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GEOCHEMICAL FACIES ANALYSIS OF GROEDEN SEDIMENTS AND ORE FORMING PROCESSES IN ŽIROVSKI VRH URANIUM MINE, SLOVENIA, YUGOSLAVIA

GEOKEMIJSKA FACIJELNA ANALIZA GREĐENSKIH SEDIMENATA I RUDONOSNI PROCESI U RUDNIKU URANA ŽIROVSKI VRH
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The Zirovski Vrh uranium deposit is located on the northeastern slopes of the same called mountain. The ore bodies are placed in the upper part of the grey Groeden sandstones, having lenticular and inbedded forms. It belongs to the peneconcordant deposits in fluvialite sandstones, with signs of epigenetic origin, as corrosion of detrital grains by ore forming solution, decoloration (leaching) of red beds, and zonation of concentration of uranium and chalcopyrite elements around an ore body caused by differentiated Eh-pH profile and differences in their geochemical behaviour.

The subject deals mainly with distribution of trace and major chemical constituents in an uranium ore body and its close vicinity. The leading idea was to investigate and interpret syn— and epigenetic signs of ore forming processes.

The results of undertaken investigation are in good agreement with general statements of epigenetic origin, bringing some new ideas in connection with unusual appearance of low FeO/Fe₂O₃ ratio in the center of the ore body, estimation and explanation of elemental grouping and zoning, suggesting an epigenetic-exogenic model in accordance with the recent ideas in the geochemistry of uranium ore formation.

* * *


Rad se bavi distribucijom mikro i makro kemijskih komponenta u uranskom rudnom tijelu i njegovoj blizoj okolici, rano i kasno diagenetskim i epigenetskim promjenama na detritusnim mineralima, porijeklom boje sedimenata i njezine veze s rudnosnim procesima.

Istraživanja ukazuju na epigenetsko-egzogeni način oruđenja. Znalost distribucije halkofilnih elemenata oko uranskog rudnog tijela

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uzrokovana je infiltracionim mehanizmom njihovog unašanja u geo
dolomitne ceđe (bajiruru) sa izdiferenciranim Eh-pH profilom. U radu
se također predlaže genetski model koji uzima u obzir paleogeografske
i klimatske uvjete i promjene u srednjem i gornjem permu, te kroz
geoakmatsku facijsku analizu objašnjava genozu rudnog ležišta.

1. GEOLOGICAL SETTING

The Žirovski Vrh Paleozoic sedimentary complex belongs to the Idri
da-Ziri region (allochton, overthrust) and the autochton to the Poljana-
Vrhnika sequences, O r m a l j e v (1965), Fig. 1. The basic structure in the
deposit is interpreted as an overturned Paleozoic syncline, overthrusted
onto the Triassic sediments. A part of the structure in the mining ex
doration area is presented in Fig. 2. On the basis of detailed under-

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**Sl. 1. Geološka karta okolice Žirovskog Vrha**


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44 [2]
Fig. 2. The position of the investigated H.52 corridor on the 480 m level of the Zirovski Vrh mine. The double Sr structure of the ore-bearing sedimentary series (according to L. K. G. and F. T. J. F. 1974).

Fig. 3. Geological profile of the H.52 corridor (profile, diagram).


Sl. 3. Geološki profil hodnika H.52.
ground exploration by means of tunneling and drilling, as well by opening of three new mining horizons downwardly, Lukács & Florijančič (1974) interpreted it as a double S structure.

The investigated corridor H-52 is situated at the 480 horizon, and due to its specific position in "the double S structure" superposition of sedimentary layers is inverse.

The Paleozoic sedimentary series is presented by two lithofacies and stratigraphic units: clayey shales, probably of marine origin (Omaljev, 1978), and terrigenous clastics, predominantly sandstones (the Groeden deposits).

Earlier comprehension, that the black shales belong to the Middle Carboniferous, separated from the Permian sandstones by a great hiatus, are nowadays under doubt since discovering of clastics inside of them.

By means of sedimentological analysis a sequence of geological events was reconstructed. After deposition of clayey sediments at the transition Carboniferous-Permian in marine environment, a prolonged emergence phase gradually caused rhythmic retreat of the marine facies. In the course of the Permian time, dry land phase dominated in the entire region. Due to the Saalic orogenic phase, a new mountain range arised in the hinterland became a source of great quantities of clastic material so called molasse. At that time, the surrounding of Zirovski Vrh was terrain with fluvial system (braided river) in whose domain started volcanic activity (quartzkeratophyre, quartz-porphry).

The Groeden clastic sediments are widely spreaded in the Alpine and Dinaric geosyncline regions. In the Zirovski Vrh area, there are two series of the Groeden deposits. An older, gray one is laid directly over the Carboniferous shales. It starts with basal conglomerates, followed by alternation of pschphites, psammites and pelites. Wedge-shaped intercalations of red psammites and pelites are of limited dimensions. A red series is presented by fine-grained clastics, especially in the lower part, although all other sorts are present too. The thickness of the gray series is estimated at 200 m and the red one at 300 to 500 m. The Groeden sandstones consist of fragments of volcanic, sedimentary and metamorphic rocks. Particularly characteristic are white and pink quartz, red quartz porphyry, argiloshist and limestones.

2. URANIUM MINERALIZATION

On the basis of the previous and recent explorations, it is definitely clear that mineralization is situated only in the upper part of the grey series. In turn, the ore bodies are often placed in a sandwich, which begins with red rocks, passing over a green zone into grey ore bearing sandstones and terminating with a green zone before a next red package (Fig. 14).

There is a gradational transition from the grey series, into the red one over a narrow zone of green and grey-green rocks. Exceptions, like implantation of green rocks in the grey ones as well as direct contact of red and grey rocks (and the green ones inside the red rocks), however, are present too.

The ore bearing sandstones are hardly distinguished from the barren ones, although, there is a tendency of accumulation of uranium mineralization at darker sites rich in organic matter and sulfides. The warrant determination of an ore body position and its shape is possible only instrumentally.
The shape of the ore bodies is variable. The transition barren-ore bearing rock is sharp (inside several cm), and the concentration of uranium inside the ore body is irregular.

The younger strata, overlaying the Groeden sandstones are Bellero-phonian limestones and dolomites (Zhazharian layers) of the Upper Permian age. It was the only criterion for age determination of the clastic series.

The ore bodies are mostly lens-like pseudolayers. The limit of exploitable concentration is 0.03% of Uranium and concentration above 5% are rare, Radosinović (1967). The ore is sufficiently rich to undergo exploitation dilution and to be used for production of «yellow cake» (U₃O₈).

The main ore mineral in the deposit is pitchblenda, always followed by sulfide mineralization. Radosinović (1967) determined following paragenesis: pitchblenda, pyrite, galena, sphalerite, chalcopryite, arsenopyrite, tetrahedrite, chalcocite, covellite, bornite, markasite. Ore minerals are exclusively in cement of clastic rocks. Secondary uranium minerals in oxidation zone are: dumontite, torbernite, metatorbernite, autunite, phosphuranylite, renardite, humite, malachite, azurite and arsenolite. Kuraš G. et al. (1977) determined also coffinite and soddyite, hydrated uranium silicates and cobaltite (microprobe). Pitchblenda is bigger than 10 (microns) rarely and comes in association with galena, pyrite and chalcopryite. Direct contact between pitchblenda and organic matter is sporadic.

3. ANALYTICAL METHOD

Common characteristics of the epigenetic sedimentary uranium deposit is zonal distribution of elements associated with uranium mineralization, (Harsman, 1974; Jensen & Qidwai, 1979). It is a consequence of infiltration mechanism of water with metal ions into the geochemical barrier with more or less differentiated Eh, pH, and pH-S conditions. Epigenetically introduced metals are concentrated in matrix and cement of clastics. Detrital minerals also bear certain quantity of trace elements and data on their «total» content are less useful for studying of epigenetic zoning (Shoemaker, 1959). That problem may be practically solved by choosing appropriate analytical method, i.e. by «partial» extraction of metals. Number of interesting elements for investigation of primary halos of sedimentary uranium deposits is very high because of especially rich paragenesis of theirs. The choice of elements, to be analyzed in this work, was restricted by available analytical facilities in the laboratory of the Institute at the time. Se, Mo, and V, as particularly typical and interesting elements for this type of deposits, for that reason have not been analyzed, (analyzed components in Appendix I and II).

3.1. Sampling

Lack of some systematic study of trace element distribution in the mine was the reason to choose linear method of sampling. In that way, the samples were collected along the corridor H-52, 1 sample/m, representing all lithological units of grey, green, red and ore bearing clastics (Fig. 3). Special attention was paid to «ore body I and II» and their close vicinity. The size of the rock sample was about 1 kg, what was enough to avoid local variation because of inhomogeneity. The rock was then crushed and ground in an agate mortar to avoid metal contamination.
3.2. Trace element analyses

3.2.1. Extracting of metals

A preferable analytical method would be the one with selective extraction of elements, which are in cement and matrix of investigated clastics, whose accumulation was caused by processes of diageneis and epigenesis, i.e. in exogenic conditions. Endogenic concentration of elements in crystal lattices of petrogenic silicates (detrital grains), in this way is not of interest. Appropriate methods would be those giving >partial< but not >total< content of trace elements.

