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Aragonite in Kerogenous Lower Cretaceous Carbonate Rocks of Mt. Dinara

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Key words: Aragonite, Algal fragments, Kerogen, Strontium, Mt. Dinara, Lower Cretaceous

The first aragonite occurrences in kerogenous Lower Cretaceous rocks of Mt. Dinara are described. Aragonite occurrences are correlated to the favourable conditions of its formation and preservation. In the preservation of aragonite, organic matter had an essential part as protection against meteoric water impact but also a strontium content in aragonite. Aragonite appears mostly in stromatolitic laminae, and rarely in algal fragments in kerogenous dolomites as well as in kerogenous dolomitized and recrystallized limestones.

Ključne riječi: Aragonit, Algalni framenti, Kerogen, Strocij, Dinara, Donja kreda

Opisani su prvi nalazi aragonita u kerogenim donjokrednim karbonatnim stijenama Dinare. Pojave aragonita povezuju se za pogodne uvjete njegovog postanka i očuvanja. Pri očuvanju aragonita bitnu ulogu imala je organska tvar kao zaštita od djelovanja meteorskih voda, no i sadržaj stroncija u aragonitu. Aragonit se nalazi pretežno u stromatolitnim laminama, a rjeđe u algalnim fragmentima, kako u kerogenim dolomitima, tako i u kerogenim dolomitiziranim i rekristaliziranim vapnencima.

Introduction

In this paper aragonite occurrences in younger Lower Cretaceous kerogenous carbonate rocks of Vrdovo and Bitelić in Mt. Dinara are described.* Parts of stromatolitic laminae type LLH–S are prevalently built of aragonite. As far as we know, these are the first aragonite occurrences discovered in Mesozoic sediments in Yugoslavija. Aragonite, which is formed in shallow sea, at the high Mg/Ca ratio transforms in the diagenesis due to the impact of meteoric waters into stable calcite. Therefore, there are rare occurrences of aragonite in old carbonate beds. In such deposits aragonite is often preserved in fossils. The preservation of aragonite is explained in literature on account of protective effect of organic matter, due to clay. or due to the increased content of strontium in aragonite (Füchtbauer, 1974).

In rock samples of Mt. Dinara aragonite has been stated by means of X-ray powder diffraction and by microscope after painting of cross sections in Feigel solution (Leitmeier and Feigl, 1934).

Description of kerogenous carbonate rocks with aragonite content

There are more kerogenous occurrences in Mt. Dinara. The following occurrences have been sedimentologically and mineralogically tested:

1. four occurrences from Vrdovo (one from Briščić and three from Golo Brdo)
2. one aragonite occurrence in Bitelić (Fig. 1).

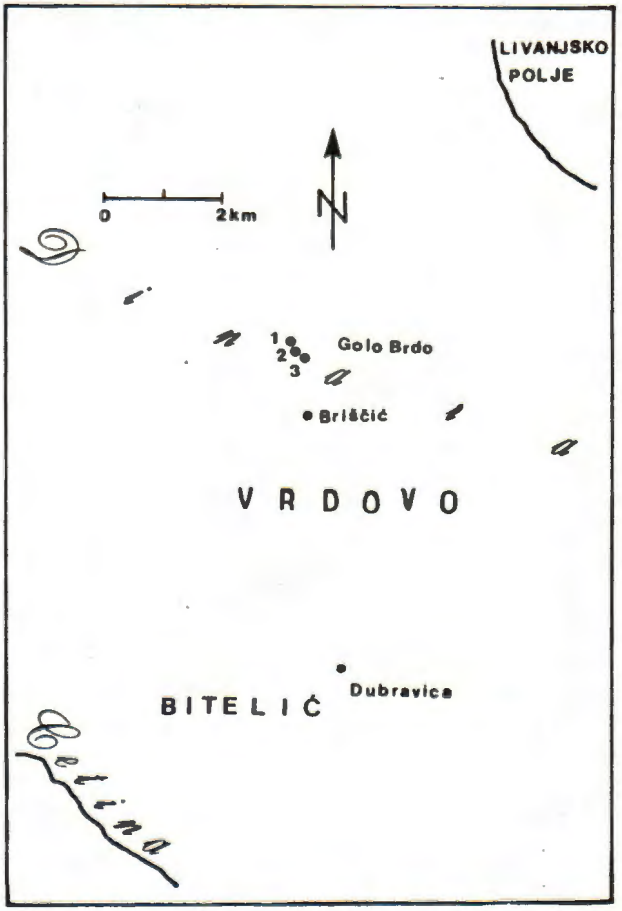

Fig. 1. Situation map of the researched kerogenous occurrences of Vrdovo and Bitelić.

