90	1,05
The rest on the sieve 45μ, %	0,0	0,0	0,0	0,0	0,00
Watersoluble salts, %	0,08	0,09	0,18	0,16	0,15
Loss by ignition, %	12,0	13,0	0–5	0–5	6–10
Spec. weight (g/cm <sup>3</sup> )	4,0	4,0	4,8	4,8	4,5
Most common particles d=95% mm	5	5	5	5	8
Volume charging (cm <sup>3</sup> /g)	0,9–1,0	1,01–1,06	0,95–1,05	1,02–1,08	1,03–1,08
ph	19,6	25	22,7	28	26

On the basis of the presented test results, using the technical and application characteristics, different types of application of iron oxide on the basis of the brand have been approved, which have satisfactory technical, protective and decorative properties, as follows:

1. Construction (production, protection, decoration)

- organic and aquatic systems for finishing interiors and exteriors, mineral and plastic plaster, concrete semi-finished products and flooring, brick products, etc.,
- concrete facades, interiors, flooring of roofs and roof structures, etc.,
- concrete brick products, floors, facades, interiors.

2. Anticorrosives (production, protection, decoration)

- base colors based on: alkyd resins and polyurethane binders, semi-aqueous dispersions, etc., colors on the basis of said binders, etc.,
- covered lacquer paints full of tones (red, brown and black, blending them),
- steel and sheet structures, transport means, ships, reservoirs, etc.

3. Ceramics (production, decoration)

- ceramic pigments, glaze of different types, etc.,
- in addition to the decorations given by these products, suitable technological conditions can be obtained: gray to dark gray tones, matt surface, green, yellow brown to brown tones.

4. Wood (production, protection and decoration)

- basic and cover colors and lacquer in organic and aqueous systems for protection and decoration, transparent colors and glazings for protection and decoration,

- protect the wood from the harmful effects of atmospheric and ultraviolet radiation,
- full basic tones (ocher, brown, red and black) and other combinations by mixing these pigments, as well as mixing with inorganic and organic pigments, give an unlimited range of transparent shades.

5. Leather (production, protection and decoration)

- covering colors (for leather finishing) in aquatic (casein, acrylate, etc.) and hydrophobic systems,
- protect the leather and leather products from the influence of ultraviolet radiation,
- Full tones (ocher, brown, red and black) interact with each other and with other pigments give an unlimited range of transparent shades.

6. Plastics (production, protection and decoration)

- paints and lacquer for plastics, coloring of plastics in the mass of dry pigments, preparation of sterile mixtures, etc.
- protecting plastic and its products from the influence of atmospheric and ultraviolet radiation,
- full basic tones (ocher, brown, red and black) with each other and with other pigments give an unlimited range of transparent shades.

Qualitative characteristics meet the requirements of ISO standards for the listed areas of application. The more detailed overviews related to the treatment of brands as non-metallic raw materials, or raw materials for the chemical industry, as final products and market articles, give a clear picture of unhindered use, which is still insufficiently understood, even sometimes negated, and the previous production and market verification allows unhindered development.



## 6. CONCLUSION

Deposits of brands of the Tomašica ore field brand have been a significant economic – geological type for years as a raw material for metallurgical processing, while today they are conditionally potential. As a raw material for mineral pigments, these deposits are the first and so far the only geological-economic type, which will, with significant geomarketing activities, give more economic effects.

The Ljubija ore region has been composed of several formations belonging to Carboniferous, Permian, Triassic and Cenozoic. Of all of them, only two are ore – bearing brands: the Middle Carboniferous olistostrome formation and Neogen – Quaternary lake formation of the Prijedor basin. In the first formation, there are primary siderite and ankerite partly of the limonitised ores and the secondary autochthonous brands, and in the second only the redeposited limonite (a piece of limonite and pulverized limonite, known under the commercial name „brand”).

Brands deposits are integral parts of two ore formations: secondary autochthonous brands of the Ljubija and secondary allochthonous brands of the Tomašica. The first ones, autochthonous, were created by surface decomposition of primary siderite – ankerite ores in the continental phase. These concentrations of pelitoid ores are widely represented throughout the entire area of the Ljubija ore region. They do not form homogeneous bodies of continuous distribution, therefore they do not have economic significance.

Secondary allochthonous brands deposits belong to the Pliocene – Quaternary continental crevices with redeposited ore material from older, primary deposits of limonite. They come to the complex where the horizons of the clay brand and brand clay with lenses of the brand, that is, the pulverized limonite, are alternations and replaced. Commercial ores are usually represented by two to three such lenses, mostly 10 to 30 m thickness, but locally they also have 100 m thickness – connected with clay – limonite mass.

Secondarily, redeposited iron ore was carried out only in Neogene, and therefore they are found exclusively in Neogene – Quaternary sediments. It was finally established that there are no redeposited iron ores between the Javorik formation and the Permo – Triassic clastite. This erroneous assumption was based on the occurrence of wires mineralized in Permo – Triassic clastics.

Fe oxide and Mn – Fe oxide pigments have the highest distribution and significance. Chromophores represent oxides and hydroxides of iron (30 –

60%) and manganese, where the hematite gives the tones of red and dark – red color. The presence of manganese minerals gives the tones of brown to dark – brown. Manganese pigments are rare and clay pigments belong to differently colored clays and clay rocks with low chromofore content, which usually ranges from 5 to 12%.

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#### ГЕНЕТСКИ МОДЕЛ ЛЕЖИШТА ЛЈУБИЈСКИХ БРАНДОВА – СИРОВИНЕ ЗА ДОБИЈАЊЕ МИНЕРАЛНИХ ПИГМЕНАТА

**Сажетак:** Посебне карактеристике лежиштима гвожђа Љубијског рудног рејона дају пелитоидне руде („brand“), које заузимају значајан дио минералних ресурса гвожђа, а на којима се заснива и индустријска производња природних оксида гвожђа – пигмената. Тај посебни технолошки тип руда гвожђа лежишта Љубије је до недавно био јаловина код рудничке производње, да би као посљедица примјене нових технолошких поступака постао значајан комерцијални производ. У раду су представљени резултати вишегодишњих детаљних геолошких истраживања, лабораторијских и технолошких испитивања. Презентовани су нови подаци о металогенетским карактеристикама средине у којој су настали оксиди гвожђа као сировина за минералне пигменте. Дати су одговори и решене дилеме о припадности брендова адекватним генетским типовима руда гвожђа Љубијског рудног рејона, њихова специфичност као рудне формације и геосторијског развоја. Кроз технолошку карактеризацију руде и њен домен примјене, дата је основа за економску оцјену лежишта овог веома значајног минералног ресурса.

**Кључне ријечи:** Љубијски рудни рејон, минерални пигменти, рудна формација, геолошка истраживања, лабораторијска испитивања.