In the clastic Permian sediments, which underwent a low grade metamorphism, metals in trace or macro quantities are present in different chemical forms. Cu, for example, might be: included in petrogenic silicates, or like sulfide, adsorbed or incorporated in clay minerals, adsorbed onto organic matter in organo-metallic compounds, coprecipitated by Fe-Mn oxides, built in secondary carbonates etc. By using different digestion procedures it is possible to extract it from particular chemical form.

The investigated Permian clastics contain up to several percentages of organic matter, which is known as an efficient extractor of metallic ions from water solutions. Binding mechanisms are diversified and differ from simple adsorption to cation exchange on active radicals like —OH, —COOH, —CNH₂, etc., or organo-metallic complexing by electron donor-acceptor mechanism. Aging of sediments and low grade metamorphism transformed organic matter into anthracite. Primary forms of complex organic molecular structures with functional groups have undergone polymerization, condensation and loss of volatiles. Bound metals were partly released from organic matter, since breaking of bonds, and newly formed compounds are mostly in reduced forms. For that reason, digestion agent has to have strong oxidizing character to destroy organic matter. Strong oxidizing acids with or without addition of H₂O₂ are mostly in use for that purpose. HClO₄ in that case is not recommendable for permanent explosion hazard.

Trace elements are also concentrated in mineral colloids present in pore space of water permeable sediments. Fe-Mn hydroxides are known as very good metal acceptor, whose dehydration in the course of diageneis and katagenesis leads to formation of hematitic cement, enriched in manganese or some manganese minerals.

Clay minerals are also ion-active matter. Metal accepting mechanism is complex and ranges from simple physical adsorption in space between two and three sheet layers, cation exchange on vacant hydroxyl groups —SiOH or —AlOH as well as isomorphic substitution in the octahedral Al-sheet. The last one usually enhances capacity of physical adsorption because of induced electrostatic disequilibrium if an introduced atom differs in charge from Al³⁺. Primary clay minerals were transformed by low grade metamorphism into micas and chlorites.

Carbonate cement is easily dissolved by acids and extraction of trace elements should not be particular problem.

Sulfides associated with uranium mineralization are digestable by hot mineral acids. Certain difficulties might be encountered with molybdenite (MoS₂).

Taking into consideration materials, probable bearers of trace elements, and consulting literature data, as most promising and efficient digestion agent would be a mixture of HCl—HNO₃ (1:6). The acid is able to dissolve all foregoing materials and to give persistant values of repeated measurements on a randomly chosen sample, what is necessary for reliable statistical procedure. Other acids were testified too, in order to compare efficiency of extraction, (K u n z e G. W., 1965; R o s e A. W. & S u h r N. H., 1971).
3.2.2. The choice of digestion agent and optimal extraction conditions

A choice of digestion agent was done by treating a ground sample by following acids: 10% CH₃COOH, 0.5 N CH₃Cl—COOH, HNO₃ conc., HCl conc., HCl—HNO₃ (3 : 1), HCl—HNO₃ (1 : 6) and total content by HF—HNO₃. To avoid matrix effect, the total content was analysed by standard addition method. The results of partial extraction efficiency are shown in Fig. 4.

The optimal quantity of digestion acid was determined on 5 samples. From the presented graph (Fig. 5) it is obvious that the maximum concentration of extracted metal is obtained by using 10 ml of HNO₃—HCl 6 : 1 mixture.

The optimal digestion time is determined on seven samples. The graph in Fig. 6 shows, that the highest extraction coefficient with chosen acid is obtained after 1 hour. To avoid lesser errors because of too short digestion, a time of 2 hours was satisfying.

Temperature of digestion is an essential factor for extraction coefficient. The graph (Fig. 7) shows that temperature of the water bath (about 90°C, measured in the digestion beaker) is sufficiently high to avoid greater fluctuations caused by lesser temperature change.

The foregoing tests proposed following procedure: 1 g of sample in the glass beaker (250 ml) is covered by 10 ml of HNO₃—HCl (6 : 1) mixture and carefully mixed. The beaker is covered by watch glass and digested on a water bath for 2 hours, cooled and transferred in a cuvette and centrifuged. The residue is washed out till it shows an acidic reaction. Centrifuged solution is quantitatively brought over into a plastic beaker and covered by a plastic stopper.

Precision of measurements is determined on 14 probes of two randomly chosen samples on Cu, Zn, Co, Ni, Pb, and Mn. The test determinations proved that detection limit is by far below the present metal concentration in rock samples.

The analyses were performed by «Beckman 495» autolaminar atomic absorber.

3.2.3. The analysis of uranium

The analysis of uranium was made by fluorescence method using a nitrogen laser fluorimeter UA—3 «Scintrex», Canada, with intensive pulsing emission in ultraviolet region (3371 Å).

Results of silicate and calcimetric analysis, analyses of sulfur, organic matter and extracted metals are given in Appendix I and II without describing of well known and common analytical methods, with exception for U and extracted metals which were described in the foregoing chapter.

4. STATISTICS

Statistical treatment of chemical data included testing of population, univariate, multivariate regression analyses and cluster analyses.

The total number of samples in the corridor H-52, on the level 480 was 77. The basic statistical treatment used to determine characteristics of chemical data populations was calculation of means, standard deviations and variance coefficients. Frequency distribution diagrams of row data and their logs were constructed and testified for »goodness of fit« between normal, lognormal, and empirical distribution by means of »Smirnov-Kolmogorov test«. The results are presented in Appendix III, Table B.
Fig. 4. Extraction efficiency of some testified agents
Sl. 4. Stupanj efikasnosti nekih ekstrahirajućih sredstava

Fig. 5. Determination of optimal quantities of digestion acids
Sl. 5. Određivanje optimalne količine digerirajuće kiseline

Fig. 6. Determination of optimal digestion time
Sl. 6. Određivanje optimalnog vremena račinjavanja

Fig. 7. Determination of optimal digestion temperature
Sl. 7. Određivanje optimalne temperature digeriranja
On the basis of clear appearance of two distributions, as well as bad 
goodness of fit of empirical and theoretical normal and lognormal 
populations and higher variance coefficients, one can distinctly observe 
epigene components, i.e. uranium and trace elements Zn, Pb, and Co 
as well as two generations of CaCO₃ and Sr.

Afterwards, grouping on the basis of rock colour detached 3 groups 
of 16 gray, 8 green and 13 red samples. A separate group of ore samples 
from the ore body I and ore body II, distinguished by radiometric 
measurements (41 samples) were chosen. Each particular population was 
described by calculated mean (x), standard deviation (o) and coefficient 
of variance (o/x), (Appendix III, Table A).

The ore samples show high variance coefficient especially for chalco-
phile elements and uranium. Microscopic examination of thin and polished 
sections discovered much bigger number of transitive varieties, green-
gray, green-red, red-green etc., what definitely influences statistical eval-
uation of chemical characteristics of a particular sample group.

Multivariate regression analyses and T-test, and analyses of regression 
variance (F-test) were made in order to determine geochemical relations 
among particular components and uranium. The obtained results were 
supposed to be used for determination of efficient uranium pathfinder 
elements, better understanding of genetic processes or characteristic as-
sociation of elements for successful exploration works. As an example 
of multivariate regression analysis, there is an equation for uranium.

\[
U = -110.44 + 101.21 \text{ L.o.i.} - 38.89 \text{ CaCO}_3 + 0.18 \text{ Zn} + 0.08 \text{ Pb} - 0.01 \text{ Cu} + 2.85 \text{ Co} + 1.14 \text{ Ni} - 0.45 \text{ Sr} + 1.26 \text{ Li} - 2.99 \text{ Cr} - 112.21 \text{ Fe} + 0.09 \text{ Mn}
\]

Standard error of estimate is 135.77 and multiple correlation 0.67.

Technical reasons prevented presentation of all statistical calculations 
made by a computer.

Cluster analysis was preceded by inserting of all correlation coeffi-
cients (r), does not matter of assigned T-values, into correlation matrices. 
In that way a review of all mutual dependences of all particular compon-
ents in four groups of samples (Appendix IV) was obtained. The pro-
ceding cluster analyses by unweighted pair-group method enabled con-
struction of dendrograms of geochemical affinity, (Davis, 1973). The 
dendrograms point out gathering of elements into groups of affinity, 
which confirmed and accomplished understanding of genesis of the depo-
sit.