Sl. 1. Položajna karta istraživanih kerogenih pojava Vrdova i Bitelića.

* Chronostratigraphic characteristics according to the personal communication of M. Vitezić, B. Sokač and I. Gušić, from the Geological Institute in Zagreb.

Vrdovo

Briščić. A very small quantity of aragonite is registered above the adit (Plate I. fig. 1) in hardly visible and slightly preserved fragments of algae in biogenetic limestone. While colouring in Feigel's solution the algal fragments became grey, i.e. they were equivalent to 5Y 5/1 colour (Munsell, 1988). According to the lithotextural relations in the sample, laminae of highly kerogenous fossiliferous micrite (M-w) interchange with slightly kerogenous, partly dolomitized biomicrite (w). Algal fragments have been observed in dolomitized biomicrite. The contact between laminae is slightly wavy. The same microsequential relations appear also on the top of adit, where also in biomicrites (w) of algal fragments were found. Their taxonomic characteristics could not be determined. It can be particularly stressed, that these biomicrites contain stromatolitic intraclasts enriched by organic matter (Plate I, fig. 2), similar to those previously discovered on Pelješac (Šebečić et al., 1983) and Mljet (Tišljar, 1986). The thickness of laminae and limestone leaves varies from 0.25 to 4 mm.

Golo Brdo. Aragonite has been observed in three kerogenous occurrences (fig. 2). In relatively the oldest occurrence (occurrence No. 1) successively are placed kerogenous dolomitized and recrystallized limestones: dolomitized laminated biomicrites (w) and fossiliferous (ostracode) micrites (M), fossiliferous pseudomicrosparites and dolomitized stromatolitic limestones (B). In fossiliferous pseudomicrosparite aragonite is registered in the shade of algae. The needles of radial ribboned aragonite became grey by means of colouring (N4).

In the medium kerogenous occurrence (occurrence No. 2) the highest aragonite content has been stated (to 8%) in laminae of kerogenous dolomitized stromatolitic (LLH–S) limestone to calcite dolomite (Plate I, fig. 3 on the left – a). Laminae are parallel to slightly wavy; microfaulted with micro displacements of laminae to 5 mm. In somewhat younger stromatolitic calcitic dolomite (Plate I, fig. 3 on the right – b) the occurrence of aragonite has been registered. By colouring the differences in aragonite contents have been observed. Single laminae were coloured black (2.5 Y 2/0), and some dark grey (5 Y 4/1). By this, laminated stromatolitic lithotexture is stressed. In kerogenous stromatolitic dolomite the occurrence of convoluted laminations (Plate I, fig. 4) is outstanding, as well as the occurrrence of calcite cemented fenestral pores and pores with geopetal filling.

In the youngest kerogenous occcurrence (occurrence No. 3) aragonite has been found in a small quantity (to about 2%) in algal fragments of calcitic dolomites. The thickness of stromatolitic laminae in kerogenous dolomites varies from 0.05 to 0.25 mm. Dolomites are sporadically silicified with changing intensity. They are wavy and parallely laminated. Except kerogenous dolomites there are also sedimentary microbreccias and brecciated dolomites with prevalently stromatolitic dolomite fragments, mostly larger than 5 mm.

Kerogenous occurrences of Golo Brdo are built from more smaller outcrops which can be contoured on the surface lenslike the size of the lenses being 50-100 m. The thickness of carbonate deposits with the interstratified kerogenous carbonate layers is from 10 to 45 m. The occurrences of Golo Brdo have been researched by mining by means of trenches and cuts, and in Briščić and Bitelić also by means of adits.

Part of the excavated raw material from Mt. Dinara was transfered to Ruda between 1949 and 1951, and was there processed into a high quality poduct (Čubranić-Ajduković, 1980), while the rest (larger part) remained storaged in the field.

