Pyritized bauxites from Minjera, Istria, Croatia

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faune tih područja i južne Dalmacije. Iz toga možemo zaključiti da i kod leptira, insekata koji su veoma pokretljivi, najčešće s velikim područjem rasprostranjenja, postoje zanačajne razlike u strukturi i sastavu faune na određenim područjima koja su pod utjecajem karakterističnih i za njih specifičnih ekoloških uvjeta. U ovome slučaju to se prvenstveno odnosi na klimu (Gorski kotar – dominantni utjecaj planinske klime, Turopolje – kontinentalne i južna Dalmacija – mediteranske) vegetaciju i pedološke karakteristike, koji djeluju na sastav faunističkih elemenata koji dolaze na tim prostorima. Sa porastom njihove sličnosti, raste i sličnost faune.

Zaključci o karakteristikama faune sovica tih područja možda se mogu primjeniti i za cjelokupnu faunu leptira tih regija, kao i većih geografskih prostora kojima pripadaju (kontinentalni nizinski dio-Turopolje, centralno-planinsko područje-Gorski kotar i mediteransko područje-južna Dalmacija), što će moći potvrditi tek rezultati idućih entomoloških istraživanja različitih skupina i porodica leptira na tim područjima.

Zoogeografska analiza (Tab. 5) pokazala je da u fauni Macrolepidoptera Risnjaka i Ličke Plješevice prevladavaju eurosibirski zoogeografski elementi, što je uvjetovano ekološkim karakteristikama koji vladaju na tim planinskim prostorima. Relativno visoki udio orjentalnih elemenata uvjetovan je znatnim utjecajem mediterana na ta područja, kao i migracijskim letovima nekih vrsta leptira iz južnih dijelova Europe, sjeverne Afrike i Azije u hladnija područja srednje i sjeverne Europe. Ti rezultati podudaraju se sa rezultatima sličnih zoogeografskih analiza provedenih za područje centralno-planinskog dijela Republike Hrvatske (KUČINIĆ, 1992; MLADINOV, 1977, 1980). U fauni sovica Turopolja dominantni su također eurosibirki faunistički elementi (KUČINIĆ & PEROVIĆ, 1992/1993), za razliku od područja Dalmacije u kojoj prevladavaju orjentalne, vrste (KUČINIĆ et al., 1993; MLADINOV & KUČINIĆ, 1993). I ti podaci ukazuju na veći stupanj sličnosti faune Macrolepidoptera Turopolja i Gorskog kotara, u odnosu na područje južne Dalmacije.

Rezultati ovih kao i istraživanja ostalih autora koji su obrađivali faunu leptira centralno-planinskog područja Hrvatske (ABAFI-AIGNER et al., 1896, LORKOVIĆ, 1977, 1985; LORKOVIĆ & MLADINOV, 1981; MANN, 1867; MLADINOV, 1977, 1980, 1983, 1985, 1986; MLADINOV & LORKOVIĆ, 1985) ukazuju na značajne faunističke specifičnosti toga područja Hrvatske. Buduća entomološka istraživanja (u slučaju leptira posebno skupine Microlepidoptera) trebala bi prvenstveno usmjeriti na područje NP "Risnjak" kao i na neke druge do sada nedovoljno istražene planinske dijelove (Snježnik, Lička Plješevica, Velika i Mala Kapela, Velebit).

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PYRITIZED BAUXITES FROM MINJERA, ISTRIA, CROATIA

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Pyritized bauxite was exploited in the valley of Mirna river in Istria already 400 years ago. It was used as a raw material for production of vitriol and alum. The pyritized bauxite contains both pyrite and marcasite. The conditions of their formation are interpreted in terms of the pH of the micro-environment and the concentration of sulfur and iron. Two phases of pyritization of bauxite have been recognized. Sulphur from the first phase of pyritization originated from organic matter of hangingwall sediments, while during the second phase sulfur mainly originated from the sea water. Pyritization is in some places accompained by diasporization.

Key words: pyritized bauxite, diaspore, Paleogene, old bauxite mining, Minjera, Istria

Šinkovec, B. & all: Piritizirani boksiti "Minjere", Istra, Hrvatska. Nat. Croat. Vol. 3, No. 1, 41-65, 1994., Zagreb.

U dolini rijeke Mirne u Istri piritizirani boksit otkopavan je još prije 400 god. a upotrebljavan je za proizvodnju vitriola i alauna. Piritizirani boksit sadrži pirit i markazit a njihov nastanak ovisio je o promjeni pH i koncentraciji sumpora i željeza mikrookoline. Piritizacija boksita izvršena je u dvije faze. Sumpor prve faze piritizacije potječe od biljnih ostataka krovinskih sedimenata, a u drugoj fazi sumpor je pretežno dolazio iz morske vode. Piritizacija je mjestimično praćena dijasporizacijom.

Ključne riječi: piritizirani boksit, dijaspor, paleogen, staro rudarstvo boksita, Minjera, Istra.

INTRODUCTION

Pyritized bauxites often occur in bauxite bearing areas worldwide and have been the subject of interest of many authors such as CAILLERE and POBEGUIN (1963), DUDICH (1965) and KOMLOSSY (1968). The general opinion prevails that pyritization of a bauxite is an epigenetic process stipulated with the presence of swampy environment in the immediate cover. Due to a decay of organic matter, an anaerobic environment is formed which produces hydrogen sulfide. Ferric ion is reduced to ferrous ion that reacts with hydrogen sulfide, forming pyrite. Sulfur originates from organic matter.

In Istria pyritized bauxites are situated mainly in the northern part of the Early Paleogene bauxite bearing area. They are of interest both from the point of view of their frequency and their exploitation for alum production. They were used for sulfuric acid and alum production since the 16^{th} century and especially in the late 18^{th} and in the early 19^{th} century. The production took place in the valley of Mirna river in the vicinity of Sovinjak (Sovignacco) at Minjera locality. There are no relevant data on the mineralogy and chemistry of pyritized bauxites of Istria. The aim of this paper is to present new data on both the mineralogical and the chemical composition of pyritized bauxites and to develop ideas on their genesis. In this paper, for bauxites containing both pyrite and marcasite the term "pyritized bauxite" is used.

STUDY AREA

The Istrian peninsula is situated in the western part of the Outer Dinarides region and is composed of Upper Jurassic, Cretaceous, Tertiary and Quaternary sediments. The southern, western and south-eastern parts of the peninsula are made up by Upper Jurassic and Cretaceous, mainly shallow marine carbonate sediments. Tertiary sediments are known in the northern and north-eastern parts. They consist of Kozina beds, foraminiferal limestones and flysch sediments. During the Neogene and Quaternary, superficial sediments (e.g. aeolian sediments) as well as heterogeneously developed paleosols and soils have formed (Fig. 1).

The regime of shallow marine sedimentation was interrupted at the end of Kimmeridgean by local emersions that caused the formation of clayey bauxites and karst breccias (TIŠLJAR et al., 1983). The clayey bauxites are red in colour and of kaolinite-boehmite type (ŠINKOVEC, 1974). In the uppermost part of some deposits a thin layer of pyritic clay developed. The bauxites are overlain by shallow marine carbonates of Tithonian age. The regime of carbonatic sedimentation lasted (with a few local emersions) until the Early Campanian. As the result of Laramian movements which started in the Late Senonian, a large anticline was formed with the b-axis extending in NE-SW direction, inclining gently towards NE. The extension phase generated deep decametric joints which developed parallel to the C-stage axial plane cleavage and B-stage tension joints (MARINČIĆ and MATIČEC, 1991). The uplifted carbonate rocks were exposed to

weathering and a network of deeply karstified and intensely eroded landforms opened along extension joints. Due to subaerial exposure, bauxites were formed which fill a tectonically controlled relief of shallow marine carbonates which are Albian to Senonian in age. Bauxites generally appear at the intersection of the two joint systems mentioned (MARINČIĆ and MATIČEC, 1991).