The dendrogram of geochemical affinity in the ore body (Fig. 8) points 
out conspicuously «the carbonate group»: loss on ignition, CaCO₃, Sr, 
Mn, and unusual join of Cu. The group «organic matter-sulfur» links 
chalcoophile elements Zn, Co, Pb, and uranium. Fe and Li are in a separate 
group joined to clay. Cr and Ni are particularly firmly tight, likely by 
presence of a sharing mineral of a phyllosyllicate group.

The dendrogram of the gray rock series (Fig. 9) also has «the carbo-
nate group»: loss on ignition, CaCO₃, Mn, but it is linked with Ni, Co, Cr 
and Pb too. Weak, but otherwise illogical association of chalcoophile 
elements is due to lack of data on sulfur and organic matter in the gray 
rocks. Zn, Mg, Fe, and Li are connected to the clay group. U and Cu stay 
separately, geochemically unrelated, not showing special affinity for some 
common adsorber of trace elements, or are being grouped in all present 
ones.

The dendrogram of the red rock series (Fig. 10) shows similar features 
to the gray one, CaCO₃, loss on ignition, Sr, and Mn are separated from 
the clay group Cr, Pb, Ni, Co, Zn, Fe, Mg and Li. U and Cu are again 
nonaligned to any particular group.
Fig. 10. Dendrogram of geochemical affinity in the red rock series
Sl. 10. Dendrogram geokemijske povezanosti u crvenoj seriji stijena

Fig. 11. Dendrogram of geochemical affinity in the green rock series
Sl. 11. Dendrogram geokemijske povezanosti u zelenoj seriji stijena
The dendrogram of the green rock series (Fig. 11) is different only in a detail, that Pb is joined to the carbonate group. That is even more expressed in the gray group, while in the ore series the chalcophile group is definitely apart.

5. GENESIS

5.1. Case history

Omaljev V. (1967 a,b) considered the Val Gardena sandstones as being formed in a sublittoral region of a vast sedimentary basin (a lake). The border between dry land and water (paleoshore line) was responsible for development of gray and red members of the series which alternate vertically and laterally. Uranium was brought into the deposit exclusively in water solution and process of mineralization terminated with diagenesis (cementation). Source of uranium was preexisting quartzporphyry massif, whose fragments are present in the sandstones. Organic matter provided anaerobic, reducing conditions (geochemical barrier), but otherwise, did not take part in uranium precipitation. Sulfide mineralization became in the same way, but was remobilized several times by pseudohydrothermal waters. Sulfur came from the organic matter and heavy metals were brought into the deposit likewise uranium. A part of lead is radiogenic. The deposit is of epigenetic-syngenic origin.

There were two papers at the symposium «Formation of Uranium Ore Deposits» in Athens in 1974, sponsored by IAEA (International Atomic Energy Agency).

Markov C. and Ristic M. (1974) concluded that the deposit was formed by epigenetic introduction of uranium and other chalcophile elements in the sandstones, which were washed out from primary dispersion haloes in the surrounding quartzporphries. Reducing geochemical barrier caused by H₂S (product of anaerobic bacterial metabolism) was a place of deposition of immobile uranium forms. Lesser quantities were precipitated by humic matter in a marine basin. Sulfur isotope composition points out bacterial origin. Uranium was transported in water solution from primary dispersion haloes and partly on the clay micelles. Hydrothermal introduction of uranium into groundwater, however, was not excluded either.

 Lukacs E. and Florjančić A. P. (1974) maintained that uranium was brought into the sediments during the time of deposition and subsequently redistributed. Structure of the sedimentary series is typically fluviatile (meandering type). Uranium transport was carried out by oxidizing waters at pH 7–8 as uranylcarbonate or hydroxy complex or maybe as uranylhydroxy sol. Precipitation started at places with stagnant water by means of organic matter and silicate minerals. Increased quantity of plant remnants enhanced production of H₂S, which reduced uranium from solution at the site of the ore body. The concentration gradient caused remobilization of primary poor accumulation by diffusion. Formation of the ore body was completed by accession of uranium leached from the red series.

At the 8th Yugoslav Geological Congress, held in Bled in 1974, Omaljev V. modified his original theory explaining origin of red clastics by oxidation of primary gray marine sediments, rich in organic matter, in the course of an emersion phase. The deposit is of epigenetic-infiltration type with recycling of uranium, something similar to «cementation» process, leading to enrichment of primary mineralization during dry-land phase.
On the basis of extensive underground evidences in the mine Budić T. (1978) confirms an idea of fluvialite origin (braided river). Mineralization is mostly connected with intraformational erosional unconformities (river beds of intermingled streams) predominantly in the most permeable, poorly sorted, basal, sandy conglomerates, which gradually pass into less coarse, parrelally laminated sandstones and dark claysones. Ore could also be found in the footwall claystone in the vicinity of anthracite lenses in fine and medium grained sandstones and even in the anthracite lenses themselves if they are in permeable parts (paleo-channel), although, does not explain geochemical mechanism of uranium distribution between claystone and sandy basal conglomerates.

Drovenik M. (1979) in his paper links diagenetic origin of Cu mineralization with formation of the uranium deposit in the lower part of predominantly gray series of the Val Gardena sediments. Diagenetic model of genesis is supported by number of geological, lithological, mineralogical and geochemical observations which according to the author disprove magmatic-hydrothermal origin.

5.2. Criticism on some possible ore forming processes

As it has been mentioned in the introductory part, we are dealing with »peneconcordant type of uranium deposit in sandstones«. The ore bodies have got irregular shape, but they might be considered as lenslike, pseudolayered forms, bound solely for gray sediment members of the clastic series. Mineral association of sulfides and reduced forms of uranium in the sandstones might have become in four different ways regarding time of the host rock formation and mineralization as well as source of metal: 1. syngenetic-exogenic, 2. syngenetic-endogenic, 3. epigenetic-endogenic and 4. epigenetic-exogenic, or eventually by their combination.

Before we start to discuss a genetic model, it is necessary to clear up the terms diagenesis, syngenesis or epigenesis, since there is in literature fairly free treatment of these notions.

In that paper an interpretation of Chilingar G. V. and Larsen G. (1967) was used. According to them, diagenesis is process of lithification of sedimentary material, which starts with its deposition and terminates with metamorphism. It is devided into three phases: 1. syntogenesis, 2. anadiagenesis, and 3. epidiagenesis. Syndiagenesis embraces diagenetic processes at or just below sedimentary interface »water-sediment«. Anadiagenesis acts during burial, while epidiagenesis is related to processes when sediments are exposed to influence of meteoric water after an emergence phase. The scheme is adapted to a marine type of sedimentation as the most frequent one.

Most sedimentary host rocks of exogenic uranium deposits were formed during a dry-land phase and mentioned succession is essentially different, i.e. syndiagenesis, epidiagenesis and eventually, anadiagenesis. It substantially changes character of diagenesis and spots up epigenetic processes. That is why, in description of uranium mineralization formation in sandstones and generally ore deposits in red beds, it is convenient to use expression »epigenesis« for processes often described imprecisely as »diagenetic«.

Among four possible situations, syngenetic-endogenic model might be refused as useless. Injection of hydrothermal water in a river environment (positive Eh and CO₂ saturation) will not produce chemically stable uranium-sulfide paragenesis.
Epigenetic-endogenic model does not fit well to some very common evidences like:

- sulfur isotope studies show $\delta^{34}S$ enrichment microbiological separation,
- appearance of mineralization in sandstones all over the world on a massive scale and its spatial characteristics (often stratabound) requests extraordinary dimensions and unusual mechanism of proposed hydrothermal processes,
- most often absence of appropriate signs of magmatic activity in the clastic sedimentary series and its close vicinity,
- absence of typical hydrothermal activity signs, like alterations, infiltrations channels, etc.

In spite of conviction of mentioned proves negating hydrothermal activity, there is still at least minor possibility of hydrothermal metal contribution. Complexity of the mechanism, however, as well as frequency and spatial distribution of the deposit type and existence of alternative much simpler models make epigenetic-endogenic or any similar, combined process less probable.

More attention should be paid to syngenetic-exogenic model but not as final, rather preconcentrating (Lukac E. and Florjančič A. P., 1974). Supposing that question about sedimentary environment is solved, i.e. it belongs to »braided river« facies, syngenetic formation of economic uranium mineralization is hard to imagine.

»Braided river« environment is a site where deposition of medium or coarse grained clastic sediments took place. Pelitic fraction is accumulated locally, like mud flows, during the time of great floods or at lowlands or flood plains with stagnant water, which evaporates quickly or dries.

Big marshes or muddy plains accumulating excessive masses of humic material did not exist (high energy water). The sediments of »the Zirovski Vrh braided river«, however, are well sorted with frequent fining upward grading from intraformational unconformities (paleoriver beds). The regularity is almost ordinary and Budkovič T. (1978) takes it as a basic sedimentary sequence or unit. It suggests more to a transition zone »braided river« — »low sinuosity river« (Reading H. G., 1978), or »low sinuosity meandering river«, as was mentioned by Lukac E. and Florjančič (1974). At such circumstances, greater quantities of humic material were capable to adsorb »significant« but not »ore« concentration of uranium, what should be argued through proceeding consideration.