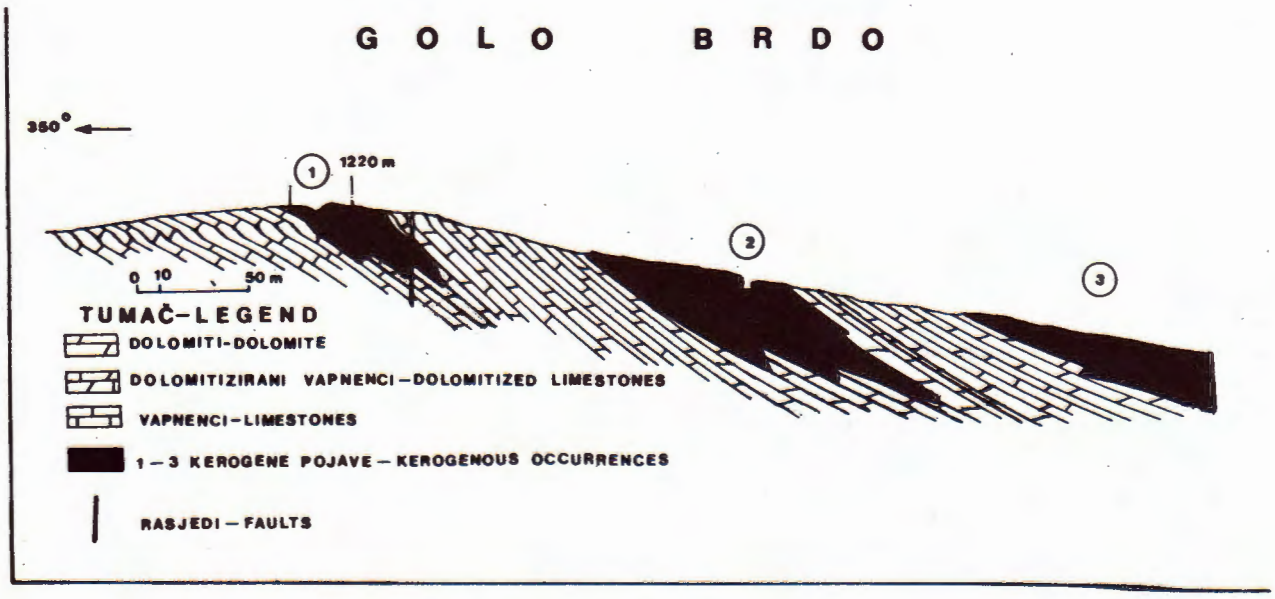

Fig. 2. Profile of kerogenous occurrences (1–3) Golo Brdo.

Sl. 2. Profil kroz kerogene pojave (1–3) Golog Brda.