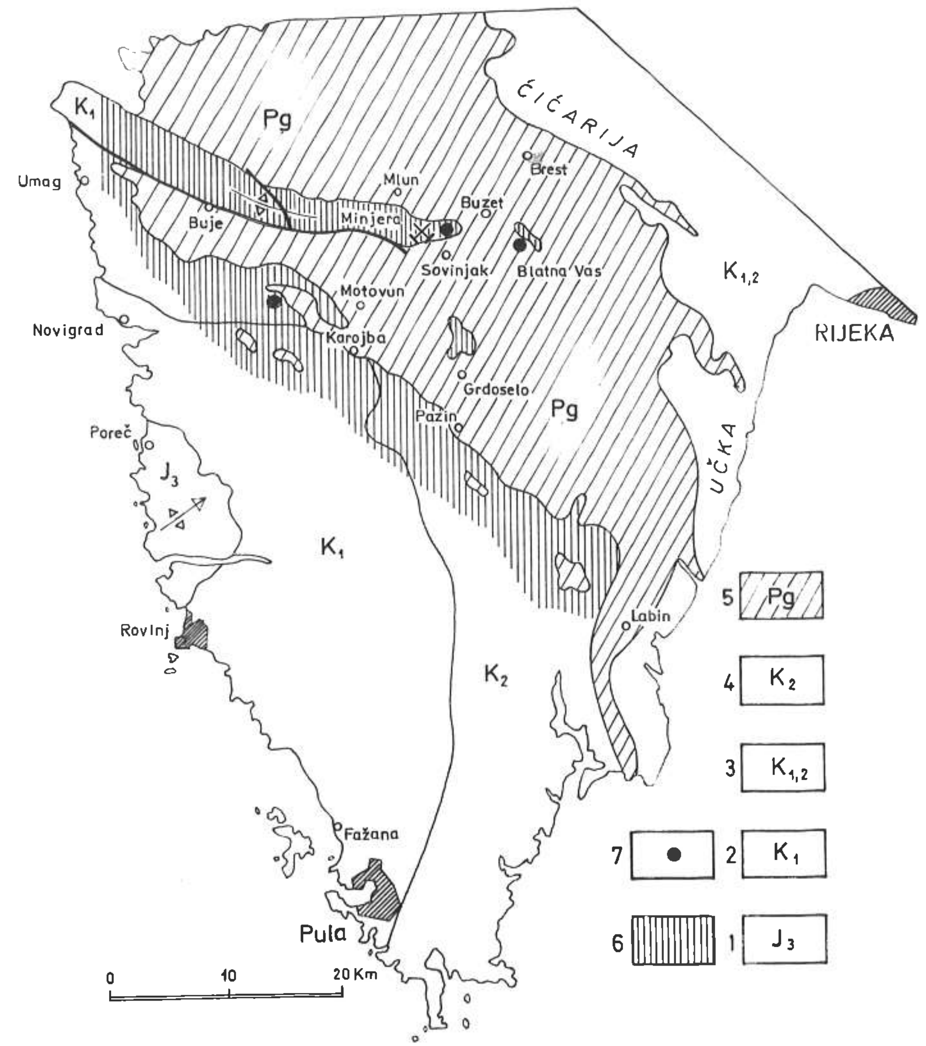

Fig.1. Geological sketch of Istria. 1 Malmian beds. 2 Limestones and dolomites, Lower Cretaceous. 3 Carbonate beds, Lower and Upper Cretaceous. 4 Limestones, partly dolomites, Upper Cretaceous. 5 Kozina beds, Foraminiferal limestones and Flysch, Early Paleogene. 6 Bauxite bearing area. 7 Sample location.

During Palaeocene to Eocene times, the paleorelief developed on carbonate rocks was unconformably overlain either by fresh water - brackish water sediments (Kozina Beds) which may contain organic remnants and numerous coal seams, or by foraminiferal limestones. Namely, due to irregular subsidence, the lows of the Cretaceous paleorelief were covered by Kozina beds, being overlain in turn by foraminiferal limestones, while the highs were directly overlain by foraminiferal limestones. DROBNE (1971) showed that the transgression was progressing from NE.

At some localities in Istria along the Slovenian coast DROBNE (1979) recognized a continuous succession from the Cretaceous to the Paleogene that indicates that the Kozina beds represent a regressive sequence. In present paper, however, we consider Kozina beds to be a carbonate transgressive lithofacies in the sense described by DRAGIČEVIĆ et al. (1992).

The stratigraphic position of these beds varies in the time span Paleocene - Early Eocene and depends on the hypsometric position of a paleorelief at a given site. The foraminiferal limestones are overlain by flysch sediments.

The Early Paleogene bauxite bearing area of Istria extends along the Cretaceous/Paleogene unconformity from Umag in the NW part of Istria to Labin in the SE. This area is approximately 60 km long and 4-6 km wide. Early Paleogene bauxites are also situated along the Buje-Buzet anticline, in the wider area of Pula and on Mt. Učka and Ćićarija. Bauxites occur as small ore-bodies that were formed by filling of sinkholes. The surface of an outcrop usually amounts to 100 to 300 square m, the depth being 8 to 30, rarely 45 m. Bauxite reserves of the individual deposits range from 50 to 25,000 Tons. Deposits without cover are smaller and estimated at 3 to 4000 T each. One can tentatively conclude that both the number and size of deposits increase in the vicinity of the Cretaceous/Paleogene boundary. By the investigation of Early Paleogene bauxite of Istria it has been established that the source material of bauxite derived in its major amount from insoluble residue of footwall limestones (ŠINKOVEC, 1973).

Although mostly red and yellowish-red in colour, in some deposits pyrite occurs instead of hematite and goethite. This gives to the bauxite gray, green and black colours. Pyritized bauxite is usually found in the form of irregular bodies in the red and yellowish-red bauxite. In some deposits, the process of pyritization has affected the major part of a deposit.

Pyritized bauxites, the origin of which is stipulated by the presence of organic matter in the immediate cover, are situated in the northern part of the bauxite bearing area, in the wider area of Sovinjak (Minjera), Grdo selo (near Pazin) and Blatna Vas (south of Roč).

The main tectonic feature in the wider area of Sovinjak is a brachianticline that extends along the canyon of Mirna river and is composed of Cretaceous sediments. Paleogene sediments are situated along both limbs of the anticline mentioned. Upper Cretaceous and

Paleogene sediments are gently inclined toward NE and SE, respectively. No clear angular unconformity could be observed between these sediments. Obvious erosional unconformity is clearly marked by the uneven thickness of the Kozina beds.

The pyritized bauxites in Grdo selo and Blatna Vas are related to small outcrops of Cretacous sediments. In the area of Sovinjak the footwall rocks of the pyrite bauxites are represented by the pale-gray to white coloured shallow marine limestones with fossil shales of rudists and Chondrodonta. Due to the common presence of *Radiolites praesauvegesi* TOUCAS in the upper part of these limestones, they are assigned to the Lower Turonian (PLENIČAR, 1973). The Kozina beds, which represent the hanging wall of the pyritized bauxites display a marked erosional unconformity towards the underlaying Cretaceous limestones. These beds are composed of thin-bedded, clayey, micritic limestones rich in organic matter, up to 10 m thick. At places where they contain thin layers of coal and clays rich in organic matter, fresh water flora and fauna species can be found such as *Chara oogonies* (genera *Nitella* and *Lagynophora Melanoides solitaria* STACHE and *Anomia liburnica* STACHE. These layers were undoubtedly formed in a freshwater and brackish water environment. They alternate with layers containing abundant miliolids (the genus *Peneroplis* being the most common) and *Stylophora sp.* which points to a periodical marine influence. (Pl. I).

REVIEW OF PREVIOUS RESULTS

Several papers have been published on the pyritized bauxite deposits and their exploitation and processing in Minjera. While a few of these were published in the 19th century, the majority has come out quite recently. An overview of these publications as well as a detailed description of Minjera was given by SAKAČ et al. (1993) and MARUŠIĆ et al. (in print).

The oldest known published data on Minjera was given by TOMMASINI (1646) who was the bishop of Novigrad in Istria. He stated that the "Miniera di allume" situated at Sovinjak in the valley of Mirna river was abandoned by "minatori ... tadeschi". He also pointed out that the mines had been reactivated and exploited by Battista Cavanis of Venice but the operations were suspended after his death. No detailed data on exploitation and processing have been included in his publication. TURINI (1808) pointed out that in the valley of Mirna river he had found an ore (he used the name "pirite") favorable for alum production. After a few years of preparation Turini activated a mine and built a chemical processing plant. In his comprehensive monograph he presented the physical and chemical characteristics of the ore and described the technology (he himself innovated processing procedure) of vitriol, sulfuric acid and alum production. Turini's monograph was published 13 years before the publication of BERTHIER (1821) was presented. This fact indicates that priority regarding the first published data on the physical and chemical characteristics of bauxite has to be given to the pyritized bauxite from Istria and not to the bauxite from Les Baux in France.