Experiments of Szałaj (1959, 1964) showed an exceptional ability of peat to adsorb uranyl ions (UO$_2$$^{+3}$). In addition, he proved that an active adsorbing part of peat are humic acids since after its alkaline treatment and leaching of humic acids adsorbing ability disappears.

According to Bregér J. (1974) fulvic acids also take an important role in that process. Uranyl humates and fulvates show maximum stability in weak acid to neutral conditions i.e. at pH 5—7.

From the foregoing investigation is deducible, that adsorption of uranyl ions onto peat is a cation exchange process, which happens on —COOH and —OH groups. It has a reversible character, showing »saturation« depending on pH and concentration of uranyl ions in aqueous environment. Because of limited number of —COOH and —OH groups on macromolecules of humic acid colloids entire process might be well identified with physical adsorption (with monolayer formation), described by Langsmuir’s adsorption isotherm.
\[ \frac{C}{N} = \frac{1}{aN_\infty} + \frac{C}{N_\infty} \text{ i.e., } \frac{N}{N_\infty} = \frac{aC}{(1 + aC)} \]

- \( N \) = saturation concentration (mg equiv. \( \text{UO}_2^{2+} \)/g peat)
- \( C \) = concentration of \( \text{UO}_2^{2+} \) in water (mg equiv. \( \text{UO}_2^{2+} \)/ml water)
- \( N \) = concentration of \( \text{UO}_2^{2+} \) on peat (mg equiv. \( \text{UO}_2^{2+} \)/g peat)
- \( a \) = coefficient characteristic for chosen adsorbent and adsorbate

The whole expression may be simplified for low concentration of \( \text{UO}_2^{2+} \) in natural waters,

\[ \frac{N}{N_\infty} = aC, \text{ that is } \frac{N}{C} = N_\infty a, \]

whereas \( N/C \) is a saturation coefficient or ratio between \( \text{UO}_2^{2+} \) on peat and in water solution. According to Szalaj's experiments (1964), saturation coefficient is about 10,000, what means that there is 10,000 times more uranium on the peat than in natural water being in mutual contact with (under equilibrium conditions).

Diagram in Fig. 12 represents equilibrium line »iso-pH« biolite-water with saturation coefficient \( N/C = 10,000 \). It is obvious from the graph,
that formation of «ore» concentration of 1000 g U/t biolite requests natural waters of 100 ppb, what is exceptionally high value seldom encountered at natural circumstances. Waters with lower uranium content (10 ppb and lower) enable preconcentration of 100 g U/t biolite. Convenient pH conditions (5-6), caused by organic matter decay, fermentation and production of humic acids in muddy environment, promotes transfer of $UO_2^{2+}$ ions from carbonate complex $UO_2(CO_3)^{2-}$ to uranyl humates (Fig. 13).

The foregoing consideration proves possibility of syngenetic preconcentration at muddy plains with stagnant water. In this way, we can explain low concentration of uranium in syngenetic deposits, i.e. marine bituminous shales and coals. The Groeden sandstones contain up to 3.5%...
of organic matter and on an average 0.14%. The present ore concentration of 1000 g U t sandstone requests higher concentration of uranium on organic matter in two orders of magnitude, with supposition that uranium was linked by humic acids and peat material primarily. The diagram (Fig. 12) shows clearly a necessity for natural waters of 10 000 ppb what is practically impossible.

Upon these premises we can draw a conclusion about syngenetic-exogenic model: ore concentration in the Zirovski Vrh mine had not been formed by syngenetic precipitation of uranium from surface waters onto organic matter since it would have required abnormal concentration of uranium in water; ore concentration might have been obtained only in the case of simultaneous adsorption and reduction of $\text{UO}_2^{2+}$ to $\text{U}^4+$, what is in well aerated and drained »braided river« environment in superficial conditions improbable.

5.3. *Epigenetic-exogenic model*

Attention in the proceeding exposition will be paid to epigenetic-exogenic model which had been preceded by syngenetic preconcentration that played an episodic role but not negligible.

5.3.1. *Organic matter and its importance in formation of geochemical barrier as well as in redoxomorphic stage of diagenesis*

Formation of the deposit had started with fluvialite sedimentation and deposition of the clastic sedimentary series. The host rocks consist of medium to coarse grained material possessing good permeability what is an important prerequisite for formation of an infiltration deposit. The gray rock series had been deposited under influence of humid climate, convenient for growth of vegetation, whose fossil remnants are being met in all gray lithological members. Organic matter in the Groeden sandstones is represented in three ways:

1. Anthracite plant remains, ranging in size from microscopic scale to several cm, very often impregnated with siliceous matter (Plate I, Fig. 1). This is a vegetation detritus buried together with other clastic material.

2. Flows of colloidal organic matter formed by infiltration of colloids and real solution of humic acids and humates from water streams and marshes. This is a well known recent process in the coastal side of the Mexican Bay (Texas and Florida). Humic acid formation is a fermentation process in weak acid environment and at low oxygen concentration. Oxygen is necessary for bacterial metabolism. Too high concentration, however, causes destruction of complex organic structure of humic acids, providing formation of $\text{CO}_2$ and other simple organic acids. A part of buried and carbonized remnants may again undergo the same process of humification after repeated invasion of oxidizing waters through permeable sediments (Plate I, Fig. 2).

3. Organic matter with high reflectance and pseudocrystal habit in carbonate and quartz veins. Origin of that material should be in connection with late diagenetic processes, which occur in alkaline environment of connate waters (since hydrolysis of silicate). Basic connate waters leach out carbonateous matter (humates and humic acids are soluble in alkaline conditions) and precipitate their mineralization in fractures of already compact rocks giving to the appearance epigenetic character. High reflectance of the matter is consequence of polymerization of aromatic humic material. High degree of aromatic condensation of
benzene rings from the very beginning leads the process of carbonization and metamorphism to well arranged structures similar to the graphite one (Plate I, Fig. 3 and 4).

Syngenic accumulation of vegetation debris, epigenetic infiltration of colloidal humic matter and humification of carbonized plant fragments in porous sediment made sandstones impregnated with organic matter. Higher content of organic matter in clay rich parts is also possible to explain by similar processes (clay minerals show expressed ability for adsorption of colloidal organic matter), (A d l e r, 1974).

Change in climate moderate — arid led to decreased production of biomass and diminished accumulation of plant debris in sediments respectively. This phenomenon affects redoxomorphic stage of diagenesis directly. Diagenetic processes below the water table progress in an environment depleted in oxygen and organic matter is preserved from total destruction. Early diagenetic iron sulfides and dispersed organic matter are responsible for gray colour of sediments formed at such circumstances.

Red colour of rocks is effected by oxidizing conditions in a zone of active oxygen transport above water table. After fast plant debris destruction, oxidation is transferred to ferrous minerals (amphiboles, biotites etc.) with appearance of red hematite cement (Plate II, Fig. 1).

Red and gray colour is, according to that, determined by a type of redoxomorphic stage of diagenesis. Electrochemical potential of environment depends upon quantity of organic matter and position of water table. Appearance of a red bed inside the gray series and vice versa should not be interpreted exclusively as a result of abrupt climate change.

5.3.2. Formation and activity of the geochemical barrier (geochemical cell)

The most convenient site for observing activity of an epigenetic — exogenic model in the corridor H-52 is the ore body II and its close vicinity from the point 430 to 445 (Fig. 3). According to interpretation of Skaberne mine mapping, at this part of the profile, shale between points 436 and 437 represents a paleochannel bottom, filled up with coarse and medium grained sands. Schematic view of the paleochannel profile is given in Fig. 14. Immediately on the clayey bottom (now shale) coarse grained sand was deposited. Grain size is fining upwardly and sequence terminates with clayey cover at the point 442. Sandstone impregnated by organic matter and placed between two clayey impermeable horizons has all prerogatives for development of an effective infiltration geochemical barrier of reducing type (H₂S).

After discovery of the «double S» structure and detailed geological mapping in the mine, L u k a c s and F l o r j a n č e č (1974) proved existence of only one important ore bearing pocket in a gray lithological member III]. This is the uppermost part of the gray series in Groeden sandstones, close to an immediate contact with the red series. This manifestation should be regarded with due attention, since it is typical not only for the Zirovski Vrh mine but for many deposits of red bed type in the world.

The gray series is made of material, which underwent intensive mechanical weathering and short transport (poor roundness of detrital grains, higher quantity of plagioclasses). These conditions are not suitable for uranium leaching, what is manifested in smaller ore quantity in lower parts of the gray series. At that time started formation of syndiagenetic iron sulfides in sediments impregnated by organic matter (Fig. 15).

The lowering of the water table due to climate change and eustatic uplift of hinterland led to significant geochemical changes in a zone of
active circulation of underground water. Wide region of porous sediments above water table became a space of automorphic leaching of metals and chemical weathering gains in importance. Invasion of oxidizing waters into layers with plant debris causes humification, giving to organic matter particularly convenient form for adsorption of uranium in hydromorphic zone of weathering (below water table). Change in climate from humid to semiarid effects chemical composition of underground water altering it from bicarbonate to biocarbonate-sulfate and enabling proliferation of desulfurizing bacteria and generation of H₂S in plenty.

In the ore body II coarse clastic material fills up space between two impermeable horizons. Level of the water table is high and through sedi-
Fig. 15. Sketch of sedimentary and related ore-forming processes in a braided river environment during the Middle Permian time

Sl. 15. Skica sedimentnih i rudnosnih procesa u okolišu isprepletuće rijeke u srednjem permu

ments of the paleochannel circulates water with lower redox potential. On the basis of grain size one may forecast its relative speed of streaming, i.e. quantity of infiltrating water (Fig. 14) what is reflected in kind and intensity of chemical processes on the profile. A site of maximum flow is in vicinity of the sample 437 and 439. Convenient environment for deposition of humic colloids is in medium grained sandstones (sample 440) with less intensive flow of water. In shale (sample 436) organic matter is of syngenetic origin mostly.

Microorganisms in such an environment are strict anaerobics, i.e. Clostridium cellulose-dissolvens, which otherwise suffer in presence of
oxygen. Microbiological fermentation process breaks down cellulose and lignin (humic matter) into simple organic compounds like acetic acid, succinic acid, ethyl alcohol, NH₃, CH₄, CO₂, H₂ etc. (Stanley et al., 1963). Smaller concentration of SO₄²⁻ ions in infiltrating water enables life of sulfate-reducing Desulfovibrio genus which consumes simple organic compounds formed by fermentation processes. Metabolism of this important and widespread group of microorganisms is based upon oxidation of organic matter by SO₄²⁻ ion with generation of CO₃⁻ (Berner, 1971).

Desulfovibrio genus causes expressive reducing environment from $Eh = -200$ mV to $-500$ mV and pH between 7.8 and 8.4 (Germanov, 1958). Lower energetic effect, obtained by this kind of microbiological reactions, forces microorganisms to produce large quantity of S⁻ (1.5 g of S⁻ per 1 g of biomass, Sweeney & Kaplan, 1973).

Dissimilatory sulfate reduction generates H₂S, and in syndiagenetic phase first iron sulfides are being formed like makinavite (FeS₀·₉), troilite (FeS) and greigite (Fe₆S₈). Black, colloidal, poorly crystallized iron sulfides undergo weak oxidation. A cause of oxidation of S⁻ to Sₐ⁻ might be in slight increase of Eh of the environment (Berner, 1971).

Formation of iron sulfides does not necessitate voluminous and long lasting infiltration of underground water like other metals (Cu, Zn, Pb, etc.), since iron is a major element present in different minerals (silicate, oxides, etc.). Major part of the pyrite masses became by direct chemical transformation of iron rock forming minerals in reaction with H₂S.

Statistical analysis and study observations proved mentioned processes:

— connection of organic matter and sulphides can be observed on the dendrogram of geochemical affinity in the ore body, whereas organic matter is associated with a group S, U, Co, Pb, at a level 0.38 (Fig. 8),

— in the specimens 440 and 415 «framboidal» pyrite or «ore bacteria» appear in organic matter or its vicinity (Plate III, Fig. 3),

— ferrous and ferric minerals are unstable in an environment with high pH₂S partial pressure, what is manifested by frequent pseudomorphism of pyrite after maritite and magnetite (Plate III, Fig. 1 and 2),

— intermingling of organic flows and accumulations of organic matter and sulphides, what is visible under oblique light in thin sections (Plate V, Fig. 2),

— almost complete absence of biotite and magnetite in ore bearing series is not caused only by H₂S influence, but also by humic acids and humates, which leach out Fe²⁺ and Fe³⁺ efficiently since forming of very stable complexes. Transition biotite-mica is complete and only traces of biotite lamellae are fading jellow or brownish patches inside micas or in matrix of the surrounding sandstone (Plate II, Fig. 2). Maximum leaching of Fe²⁺ and Fe³⁺ coincides with the site of the maximum permeability at points 437 and 439 (Fig. 14), (Adams, Curtis & Hafen, 1974).

The total content of dissolved solids of infiltrating water is low what is characteristics of humid climate. Along with lessening of rainfalls amount of biomass decreases significantly and the total mineralization of water together with uranium and other metals increases. Bicarbonate character of water changes to bicarbonate-sulfate one, (Pišceva, 1978). Water table lowers and water with dissolved oxygen invades into strata with organic matter, percolating through and gradually loosing its oxidi
dizing character. Organic matter is destroyed by aerobic fermentation processes with lowering of pH. Uranyl bicarbonate ions are broken apart, while humates and fulvates (the product of fermentation) take over a role of adsorbent and carrier of uranyl ions (Fig. 13). At sites of organic matter accumulation, since introduction of sulfate rich water starts intensive proliferation of desulfurizing bacteria along with H₂S generation. H₂S migrates toward edges of the paleochannel, lowering redox potential to values between —200 mV and —500 mV.

Experimental investigation has shown, that H₂S is an efficient reducing agent for UO₂²⁺ into UO₂. (Lisicin & Kuznecova, 1967).

\[
\text{H}_2\text{S} + 4\text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + 10 \text{H}^+ + 8e^- \\
\text{Eh} = 0.303 - 0.074 \text{pH} + 0.0074 \log \frac{\text{SO}_4^{2-}}{\text{H}_2\text{S}}
\]

Redox potential obtained by this reaction is sufficient to perform reduction:

\[
\text{UO}_2^{2+} + 2 e^- \rightleftharpoons \text{UO}_2
\]

In presence of CO₃⁻ ions, reaction of reduction assumes a form:

\[
\text{UO}_4(\text{CO}_3)_2^{2-} + 2 e^- + 2\text{H}^+ \rightleftharpoons \text{UO}_2 + 2\text{HCO}_3^-
\]

Necessary Eh is slightly lower but still enough high in a region of pH = 5—7 and pCO₂ = 10⁻² — 10⁻³ atm for quantitative progress of reaction (Fig. 16).

Weaker correlation link between organic matter and uranium (r = 0.36) as well as better connection between uranium and sulfur in the dendrogram of the ore body (Fig. 8) agrees well with supposition that H₂S is the main reducing agent.

Different Eh-pH conditions existing at small distances are caused by diversity of reactions, which take place on the profile.

Invasion of mildly acid waters with SO₄²⁻ at the most permeable part of the profile is evident by corroded plagioclase grains. Released silicic acid replaces clayey matrix, which recrystallizes into needle-like chalcedony-sericitic cement.

In a zone of active water circulation (with higher Eh), fermentation processes in bigger wooden fragments or logs lower pH locally and enable redeposition of silicic acid (Plate I, Fig. 1). Such places are particularly favourable for transfer of uranyl ions from carbonate complex to organic matter. High concentration of silicic acid prefers formation of coesite (USIO₄⁻ n H₂O). Silicified wooden remnants often contain higher concentration of uranium up to several percentages.

Dissimilation of sulfates into H₂S produces equivalent quantity of CO₃⁻, which in form of HCO₃⁻ diffuses toward the upper and lower marginal side of the paleochannel.

Transport of dissolved matter by infiltrating waters at the points 437 and 439 is substituted by diffusion in direction of the footwall and hangingwall rocks. Influence of anaerobic bacteria increases in the same direction as well. It is followed by rise of pH and concentration of CO₃⁻ ions, causing precipititation of CaCO₃ which replaces detrital and clay minerals (especially quartz). Origin of carbonate concretions may be explained by the same mechanism.

Due to this process, the ore bodies are surrounded by carbonate «haloes», although increased quantity of CaCO₃ can be found in the very ore body too.
Precipitation of CaCO₃ from underground waters in semi-arid regions as well as ubiquitous oxidation of early diagenetic pyrites in the gray rock series after lowering of a water table changes character of water to bicarbonate-sulfatic one. In turn, late diagenetic processes are led under lessened influence of meteoric waters. Hydrolysis of silicates keeps environment alkaline and fissures in already compact clastics are filled up by calcite and quartz. Their veinlets cut older mineral paragenesis.