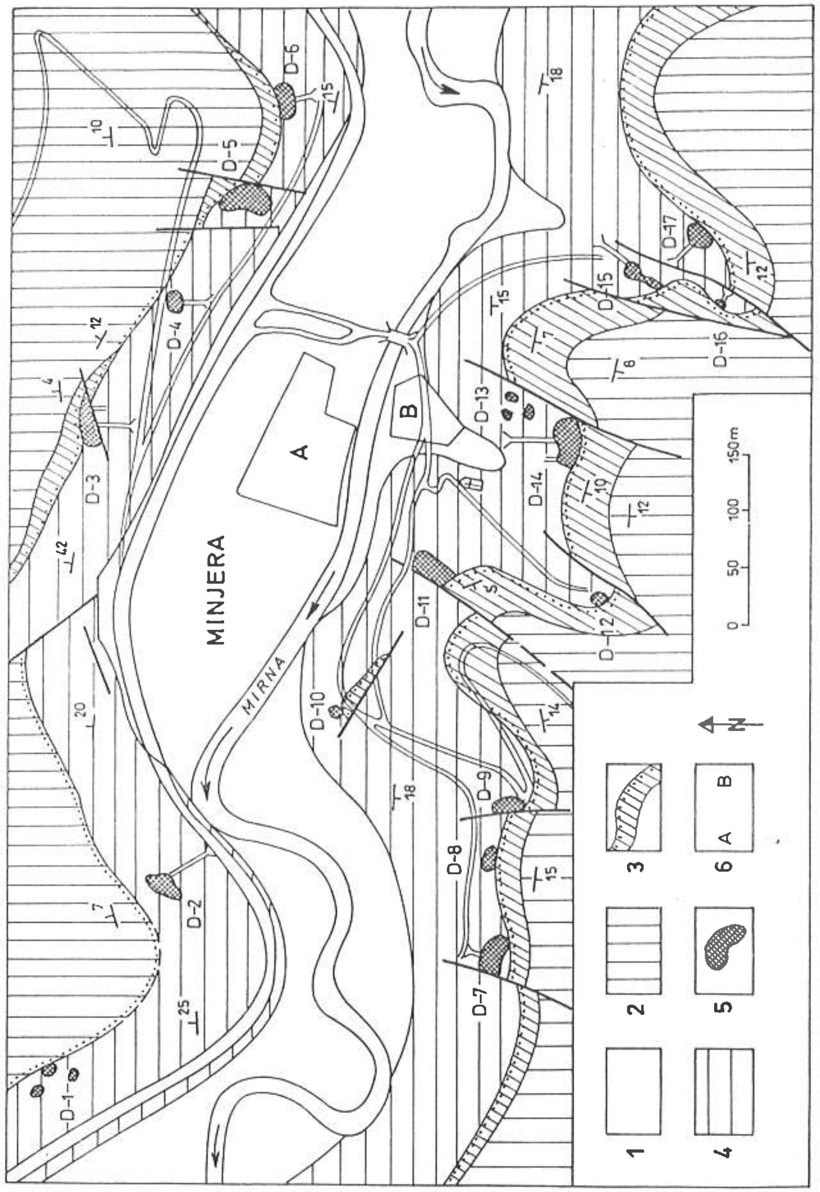

Fig.2. Geological position of the bauxite deposits in the Mirna valley.

1 Alluvion, **2** Foraminifera Limestones; Lower Eocene and part of Middle Eocene, **3** Kozina-layers: well bedded bituminous, marly or sandy limestones with coal intercalations; Paleocene and lowermost Eocene, **4** limestones with rudists; Upper Cretaceous, **5** piritic bauxite deposits, **6**: A site of the ore dressing plant, B site of the alum and vitriol factory

D'AMBROSI (1955) stated that Turini's "pirite" in fact represents a pyritized bauxite and affirmed its underground exploitation in the valley of Mirna river. Stulli (1984) found that the pyritized bauxites were also exploited in Grdo selo and Blatna Vas. SAKAČ and VUJEC (1988) presented the first drawing of a deposit in Minjera.

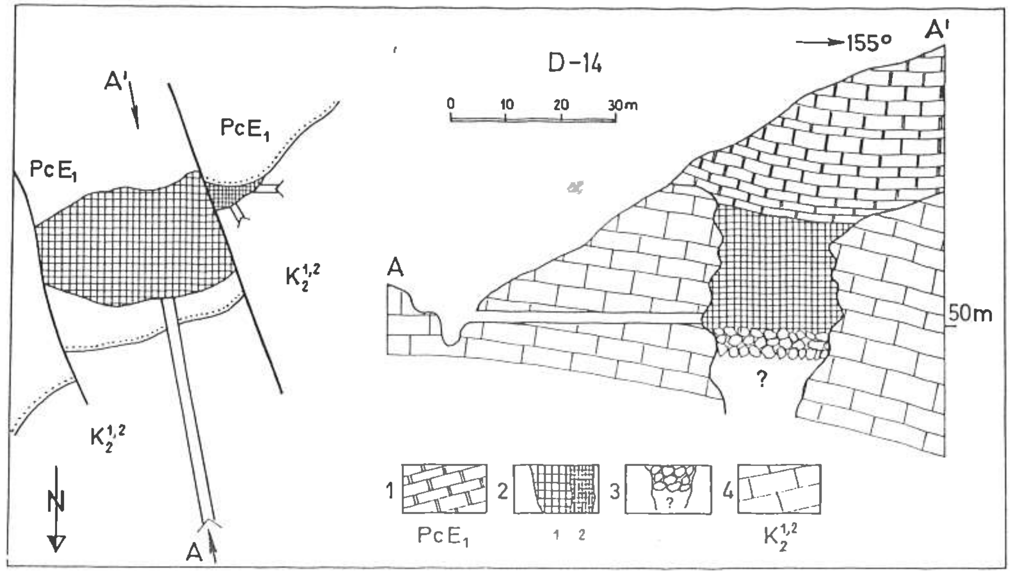

Fig. 3. Bauxite deposit E-14. 1 Kozina layers and Foraminifera limestones; Paleocene and lower Eocene, 2 Bauxite: 1 under the roof, 2 bauxite outcrop, 3 collapse structure, 4 limestones with rudists; Upper Cretaceous

FORMER MINING ACTIVITY

Bauxite deposits which were exploited in the valley of Mirna river late in the 18th century and in the first half of the 19th century are situated along the steep southern and northern slope of the Mirna river canyon in the vicinity of Sovinjak and Mlun (Fig. 2,3). Seventeen locations have been found in the vicinity of the former processing plant, covering an area of 0.9 square kilometers. The majority of deposits were covered by hanging-wall sediments and only small outcrops of the bauxite ore were exposed at the surface. Bauxites were excavated by underground mining because the configuration of a ground was in favor of adit type exploitation. Miners used adits for both carting of ore and drainage. The second reason for the underground mining was the fact that when exposed to the action of weathering pyritized bauxite is rapidly oxidated. This kind of ore is not suitable for alum production. The majority of old adits is very well preserved because they were built in the hard Cretaceous limestone. On the contrary, only dilapidated walls of the processing plant have stayed behind. It can be tentatively concluded that during the period mentioned a total of about 150.000 Tons of ore was excavated.

SAMPLING AND ANALYTICAL PROCEDURES

Twenty samples of gray pyritized, black pyritized and yellowish red mottled bauxites were collected along the steep southern and northern slopes of the Mirna river canyon in the vicinity of Sovinjak and Mlun, and from Blatna vas. Most samples belong to the gray pyritized bauxite which represents the bulk of each deposit. The black pyritized bauxite either forms a thin layer on the top of gray pyritized bauxite or is incorporated in the gray pyritized bauxite as small detrital fragments. The yellowish-red mottled bauxite is usually found on the contact with the bedrock but can also be found on the top of the deposit. Thin and polished-section studies of all samples were performed. XRD-data of selected bauxites were obtained using a Philips X-ray diffractometer unit, with Cu K α radiation generated at 34 kV and 18 mA. Thermic analyses (DTA, TG and DTG) of selected bauxites have also been made. Major and trace elements in selected bauxites were analyzed by a XRF-equipment.

RESULTS

The pyritized bauxites consist of boehmite, pyrite, marcasite, hematite, goethite, kaolinite, diaspore, gibbsite, anatase, turmaline and zircon. The main mineral constituents are boehmite and sulfides of iron. Hematite and goethite are present either in those parts of deposits which have not been affected by the process of sulphidization or in places where the gray or black pyritized bauxite has been oxidized. Gibbsite is very rare and is found both in the form of fine detritic grains and in authigenic veinlets. Turmaline and zircon crystals are of detritic origin. Boehmite and hematite are cryptocrystalline. Although kaolinite is essentially cryptocrystalline, fine grained secondary kaolinite eventually fills small cracks and cavities.

The pyrite/marcasite ratio is variable. Some samples contain more marcasite then pyrite and vice versa. Pyrites display different features as for their crystallinity and morphology, and different relationship toward other minerals. The following features have been recognized: (1) pyrite grains which often display crystal forms and vary in size from submicroscopic dimensions up to 0.6 mm (average size is 100-300 µm), (2) aggregates of cryptocrystalline pyrite of gel-like appearance with desiccation cracks, (3) framboidal pyrites, (4) pyrites filling irregular cavities and fissures and (5) fine-grained pyrites in ooides, sporadically concentrated in particular shells.