Samples 437, 438 and 439 have the lowest values of R₂O₆ on the profile of the ore body II (Appendix II), as well as for Al₂O₃, TiO₂, total iron, P₂O₅ and MgO. There is the highest value for SiO₂ in the sample 439 (79.11 %), pointing out significant quantity of quartz grains in the sandstones. The results of analyses show depletion or absence of clayey matrix in
Fig. 17. Relationship between Li and Al₂O₃ with correlation coefficient and regression line. Legend: 1. Red clastics 2. Green clastics 3. Gray clastics 4. Ore-bearing clastics


Fig. 18. Relationship between Mg and Al₂O₃

Sl. 18. Odnos izmedu Mg i Al₂O₃

the most permeable part of the profile. The sandstones in the immediate vicinity (sample 442) with similar grain size and high quantity of SiO₂ is much richer in R₂O₃. A cause for clay depletion at the sampling site 437, 438 and 439 is due to washing out of clayey matrix probably, because of more intensive water circulation. On the basis of chemical data on the profile, at the sites 435 and 443, however, a kind of underground weathering might be suggested.

Corrosion of plagioclases took place at that part of the profile, since lower pH. Magnetite, ilmenite, martite and biotite underwent chemical weathering by humates and humic acids. Released Al³⁺ and Ti⁴⁺ ions hydrolyze and build up complexe ions and molecules Al(OH)⁺捌n and Ti(OH)⁺捌n. Positive charge of these chemical species facilitates their efficient adsorption by humic acids, which are negatively charged at pH values higher than 4 (Huang and Keller, 1972).

Distribution of P₂O₅ is also possible to explain by different pH conditions, since H₃PO₄ is triprotic acid and convenient form for precipitation of phosphates appears in more alkaline environment.

Existence of pH profile is evident also by distribution of Li and Mg. Statistical analysis shows exceptionally firm correlation tie among Li, Mg and Al₂O₃ (Fig. 17, 18, 19, 20), proving their association with clay minerals. Adsorption capacity for Li⁺ and Mg²⁺, as well as for other cations on free —OH groups at the edges of crystal lattice of clay minerals depends proportionally on pH, i.e.:

\[
\begin{align*}
\text{Al} - \text{OH} & + \text{Mg}^{2+} \rightarrow \text{Al} \rightarrow \text{Mg} + 2 \text{H}^+ \\
\end{align*}
\]

Therefor, it is to be expected that ratio Li/Al₂O₃ and Mg/Al₂O₃ is higher at marginal parts of the ore body II profile.
Trace element Sr has a tight correlation link to CaCO₃ (Fig. 21) and on the dendrogram of the ore body is assigned to a group CaCO₃, Mn, loss on ignition (Fig. 8). On the diagram Sr/CaCO₃ (Fig. 22 and 23) maximum concentration is in a zone of active water circulation, where streaming of water lasted longer than at other parts of the profile, till the final cementing and lithification of the sand. Open pore space at the most permeable part of the profile, whereas clay was washed out, is filled up by calcite in a locomorphic stage of diagenesis. It points out, gradual enrichment of Sr in the course of the ore body evolution. By the time of humid climate, calcite, which was precipitated at marginal parts of the paleochannel, is poor in Sr. Change in climate from humid to semiarid one increased quantity of Sr in underground water (Pereplaten, 1967) and consequently in late calcite generation, which was crystallizing in open pore space at the most permeable parts of the profile.

Mn also has high correlation coefficient with CaCO₃ (r = 0.80). On the dendrogram of the ore body (Fig. 8) it is placed in the group of CaCO₃, loss on ignition, Sr. A diagram Mn/CaCO₃ (Fig. 24) has a minimum in a zone of active water infiltration, what agrees well with behavior of other
metal ions which do not precipitate with H$_2$S (like Al$^{3+}$ and Ti$^{4+}$, being leached out by humates and humic acids).

Distribution of iron on the profile of the ore bodies has unusual characteristics. Extracted iron is correlated well with FeO ($r = 0.94$), but much looser with Fe$_2$O$_3$ ($r = 0.37$). The reason is in efficient leaching of divalent iron from iron minerals by strong oxidizing acid (HCl—HNO$_3$). The dendrogram of the ore body joins iron with Li ($r = 0.97$), i.e. clay constituents (Fig. 8). This is fairly surprising fact, since pyrite is a frequent sulfide in the ore body and link between iron and the group organic matter, S, chalcophile elements was expected. It means that the main iron bearing mineral is not pyrite but rather silicates.

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**Fig. 21.** Relationship between Sr and CaO with correlation coefficient and regression line. Legend: 1. Red clastics 2. Green clastics 3. Gray clastics 4. Ore-bearing clastics


**Fig. 22.** Distribution of Sr/CaCO$_3$ quotient along the profile of the ore body I

**Sl. 22.** Raspored veličine kvocijenta Sr/CaCO$_3$ duž profila rudnog tijela I

68
Fig. 23. Distribution of Sr/CaCO₃ quotient along the profile of the ore body II
Sl. 23. Raspored veličine kvocijenta Sr/CaCO₃ duž profila rudnog tijela II

Fig. 24. Distribution of Mn/CaCO₃ quotient along the profile of the ore body II
Sl. 24. Raspored veličine kvocijenta Mn/CaCO₃ duž profila rudnog tijela II
Drop of H₂S partial pressure in direction of the paleochannel margins is characterized by sort and abundance of a particular chemical form of divalent iron. At the site of the highest sulfur concentration in the sample 436 and 439 gel pyrite and framboidal pyrite appear pointing out precipitation from saturated colloidal solutions. At the furthermost point of the paleochannel, in the green clastics there are big euhedral pentagon dodecahedrons of pyrite whose crystal perfection suggests crystallization from diluted ionic solutions. Because of drop of pH₂S toward the margins, Fe²⁺ is bound in authigenic leptoeliorites.

Content of FeO and Fe₂O₃ shows expressed minimum at the most permeable part of the profile, what should be explained by leaching of iron by means of humic acids and humates (Fig. 25 and Fig. 26).

Even more unusual ratio is FeO/Fe₂O₃ (Fig. 26) with a minimum value at the sites of maximum uranium concentration in the ore bodies. Limonitization is along tiny fissures, cutting detrital minerals, framboides,
organic matter, matrix and cement, i.e. all early and late diagenetic characteristics. This appearance was already noticed in the course of underground mapping with the naked eyes on the corridor walls.

Limonitization is due to pyrite oxidation, restricted to a close vicinity of uranium mineralization, since euhedral pentagon dodecachrons in the sample 443 and 435 are perfectly fresh. According to way of appearance of limonitization, it seems that oxidation took place in postdiagenesis by descending waters or by the time of the corridor construction. Fine grained colloidal pyrite, whose lattice was effected likely by radioactivity, underwent faster oxidation than coarse grained, euhedral pyrites at marginal zones in the green clastics. Oxidation is also catalyzed by Thiobacillus ferroxidans (Silverman, 1967). Catalytical activity of microorganisms speeds up pyrite oxidation about 200 times. Reaction product is sulfuric acid neutralized by CaCO₃.

On the basis of relatively small number of analyses it was impossible to conclude whether this process leads to enrichment or depletion of the ore body. The enrichment could be imagined as a cementation process. A proposed half a cell reaction would be:

\[ \text{FeS}_2 + 8 \text{H}_2\text{O} \rightleftharpoons 2 \text{SO}_4^{2-} + \text{Fe}^{2+} + 16 \text{H}^+ + 14 \text{e}^- \]

\[ \text{Eh} = 0.354 - 0.067 \text{pH} - 0.0084 \log \text{SO}_4^{2-} + 0.0042 \log \text{Fe}^{2+} \]

or a reaction of UO₂ precipitation:

\[ 2 \text{FeS}_2 + \text{UO}_2 (\text{CO}_3)_3^{2-} + 16 \text{H}_2\text{O} \rightleftharpoons \text{Fe}_2\text{O}_3 + \text{UO}_2 + 4 \text{SO}_4^{2-} + 3 \text{CO}_2 + 32 \text{H}^+ \]

or

\[ \text{UO}_2/\text{CO}_3/\text{H}_2\text{O} + 2 \text{Fe}^{2+} + 3 \text{H}_2\text{O} \rightleftharpoons \text{UO}_2 + 2 \text{Fe/OH}_3 + 3 \text{CO}_2 \]

Trace element Cr and Ni are tightly connected in the dendrogram of the ore body (r = 0.99), (Fig. 8), forming a separate group, independent of the main trace element bearers. The clue of the problem might be in presence of their common mineral, since in sample 17 and 26 concentration of Ni is 600 and 960 ppm, and of Cr 260 and 340 ppm respectively, while other elements show average values.

5.3.3. Zonal distribution of chalcophile elements and uranium around H₂S geochemical barrier — proof for infiltration mechanism of ore forming processes

Chalcophile elements Cu, Zn, Pb, Co and Ni together with uranium form a zonal distribution around the spot of the highest concentration of sulfur in the aquifer, (Fig. 27) The width of the zones is determined by precision of ± 1m. The width of each particular element zone is in excellent agreement with solubility of the appropriate metal sulfide.

Composition of infiltrating water, regarding concentration of each metal, does not effects essentially zonal sequence, what comes out from mathematical form of the isobaric potential of solubility reaction.

\[
\frac{\text{Me}^{2+} + \text{S}^- \rightleftharpoons \text{MeS}}{\text{K}_{\text{PS}} = \text{Me}^{2+} \cdot \text{S}^-}
\]

\[
\text{F}^0 = +1.364 \cdot \log \text{K}_{\text{PS}}
\]

\[
\text{F}_{\text{reaction}} = \text{RT} \ln \left( \frac{a\text{MeS}}{a\text{Me}^{2+} \cdot a\text{S}^-} \right) + F^0
\]

[29]
Fig. 27. Width of chalcophile element zones around uranium ore body (profile of the ore body I and II)

Sr. 27. Širina zone koncentriranja halkofilnih elemenata oko uranskog rudnog tijela (profil rudnog tijela I i II)

\[ F_{\text{reaction}} = -1.364 \log \text{aMe}^{2+} \cdot \text{aS}^{2-} + 1.364 \log K_{\text{PT}} \]

Change in activity of metal ions in several orders of magnitude does not influence significantly isobaric potential, since it largely depends on solubility product.

Concentration of metal ions as well as pH-S decrease toward the edges of the profile. As a result of competition for sulfide ion in a zone of lowered pH-S a zonal distribution of metal sulfides perpendicular to the flow of infiltrating water in the aquifer with geochemical cell occurred (lateral zonation has not been investigated since linear way of sampling).

On the contrary, pyrite is present all over the profile, only changing its mineral habit. The widest zone of iron sulfide, whose solubility is the highest one, in order presented in Fig. 27 \((K_{\text{PT}} = 10^{-19})\), does not agree well with the infiltration model at the first glance.

It should be noticed, however, that iron is the only major element among considered chalcophile ones in Fig. 27. It was present in the red and gray series like Fe\(^{2+}\) and Fe\(^{3+}\) in iron aluminosilicates and oxides primarily.

The answer to this question could be in a following proposed early diagenetic process. Breaking up of organic matter in sediments proceeds in a sequential manner. Under slightly oxidizing regime, above a water
In strictly anaerobic conditions in the aquifer, organic matter is further destroyed to simple, soluble and mobile organic compounds and gases \((\text{H}_2, \text{CH}_4, \text{CO}_2, \text{H}_2\text{S})\) whose transport is kept up by permanent percolation of underground water. This kind of organic matter is ideal form for feeding desulfurizing bacteria, which proliferate in less permeable parts of the aquifer, whereas the most reducing conditions exist (the lowest \(\text{E}_\text{h}\), and the highest \(p\text{H}_2\text{S}\)). At such places early diagenetic phase is characterized by fast formation of iron sulfides by replacement of detrital iron minerals or direct precipitation of \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\), carried over by organic complexes. Detrital material of the paleochannel is impregnated in that way by colloidal organic matter and iron hydrosulfides along the whole profile and prepared for a following long lasting process of epigenetic input of trace and ore forming elements.

Generation of \(\text{H}_2\text{S}\) is especially intensive during subsiding of the water table (since change of climate or/and retreating of the erosion base) when underground water is being enriched by \(\text{SO}_4^{2-}\) ions. Enrichment is caused by oxidation of early diagenetic iron sulfides in newly exposed zones of grey sediments by means of invasion of oxygenated waters and microorganisms (Thiobacillus ferroxidans).

Activity of reducing geochemical barrier generating \(\text{H}_2\text{S}\) terminates with microbiological consumption of organic matter partly.

Ceasing of \(\text{H}_2\text{S}\) generation does not stop operation of geochemical barrier, which is able to function even further by a simple cementation process in terms of pyrite replacement by metal ions of less soluble sulfides. Secondary copper sulfides, chalcolite and covellite are met regularly in the ore body replacing pyrite but also chalcopyrite and other sulfides (Plate V, Fig. 1).

5.3.4. Origin of rock colour and its relation to ore forming processes

Origin of colour of the red beds in Zirovski Vrh has been interpreted as a consequence of arid climate and of the gray rocks by humid climate inversely. It is hard to explain, however, appearance of red intercalations in the gray series, as well as gray clastics in the red ones (often wedging out laterally) by sudden climatic humid-arid change. On the basis of complete development of the Groeden sandstones it is obvious that climate had been changing from humid to arid through a longer period of time, what was followed by lowering of the water table.

The green rocks at the contact between red and gray sediments are met regularly. Examination of thin sections determined mineralogical similarity among three rock types. The main constituents are: quartz, feldspars, rock fragments, silicic-sericitic matrix and calcite cement. Calcite replaces all detrital minerals especially quartz and matrix.

There has been observed microscopically a gradual transition from the gray to the green rocks and from the red to the green ones in a number of specimens otherwise specified as the pure gray, red or green rock type by naked eyes.

The main distinction among the three colour rock types is in their phyllosilicates (authigenic and allogetic), which underwent three different diagenetic phases, i.e. redoxomorphic, locomorphic and phylomorphic ones.

Mica in the gray series possesses biotitic yellow-brownish lamellae, gradually loosing pleochroism or even colour changing themselves to homogeneous mica (Plate II, Fig. 2). Similar irregular yellow patches
may be extended from micas to surrounding matrix. This phenomenon, in addition to corrosion of hematite, magnetite and maritite grains may be attributed to humate leaching.

In the red series one may find micas with dark lamellae in thin sections, which show red colour under oblique light. In some way this is a similar appearance to the foregoing one, but biotitic lamellae were oxidized into a fine limonite film (Plate II, Fig. 1). Matrix often contains detrital hematite, maritite and magnetite grains.

Phyllosilicates in the green series are sericite, mica and green euhedral, authigenic chlorites. Their authigenic origin proves supposition that they became at the contact between the gray and the red rock series by activity of reducing water percolating through an aquifer with geochemical barrier. They appear in several ways:

- like hematite dust, gradually passing over colloidal limonite grains with clear red colour into finegrained green chlorites,
- muscovite with hematite pseudolamellae (which became from biotite in the red series in oxidizing conditions in redoxomorphic stage of diagenesis) passes into chlorite-mica lamellae with parallel yellowish ribbons of titanium oxides, recrystallized chlorite-sericite-silicic matrix (Plate II, Fig. 3),
- authigenic chlorite which completely rims out detrital minerals (Plate II, Fig. 4),
- corrosion of magnetite and maritite (detritus) with release of titanium oxides (brookite and anatase) are often encountered in the green rock series (Plate IV, Fig. 1 and 2).

Expressed calcitization, chloritization, corrosion of hematite, maritite and magnetite and release of titanium colloidal matter point out reducing epigenesis in alkaline conditions. These conditions are favorable for calcitization and transformation biotite \( \rightarrow \) chlorite (Chilingar & Larsen, 1967). The red rocks were being reduced by water percolating in the gray rock aquifer. The main reducing agents were fermentation products \( \text{CH}_4, \text{H}_2, \text{humic acids and humates}. \) Oxidized forms of iron change to \( \text{Fe}^{3+} \). High pH enables reaction of silica and alumino hydroxides with \( \text{Fe}^{2+} \) producing authigenic chlorites. Lowering of the water table induces increase of \( \text{SO}_4^{2-} \) concentration and thriving of desulfurizing bacteria. \( \text{H}_2\text{S} \) generated during this process may be also taken as reducing agent in greening of red rocks, since big euhedral pyrite crystals can be found in them (Plate IV, Fig. 3). incomplete pyritization is consequence of low \( \text{pH} \) at the edges of the paleochannel, and high reducing capacity of \( \text{S}^{2-} \) ion, which enables release of \( 12 \text{Fe}^{2+} \) ions.

\[
4\text{Fe}_3\text{O}_4 + \text{HS}^- + 23\text{H}^+ \rightleftharpoons 12 \text{Fe}^{2+} + \text{SO}_4^{2-} + 12 \text{H}_2\text{O}
\]

Since \( \text{Fe}^{2+} \) ions can not be bound by insufficient sulfur, they are built into chlorites. Consumption of great quantity of \( \text{H}^+ \) in the reaction rises pH, facilitating chlorite formation or greening of red rocks.

While red and gray colours of the rocks are formed in redoxomorphic stage of diagenesis (syndiagenesis), «greening» is a long lasting process which terminates with closing down of open pore space and obstruction of water percolation. This is a pronounced epigenetic process related to water permeable strata, fault zones, cleavage zones etc.

This appearance is closely related to uranium formation pointing out reducing character of percolating water. Closing down of the permeable profile by late diagenetic calcite stops ore formation processes.