Table 1. Content of major elements (wt% of oxides) in grey pyritized bauxite (1) and yellowish-red mottled bauxite (2)

	1	2
SiO_2	9.75	1.93
TiO_2	2.26	3.17
Al_2O_3	55.80	63.60
Fe_2O_3	1.66	16.65
MnO	<0.05	<0.05
MgO	0.33	0.30
CaO	<0.05	<0.05
Na_2O	<.0.05	<0.05
K_2O	<0.05	<0.05
P_2O_5	0.08	0.05
L.O.I.	19.64	15.32
TOTAL	89.52	101.02
SULPHIDES		-
Fe_2O_3	6.73	-
S	5.40	-
TOTAL	101.65	101.02
LESS THE "O"-EQUIVALENT OF THE "S"	2.02.	-
TOTAL	99.63	101.02

Marcasite very seldom displays crystal forms. Then it occurs in the form of elongated grains with spear-shaped twins. Aggregates of irregular grains and of gel-like appearance are much more common (Pl. 2-5).

Diaspore was found only in a few samples and then it occurs in the form of tabular crystals ranging in size from 10-80 µm. Most often diaspore crystals fill cavities, in some of them being sporadically associated with fine-grained kaolinite crystals. Diaspore is also find in association with boehmite both in the form of fine isometric grains and in small accumulations (Pl. 4).

The textures of pyritized bauxites are identical to those of red coloured Early Paleogene Istrian bauxites, oolitic and pseudoolitic textures being predominant (Pl. 2-3).

XRD traces showed that the gray pyritized bauxite contains boehmite, pyrite, marcasite and kaolinite as the main mineral phases while diaspore and anatase are accessory (Fig. 4a). When compared to the gray one, the black pyritized bauxite is enriched in diaspore and depleted in marcasite (Fig. 4b). This was also proved by thermic analyses.

Table 2 Content of trace elements (ppm) in grey pyritized bauxite (1) and yellowish-red mottled bauxite (2)

	1	2
Ba	22	35
Co	6	39
Cr	232	443
Cu	18	45
Ga	33	48
Mo	28	<5
Nb	71	77
Ni	282	151
Pb	14	22
Rb	10	12
Sr	134	123
Th	22	51
U	17	5
V	168	287
W	7	18
Y	<5	21
Zn	44	56
Zr	241	274

Chemical analyses were performed on gray bauxite with euhedral pyrites and marcasites from Minjera and on yellowish-red mottled bauxite from Blatna vas (Tables 1 and 2). The mottling is a result of recent (sub-recent) subaerial exposure when pyrites and marcasites have been replaced by limonite and hematite (reoxidation). One sample of gray pyritized bauxite as well as one of the yellowish-red mottled bauxite were analyzed.

When compared to red bauxites (Table 3), the gray bauxite is depleted in iron and enriched in silicium. The lower iron content in the gray pyritized bauxite can be explained by the fact that after being reduced to ferrous form, only part of the iron formed pyrite (marcasite) while the rest was removed in solution. The higher silica content of the gray pyritized bauxite can be attributed to the process of resilification (neoformation of kaolinite). No conclusive statement can be given regarding the content of trace elements among gray, mottled and red bauxite on the basis of analyses shown on Tables 1, 2 and 3. The contents achieved match to the average trace element contents in Hungarian bauxites of Eocene age (MAKSIMOVIĆ et al., 1991). The lower Th/U ratio in the gray bauxite (Th/U=1.2) when compared to the yellowish red mottled one (Th/U=10.2) although indicative, is not conclusive because of the inadequate number of samples analyzed.

Table 3. Content of selected major (wt% of oxides) and trace (ppm) elements in some red bauxites from Istria (from Šinkovec, 1973). 1- Deklevi locality; 2- Serbani locality.

	1	2
SiO_2	1.98	0.20
Al_2O_3	56.48	60.50
Fe_2O_3	23.10	22.16
TiO_2	3.49	2.95
L.O.I.	12.65	13.52
Ni	250	145
Co	23	16
Cu	53	19
Cr	425	560
Zr	456	380
V	220	490

DISCUSSION

As a result of gradual transgression, on a flat, low elevation area coastal swamps developed overlaying a paleorelief sporadically filled by bauxites. At the bottom of the swamp immediately above the bauxite, due to the decay of organic matter an oxygen-depleted environment was formed which produced hydrogen sulfide. At the upper parts of, at that time, highly porous bauxite deposit ferric oxides were reduced to ferrous iron which reacted with hydrogen sulfide, forming poorly crystallized pyrite. The pyrite that was formed gives black colour to the bauxite. We consider this the first phase of pyritization. It has to be stressed that BERNER (1970) concluded that during sedimentary pyrite formation the first formed iron sulfide is not pyrite. He showed that the products of reaction of hydrogen sulfide whit ferric minerals under typical sedimentary conditions consist of one or more acid-soluble, poorly-crystallized black iron-monosulfides which are thermodynamically unstable phases relative to pyrhotite and pyrite in marine sediments, and may be converted to pyrite by oxidation. The first phase of pyritization is considered to have been relatively fast and, according to some preserved outcrops has affected only a thin upper part of the deposit. Due to periodical movements of water in the swamp (storms, rapid inflow of water) the upper parts of the pyritized bauxite body have been partly destroyed and small detrital fragments redistributed within the same bauxite layer. The shape of fragments clearly indicates that they were not completely lithified and were suffered a short transport. Band-shape black fragments noticed in the bauxite probably represent plant remnants.

We believe that the processes of pyritization and synsedimentary transportation were simultaneous. Namely, an oxygen-depleted swampy environment was periodically interrupted by storms and rapid inflow of water.

The second phase of pyritization probably started after the bauxite deposit has been overlain by a thin layer of swampy sediments. This phase occurred under slightly changed conditions because bauxite had become more compact. The circulation of a pore-waters through the bauxite was slowed down. Pyritization affected also the deeper parts of the deposit. In places, almost the entire deposit was affected by pyritization.

Pore-water which contains sulfide ions moved downwards and reduced ferric-oxides. As a result, iron sulfides were formed. An experimental study performed by ROBERTS et al. (1963) suggests that pyrite will be formed either very slowly or not at all above pH 6. Whether pyrite or marcasite will be formed depends on the chemical conditions of the micro-environment. Namely, according to BERRY et al. (1983) pyrite is about to be formed under alkaline and slightly acidic conditions while marcasite is about to be formed under lower pH conditions. FEREND (1970) showed that pyrites with crystal forms develop when the concentration of sulfur and iron in pore-waters is low, while pyrites displaying framboidal shapes develop under higher concentrations of both sulfur and iron. Due to the varying content of pyrite and marcasite in the bauxite and also to the presence of both crystalline and framboidal pyrites in some samples we may tentatively conclude that the concentrations of iron and sulfur as well as the pH of pore-waters repeatedly changed during pyritization.

When compared to the poorly-crystallized pyrites formed during the first phase of pyritization, the second phase pyrites are bigger and often visible with the unaided eye.

A significant characteristic of the pyritized bauxites from Istria is the presence of diaspore. This mineral has not been observed in red bauxites. Two types of diaspore can be distinguished, as far as the time of formation and morphology are concerned.

The older diaspore is fine, isometric in shape and uniformly distributed in the bauxite. It was probably formed during the first phase of pyritization and is more abundant in the black pyritized bauxite. The younger diaspore occurs in the form of tabular crystals and was formed by filling cavities and cracks, probably during the second phase of pyritization. The presence of diaspore veins suggests that during pyritization the pore-waters in the bauxite had gently acidic but changeable character that brought about, at slightly lower pH, the dissolution and migration of aluminum and, at slightly higher pH, the crystallization of diaspore.

The presence of diaspore in the investigated pyritized bauxites confirms the widely accepted idea that the reductive environment is favorable for diaspore formation (VALETON, 1964; BARDOSSY, 1967).

In the majority of cases worldwide the intensity of pyritization of bauxites is limited and is restricted to the occurrence of fine pyrite crystals or a thin pyrite layer in the uppermost part of a bauxite deposit. In our case, the process of pyritization has effected the major part of the deposit and must have been connected with the favorable conditions for pyritization of bauxite which prevailed in the area of study.

If swampy environment is developed on a paleorelief with associated bauxites, these are in most cases immediately overlain by clay and sediments rich in organic matter. This prevent the migration of pore-waters and the diffusion of ions from the covering sediments to the bauxites.

The cover of the investigated bauxites is composed of fresh-water limestones with organic matter, alternating with marine limestones. Considering the fact that the content of organic matter in the immediate cover is not very high, one may tentatively suppose that only the sulfur which pyritized the upper part of the particular bauxite deposit (first phase of pyritization) derives from organic matter. The rest of the sulfur originated from sea water.

Normally, during transgression, sea water which contains dissolved sulfate spreads over fresh-water sediments with organic matter. Due to the porosity of fresh water sediments which represent the immediate cover of the bauxite, the sea water might have been in contact with the bauxite. As a result of diffusion, sulfates dissolved in sea water might have migrated through the sediments with organic matter, where, due to anaerobic bacterial decomposition (sulfate-reducing bacteria) hydrogen sulfide was formed. This process was followed by reduction of ferric oxides in the bauxites and, as a result, iron sulfides were formed. As the process of iron sulfide formation proceeds, the concentration of dissolved sulfide in pore-waters decreases. The diffusion of sulfate from sea water through porous sediments, and the anaerobic production of hydrogen sulfide which is present in the form of dissolved sulfide in the pore-waters of bauxite last as long as there is enough iron available for the reaction with dissolved sulfide, or hydrogen sulfide is supplied. The amount of hydrogen sulfide produced depends on the content of organic matter present. Normally, sulfate reducing bacteria utilize organic matter to reduce sulfate and produce sulfide. Because bauxite deposits are not entirely pyritized, we believe that the content of organic matter was the main limiting factor that made the pyritization of bauxite deposits incomplete.

The ideas presented are in accordance with the investigations performed by BERNER (1969) who simulated the transport of iron and sulfur within anaerobic sediment during early diagenesis.

In some deposits gypsum can be found in the form of irregularly distributed accumulation inside the bauxite or near the contact with limestone. Due to the contact with meteoric water, pyrite and marcasite are oxidized and sulfuric acid is released. As the result of reaction with limestone, gypsum may be formed.

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SAŽETAK

Piritizirani boksiti MINJERE, ISTRA, HRVATSKA

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Piritizirani boksiti nalaze se u mnogim ležištima Istre, osobito u njezinom sjevernom dijelu. U dolini Mirne podno naselja Sovinjak, nedaleko Buzeta, na lokalitetu Minjera, taj se boksit otkopavao i koristio za proizvodnju sumporne kiseline i alauna još u 16. stoljeću, a u većem opsegu krajem 18. stoljeća i u prvoj polovici 19. stoljeća. TURINI je objavio 1808. opsežan rad u kojem detaljno navodi svojstva piritiziranog boksita, kojeg naziva "pirite", kao i tehnološki postupak njegove prerade u Minjeri To je prvi znanstveni opis (piritiziranog) boksita, a Minjera je najstariji rudnik boksita u svijetu (MARUŠIĆ et al., 1993, SAKAČ et al., 1993).

U Minjeri otkopano je 17 ležišta boksita isključivo jamskim načinom (sl. 2). Ležišta su, kao i većina u Istri, mala a količine otkopane rude iznosile su u pojedinim ležištima, koja su sadržavala osim piritiziranog boksita i uobičajeni crveni bemitno-hematitni boksit, od tisuću do dvadeset tisuća tona. Boksiti leže na okršenoj paleopovršini gornjokrednih vapnenaca, dok su im krovina slatkovodno-brakične, djelomično i marinske Kozina naslage starijeg paleogena koje se sastoje od tankouslojenih, zaglinjenih, mikritskih, organskom supstancijom impregniranih vapnenaca s brojnim ostacima pretežito močvarnog bilja, malakofaunom, te foraminiferama, ponegdje koraljima itd. (tabla 1). Kozina naslage naviše postupno prelaze u eocenske foraminiferske vapnence, dok su fliški sedimenti najmlađi dio paleogenskih naslage.

U piritiziranom boksitu Minjere utvrđeni su minerali: bemit, pirit, markazit, hematit, getit, kaolinit, dijaspor, hidrargilit, anatas, turmalin i cirkon. Glavni minerali su bemit i sulfidi željeza. Dijaspor je zapažen samo u nekim uzorcima boksita. Na tabeli 1 i 2 dat je sastav piritiziranog boksita (1), te za usporedbu i sastav žuto-crvenog boksita (2) s kojima se nalazi zajedno u pojedinim ležištima Minjere.

Piritizirani boksiti Istre nastali su za vrijeme emerzione faze koja je nastupila nakon laramijskih pokreta krajem krede, a trajala je tijekom paleocena, mjestimično i u donjem eocenu, do postupnog preplavljivanja paleokopna, odn. transgresije iz smjera sjeveroistoka (DROBNE, 1971). Preplavljivanje paleokopna nije bilo cjelovito već ritmično. Tako se početno talože, odn. djelomično izmjenjuju slatkovodno-brakični i marinski sedimenti, da bi u eocenu posve prevladali marinski uvjeti taloženja. Osim toga u jugozapadnom dijelu Istre, gdje je kopno bilo povišeno, na krednim karbonatnim naslagama izravno leže eocenski marinski karbonatni, a ponegdje i klastični sedimenti. Stoga piritizirani boksiti nalaze se u sjevernom dijelu Istre jer im je postanak povezan s organskom materijom krovinskih naslaga starijeg paleogena.

Postanak piritiziranog boksita mogao se odvijati u dvije faze. U prvoj kraćoj fazi neposredno nad ležištima primarno crvenih boksita u paleocenu bile su močvare s reduktivnim okolišem uslijed razgradnje močvarnog bilja i drugih organskih supstancija. U najvišem dijelu ležišta boksita, tada još veoma poroznog, otapao se hematit, a reducirano trovalentno željezo vezalo se sa sumporom organskog porijekla. Pri tome nastao je sitnozrni, submikroskopski, slabokristaliziran pirit, dok je izmijenjen boksit dobio crnu boju. Prva faza piritizacije boksita bila je relativno brza i zahvatila je samo tanki gornji sloj ležišta.

Druga faza piritizacije vjerojatno je započela u izmjenjenim uvjetima pošto su ležišta boksita bila prekrivena tanjim slojem krovinskih naslaga. Boksit je tada bio kompaktniji, cirkulacija porne vode kroz boksit stoga je bila usporena, kao i sam proces piritizacije. No tada piritizacija zahvaća dublje dijelove ležišta, a ponegdje i čitavo ležište. Pri tom sulfidni ioni difuzijom prožimaju boksit reducirajući željezo iz hematita i vežući se s njim stvaraju sulfide. Ovisno o uvjetima mikrookoline, odn. ovisno o promjenama pH, Eh i koncentracije iona S, mogao je nastati pirit ili markazit. Za razliku od pirita prve faze, pirit druge faze krupniji je i često vidljiv golim okom.

Piritizirani boksiti sadrže dijaspor za razliku od "običnog" crvenog bemitno-hematitnog boksita Istre. Dijaspor najčešće zapunjava šupljinice, a ima ga ponegdje i zajedno sa sitnozrnim kaolinitom. Pojavljuje se i u pločastim kristalićima dužine 10-80 μm. Ima ga i u bemitu kao pojedinačna sitna izometrična zrna, ili kao male nakupine. Mogu se razlikovati dvije vrste dijaspora s obzirom na vrijeme postanka. Stariji je sitan, izometričan. Ravnomjerno je raširen u boksitu, obilniji je u crnom boksitu nastao u prvoj fazi piritizacije. Mlađi krupniji, dijelom pločasti, nastao je zapunjavanjem šupljinica u žuto-crvenom, ili crvenom boksitu. Kristalizirao je vjerojatno tijekom druge faze piritizacije. Žilice dijaspora pri tom upućuju da su pri njegovu nastanku porne otopine bile blago kisele, ali i promjenjivog sastava. Tako je malo niži pH uvjetovao otapanje i migraciju aluminija, a nešto povišeni pH kristalizaciju dijaspora.