Character of postdiagenetic limonitization and its importance in ore body development should be examined yet.
### Appendix — Prilog I

Uranium, L.o.i., CaCO₃, sulfur and trace element content in the analyzed samples of the horizon H-52

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<th>Ord.</th>
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<th>Colour</th>
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Note: 1 = green, 2 = blue, 3 = gray

Colour of sediments

1 = red, 2 = green, 3 = gray

[33] 75
Appendix — Prilog II
Graphical presentation of chemical composition data of the ore body II and its close vicinity

Grafički prikaz kemijskih analitičkih podataka iz rudnog tijela II i njegove bliže okolice
Appendix — Prilog III

Table — Tablica A

Characteristics of analytical data distributions of ore-bearing and barren rock samples

Karakteristike skupova analitičkih podataka za rudne i nerudne uzorke stijena

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Table — Tablica B

Characteristics of analytical data distribution

Karakteristike skupova analitičkih podataka

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<th>Stand. dev.</th>
<th>Min.</th>
<th>Max.</th>
<th>Var.</th>
<th>Value</th>
<th>Value coeff.</th>
<th>Goodness of fit</th>
<th>Notes</th>
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<td>Da</td>
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Appendix — Prilog IV

Correlation matrices of the gray, ore-bearing, red and green rock series

*Korelacione matrice sivih, rudnih, crvenih i zelenih stijena*

### CORRELATION MATRICES FOR THE GRAY ROCK SERIES

**KORELACIONA MATRICA ZA SIVU SERIJU**

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<th>Cu</th>
<th>Co</th>
<th>Ni</th>
<th>Sr</th>
<th>Cr</th>
<th>Fe</th>
<th>Mn</th>
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### CORRELATION MATRICES FOR ORE BEARING SERIES

**KORELACIONA MATRICA ZA RUDNU SERIJU**

### CORRELATION MATRICES FOR THE RED ROCK SERIES

**KORELACIONA MATRICA ZA CRVENU SERIJU**

### CORRELATION MATRICES FOR THE GREEN ROCK SERIES

**KORELACIONA MATRICA ZA ZELENU SERIJU**

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6. REFERENCES


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Opća karakteristika ležišta urana u pješćencinicama je pripadnost kontinentalnoj seriji klastičnih stijena, epigenetske (vrlo rijetko singenetske) karakteristika pojavljivanja, niska i neujednačena koncentracija urana, pridruženost sulfida teških metala (Cu, Pb, Zn, Mo, Ag), te još nekih elemenata kao Se, V, Cr i drugih. Usprkos velikih razlika od ležišta do ležišta, u cjelini gledano, geokemijske karakteristike upućuju na slične mehanizme orudnjenja, čija bit je u mobilizaciji reductivnih formi urana iz kiselih erupativnih stijena i tufova ili njihovih klastičnih ekvivalenta, transportu šesterovalentnog urana nadzemnim i podzemnim vodama i precipitaciji na reductivnoj geokemijskoj barijeri.

Različita geokemijska svojstva mobiliziranih i transportiranih elemenata odražavaju se u zonalnom rasposredu mineralnih vrsta oko i u rudnom tijelu. Ta je zakonitost lijepo razvijena u »roll-tipu« infiltracionih ležišta. Zbog slabije izražene zonalnosti peneokonkordantnog tipa, kojem pripada i ležište Zirovski Vrh, proučavanje te pojave je posebno interesantno jer pomaže rješavanju genetskog modela, a može imati i praktičnu važnost u smislu pronalaženja elemenata indikatora ili repernih elemenata za uspješniju korelaciju slojeva u istražnim radovima.

Geneza rudnog ležišta započinje sa sedimentacijom detritusnog materijala i zakapanjem biljnih utrusaka. Proces fermentacijske razgradnje (CH₃, H₂, organske kiseline i drugo) prati disimilacijsko razvijanje H₂S uz pomoć sumpornih bakterija. Propusni se pješčenjak impregnira hirnsnom materijalom i željeznom sulfidom.

Promjena klime, spuštanje vodnog lica, ubrzanje automorfnog kemijskog trošenja dovodi do promjene sastava podzemnih voda (porast koncentracije sulfata, mikroelementa i urana). Proces generiranja H₂S se ubrzava, a reductivna-sulfidna barijera obara halkofilne elemente i uran, koji pokazuju jasni zonalni raspored u skladu s produktima topivosti ili izobarnim potencijalom reakcije otapanja. Široka zona pirita je pośljedica njegova ranodijagenetskog postanka. Dio metalnih sulfida je taložen cementacijskim procesom zamjene pirita.

Siva i crvena boja sedimenata nastale su u redoksomornom stadiju dijagenese u reductivnoj i oksidnoj sredini. Proces »ozelenjavanja« počinje sa sindijagenozom, a nastavlja se do totalne litiifikacije stijena. To je prijelazni »glej-sulfidni« proces u kojem organski reducensi, a naročito H₂S, efikasno reduciraju ferminerale. Količina H₂S nije dovoljna za potpuno vezanje Fe²⁺ u sulfide, već se javljaju rijetki idiomorfini kristali pirita. Veći dio dvovalentnog željeza (u bazičnoj sredini) ugrađuje se u leptoklorite koji daju stijeni zelenu boju. Dugotrajnost tog procesa ogleda se u njegovu epigenetskom načinu pojavljivanja uzduž rubnih zona propusnih kanala, rasjeda i klivažnih ploha. Cirkulacijom reductivnih voda, koje su nosile uran i teške metale, vršilo se »ozelenjavanje« crvenih klastita i formiranje rudnih koncentracija. To je jedan jedinstveni proces.
Posebno bi trebalo istražiti pojavu najniže vrijednosti koeficijenta redukcije FeO/Fe₂O₃ na mjestu maksimalne koncentracije urana, koja može imati i dublje genetsko značenje (redukcija urana pomoću ranodijagenetskog pirita).

Rudnik Zirovski Vrh je penekonkordantno infiltracijsko ležište urana u »pješčenjacima«, nastalo epigenetsko-egzogenim unašanjem uranil karbonatnih kompleksa i iona teških metala u reduktivnu — H₂S bariju, što se ogleda u mnogobrojnim epigenetskim karakteristikama mineralizacije i promjenama na stijenama u rudnom tijelu i njegovoj okolini.

Analitička metoda »atomkska apsorpcija« pokazala se veoma praktična za tu vrstu istraživanja, omogućavajući određivanje udjela epigenetsk i unašanih mikroelemenata u matriksu i cementu pješčenjaka, korišćenjem parcijalne ekstrakcije. Za tu svrhu kao najprikladnija pokazala se oksidirajuća smjesa kiseline (HCl—HNO₃, 1:6), koja efikasno razlaže prisutne sulfide, dio organske materije, limonit, okside željeza, karbonate i izvrstan dio filosilikata (klorit npr.).

Testiranjem metode na sedam uzorka dokazana je visoka ponovljivost rezultata, što osigurava pouzdano statističku obraz. Selektivno način izluživanja metala, istaknuto je epigenetsko grupiranje elemenata i jasnu stohastičku vezu između pojedinih kemijskih komponenta.

Statistička obrada obuhvatila je multivarijantnu i bivarijantnu regresijsku analizu, ispitivanje skupova analitičkih podataka i klaster analizu. Dobiveni koeficijenti korelacije uvršteni su u odgovarajuće matrice (bez pripadnih T-vrijednosti), a upotrebjavani su u klaster analizi za konstrukciju dendrograma geokemijske povezanosti.

Ispitivanje skupova koncentracija mikroelemenata ukazalo je na jasno izdvajanje anomalnih distribucija zauran, CaCO₃, Zn, Pb, Co, podcrtavajući njihov epigenetski karakter. To je svojstvo slabije izraženo za Cu, Sr i Cr.

Klaster analiza je grupirala elemente prema glavnim nosiocima mikroelemenata (glineni minerali — adsorpcija, CaCO₃ — izomorfna zamjena, organska materija — adsorpcija, redoks barijera, sumpor — redoks i sulfidna barijera).

Multivarijantna analiza dala je dobre rezultate za Sr, Li, gubitak žarenjem, CaCO₃ i Mn. Nešto slabije za halkofilne elemente a vrlo slabe zauran, što proizlazi iz slabije stohastičke veze s ostalim komponentama. Primijenjena statistika nije ukazala na postojanje efikasnog elementa indikatora ili asocijacije elemenata indikatora, koji bi uspješnije od samog urana predskazivali blizinu oruđenja. Međutim, treba napomenuti, da je uzorkovanje izvršeno na najnepovoljniji način za istraživanje epigenetskih karakteristika infiltracijskih ležišta — okomito na pružanje slojeva, gdje su zone najuži.

Sr, Li, Fe, Mg, Mn, CaCO₃ i gubitak žarenjem mogu uspješno poslužiti za bolju korelaciju slojeva.
PLATES — TABLE
PLATE — TABLA I

Fig. 1. Silicified wooden fragment. Cellular interstices filled up by pyrite and chalcopyrite (reflected light, parallel Nicols, M = 120 x)

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