Općenito se piritizacija boksita svodi na ograničenu pojavu sitnih kristala pirita, ili na tek tanji njihov sloj u višem dijelu ležišta. To stoga jer su se poviše primarnog crvenog boksita najčešće taložili glinoviti sedimenti koji su sprečavali jače migriranje pornih voda i difuziju iona u boksit iz pokrovnih sedimenata s organskom materijom. U Istri, posebice u dolini rijeke Mirne, piritizacija je zahvatila veliki dio ležišta boksita, nerijetko sve do njegovih najdubljih dijelova, jer se za taj proces postojali veoma povoljni uvjeti. Važna je činjenica da se unutar krovinskih naslaga izmjenjuju sedimenti taloženi u slatkovodno-brakičnom okolišu s onim nastalim u marinskim uvjetima. Kako količina organske materije nije zbog male debljine krovinskih Kozina naslaga velika, pretpostavlja se da tek manji dio sumpora koji je piritizirao boksit u prvoj fazi piritizacije potječe iz tog izvora. Drugi znatniji dio sumpora mogao je potjecati iz morske vode koja je uslijed poroznosti krovine mogla doći u kontakt s niželežećim boksitom. Difuzijom iz morske vode SO_4^{-2} migrirao je kroz sloj s organskom materijom, gdje se zbog bakterijske sulfatne redukcije formirao S^{-2}, a potom u boksitu reducirao željezo iz hematita stvarajući sulfide. Vezivanjem sumpora za željezo smanjivala se koncentracija iona S^{-2} u pornim vodama u boksitu, zbog čega se nastavila migracija sumpora iz morske vode naniže prema boksitu. Ta difuzija SO_4^{-2} iz morske vode u slojeve s organskom materijom, a zatim S^{-2} u porne vode u boksitu trajala je sve dok je u boksitu postojalo reaktivno željezo za reakciju sa sulfidnim ionom, odn. dok je trajala bakterijska sulfatna redukcija u sloju s organskom materijom. Taj proces bio je kontroliran količinom organske materije u krovinskim naslagama. Kako ležišta boksita uglavnom nisu u cijelosti piritizirana vjerojatno je količina organske materije bila ograničavajući faktor u procesu piritizacije boksita u području Minjere.

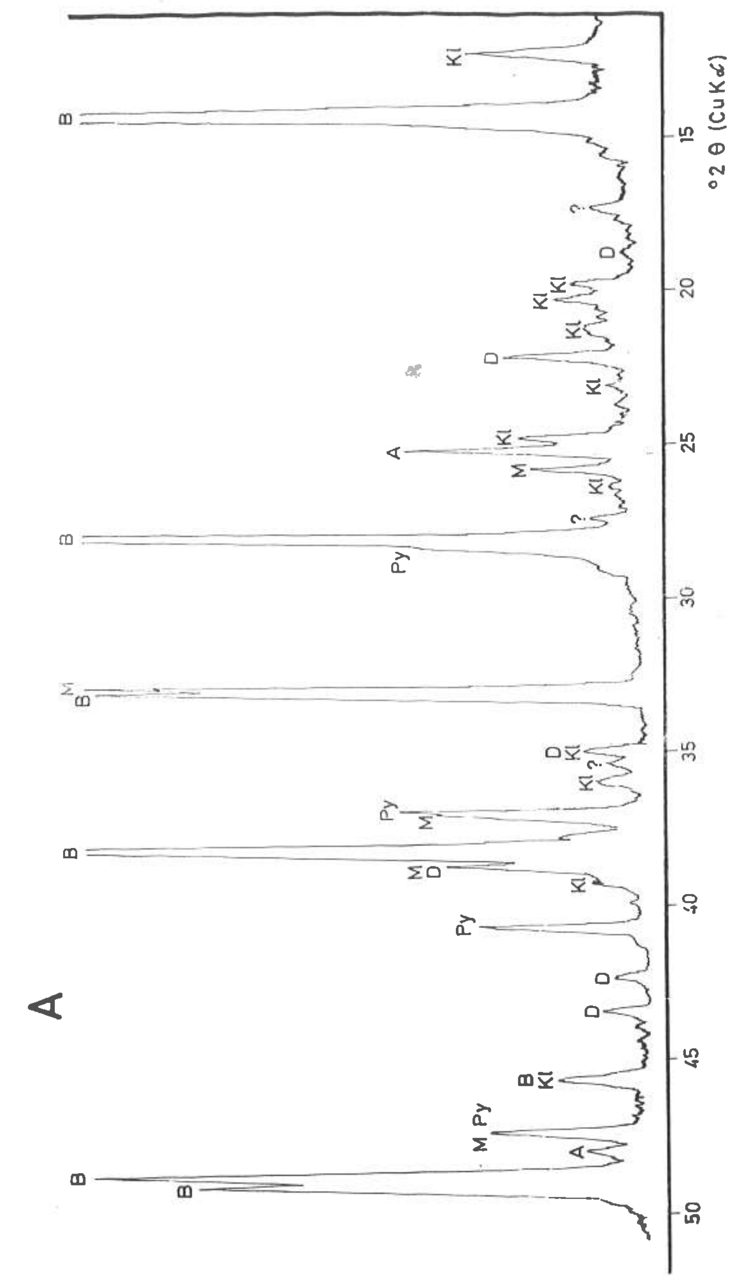

Fig.4a. X-ray powder diffraction traces of bauxites. Grey pyritized bauxite from Minjera. B- boehmite, D- diaspore, Py- Pyrite, M- marcasite, Kl- kaolinite, A- anatase, ?- unidentified mineral

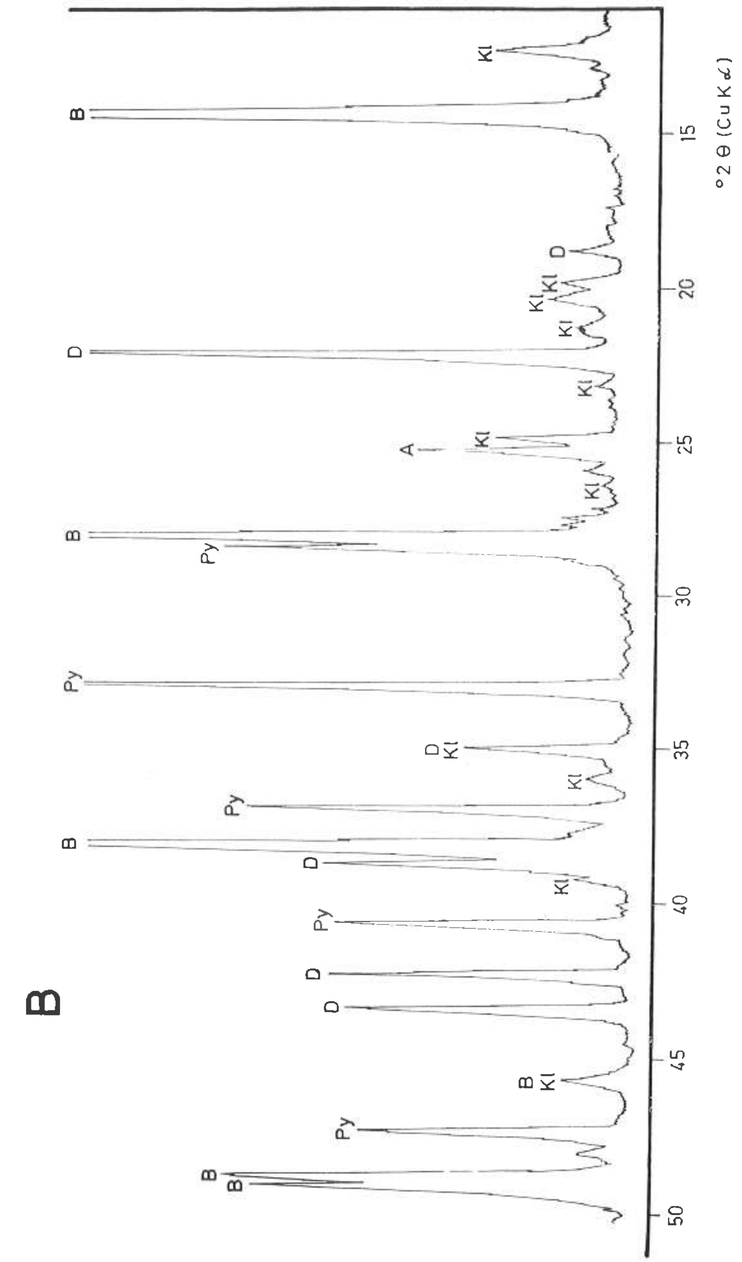

Fig.4b. X-ray powder diffraction traces of bauxites. Detrital fragment of black pyritized bauxite in grey pyritized bauxite from Minjera. B- boehmite, D- diaspore, Py- Pyrite, M- marcasite, Kl- kaolinite, A- anatase, ?- unidentified mineral

PLATE I

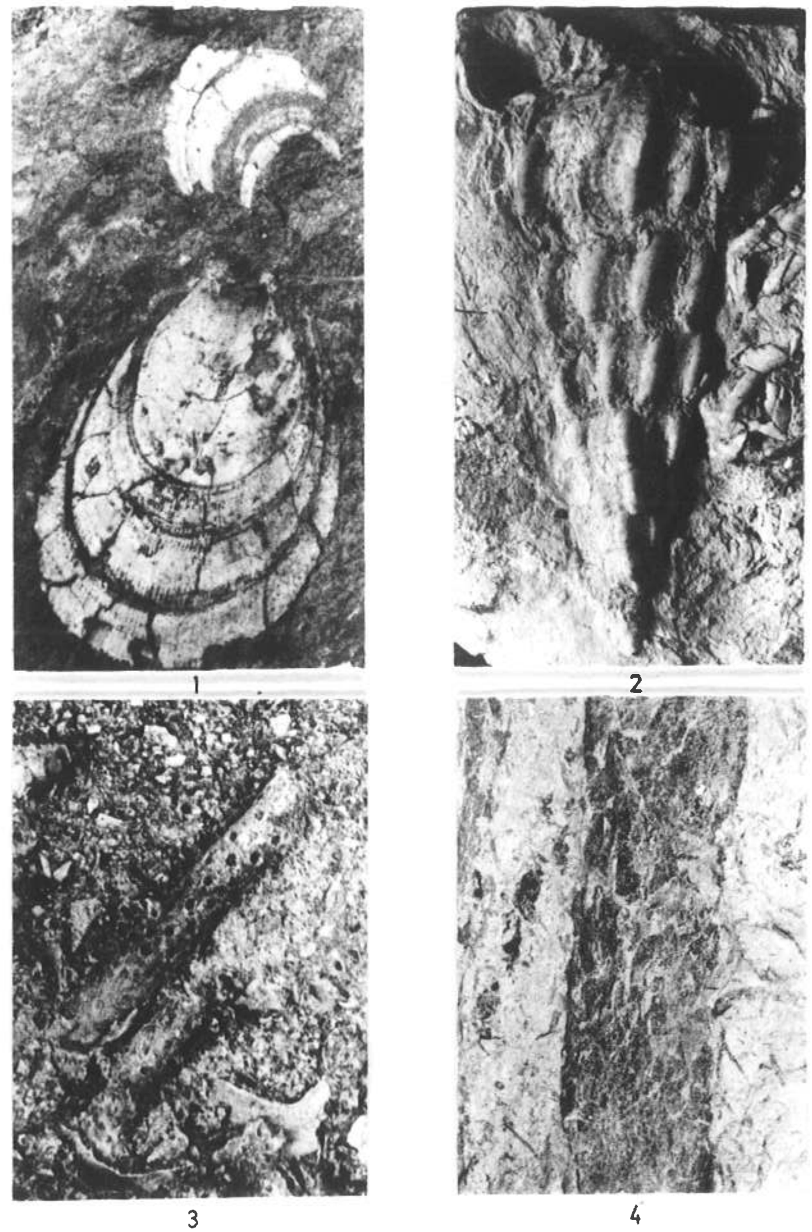

PLATE I

1 Anomis liburnica STACHE, 2x. 2 Melanoides (Melanoides) solitaria STACHE, 2x. 3 Stylophora sp., 2x. 4 Plant remnants, 2x

PLATE II

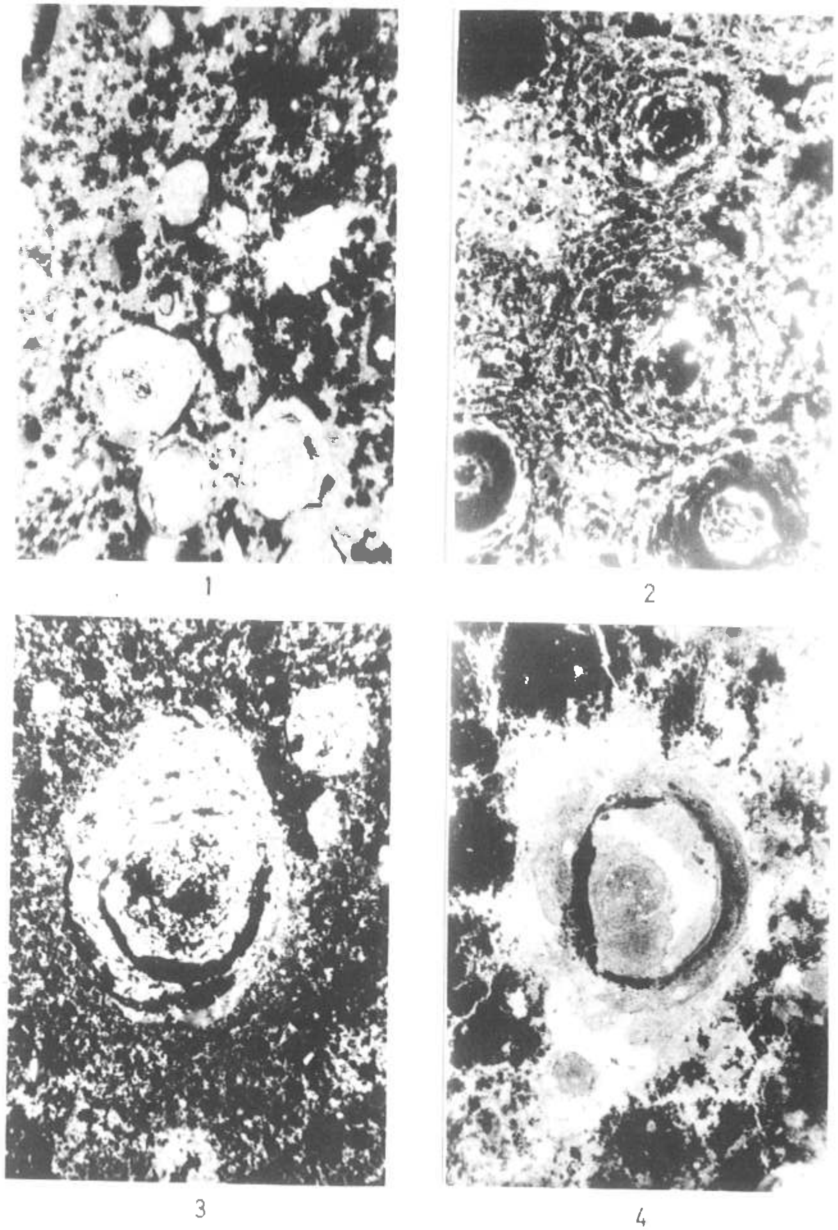

PLATE II

1. Pyritized bauxite of oolitic texture. Black-pyrite; width of photograph = 2,15 mm. 2. In situ growing of ooids. Black-pyrite; width of photograph = 1.10 mm. 3, 4. An ooid with a pyritic husk. Black-pyrite; width of photograph = 1.10 mm

PLATE III

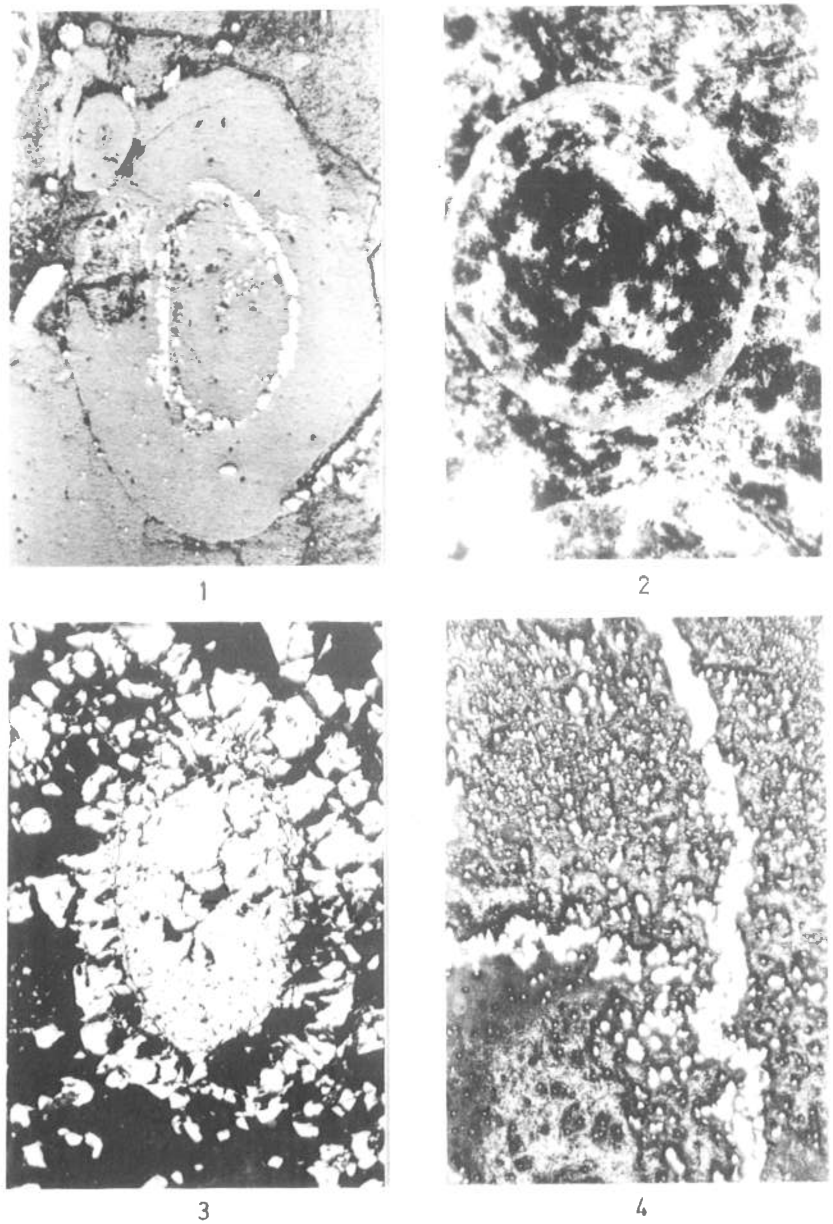

PLATE III

1. An ooid with a pyritic husk. Wite-pyrite. Reflected light; width of photograph = 0.43 mm. 2. A pyritized ooid. Young outer husk is without pyrite, width of photograph = 0.43 mm. 3. A completely pyritized ooid. Matrix contains individual pyrite grains. Reflected light; width of photograph = 0.43 mm. 4. Pyrite veins and small pyrite grains in bauxite. Reflected light; width of photograph = 1.10 mm.

PLATE IV

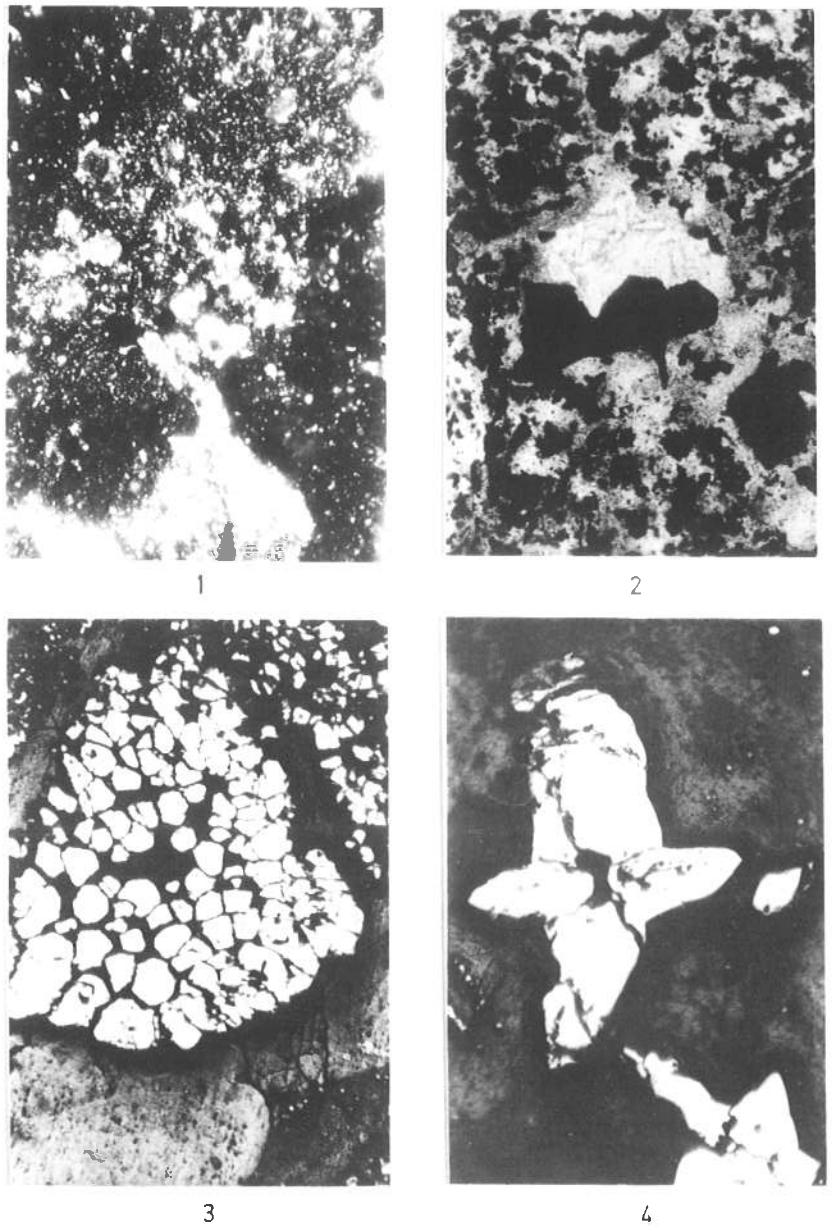

PLATE IV

1. Small grains of diaspore (white) of first generation in the bauxite; width of photograph = 0.43 mm (crossed micols). 2. Tabular crystals of diaspore of second generation (in center). Black-pyrite; width of photograph = o.43 mm. 3. An accumulation of pyrite granis. Reflected light; width of photograph = 1.10 mm. 4. Twins of marcasite crystals. Reflected light; width of photograph = 0.43 mm.

PLATE V

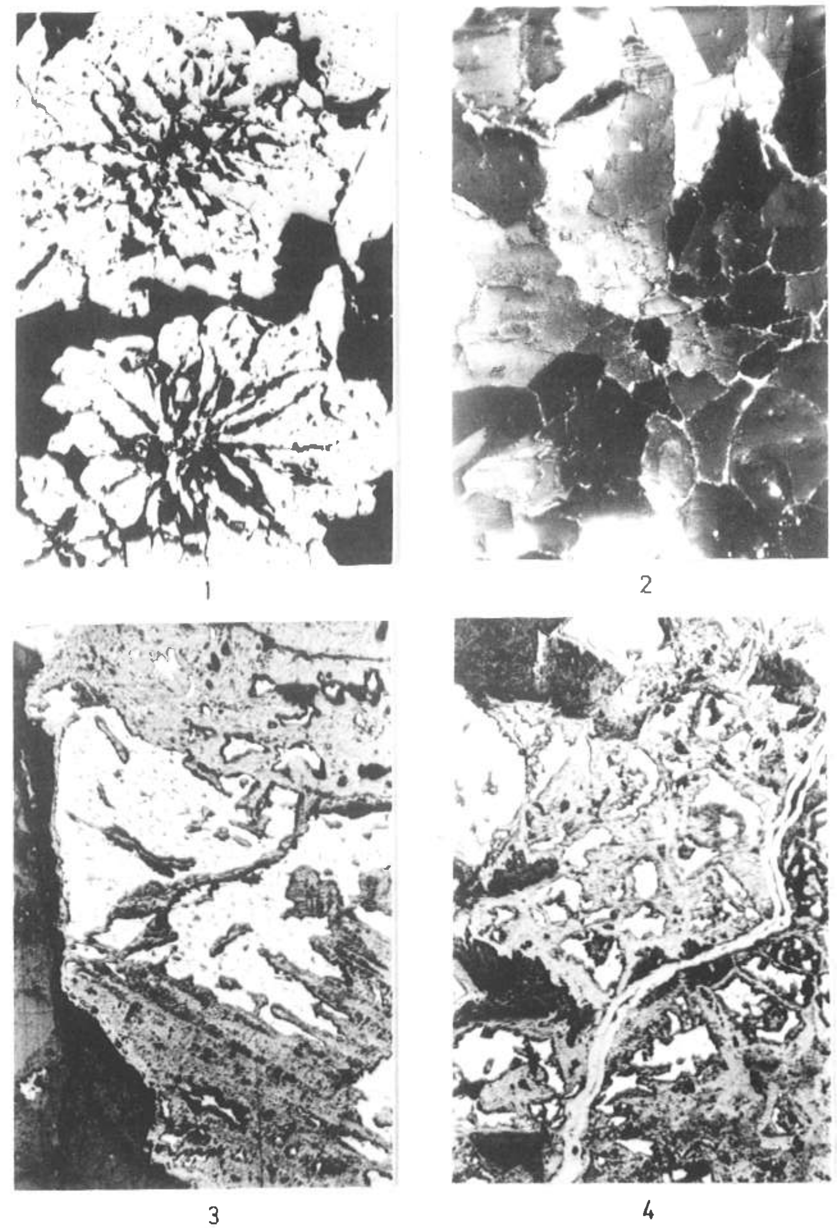

PLATE V

1. Marcasite of a gel-like appearance. Reflected light; width of photograph = 0.43 mm. 2. Anisotropic effects of marcasite. Reflected light; width of photograph = 0.43 mm (crossed nicols). 3. Replacement of pyrite (white) by goethite. Reflected light; width of photograph = 0.43 mm. 4. Limonitization of pyrite (white) and goethite vein. Reflected light; width of photograph = 0.43 mm.