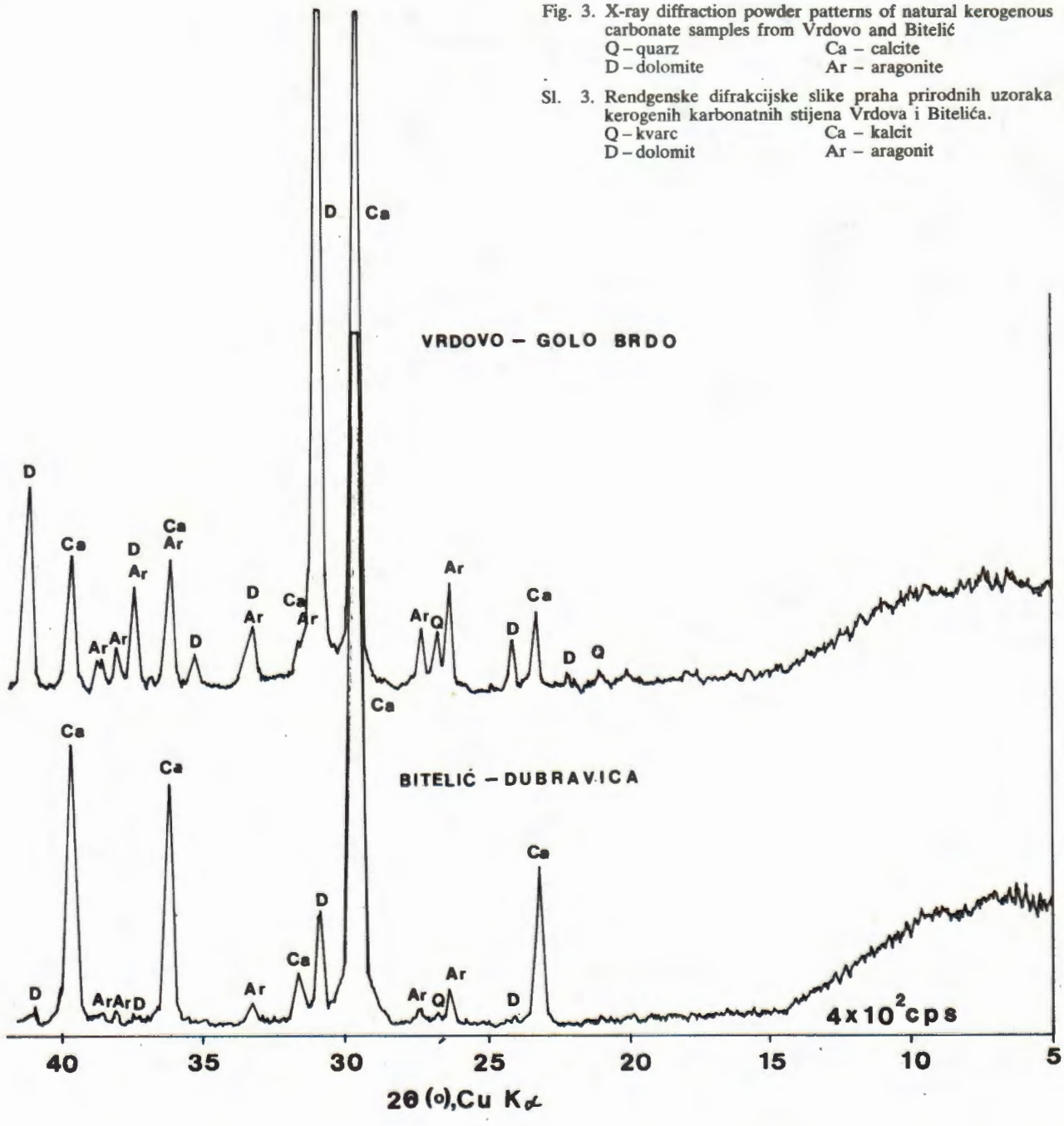

Fig. 3. X-ray diffraction powder patterns of natural kerogenous carbonate samples from Vrdovo and Bitelić
Q – quarz Ca – calcite
D – dolomite Ar – aragonite

Sl. 3. Rendgenske difrakcijske slike praha prirodnih uzoraka kerogenih karbonatnih stijena Vrdova i Bitelića.
Q – kvarc Ca – kalcit
D – dolomit Ar – aragonit

Bitelić

In the profiled kerogenous limestones of Dubravica near Bitelić the occurrence of aragonite was stated on the adit entrance in the arched adit in final kerogenous layers, similarly as in kerogenous layers, similarly as in kerogenous occurrence in Briščić. Aragonite has also been registered at the bottom of the adit in kerogenous limestone beds. By means of cross section colouring aragonite was found also in algal fragments (colour N4), within older biointramicrite (w) in which interlayers of ostracode fossiliferous micrite (M) can be found, thus building together parallely laminated (w-M-w) micro sequence, and in younger slightly wavy laminated micro sequence of the same type (w-M-w), in which micrite (M) is interbedded in fossiliferous intramicrite (w). By colouring (5Y 6/1) the previous shape of algae is stressed and it has also been found that the dark grey (N4) micrite is partly aragonitic.

Mineral composition of rocks and concentration of strontium in calcite and aragonite

After microscopic tests, ten rock samples were analyzed by means of X-ray powder diffraction, by thermal analysis (DTA, TG and DTG) and by chemical analysis (Ca and Mg in carbonates). In the operation Phillips X-ray counter diffractometer (radiation Cu K_α) and derivatograph of the firm MOM were used.

X-ray diffraction patterns of natural samples have been taken first. On these patterns visibly registered of carbonates are only the lines of dolomite, calcite and aragonite (Fig. 3). By means of adaptation of X-ray semi quantitative phase analysis and Ca and Mg data, the approximate concentrations of these minerals have been determined. In order to remove carbonates, the samples have been dissolved in warm diluted HCl (ph~3). In the undissolved residues by means of X-ray method illite, quartz and potassium feldspar were determined.

The presence of organic matter which can be seen in undissolved residues with the naked eye too, has been acknowledged by taking of thermograms (Fig. 4). Since the organic matter was not completely burnt to the end temperature of the experiment (~950^{0}C) the obtained thermoanalytic curves could not be used for the determination of the organic component participation. In order to determine the concentrations of the organic component, the undissolved residues have first been dried for one hour at 110^{0}C and then the organic matter was burnt in the burner with permanent oxygen dosage. These samples have been glowed in an oven for one hour at the temperature of 1000^{0}C. From crystalline phases which are losing mass in the course of the glowing, only illite has been determined in undissolved residues.

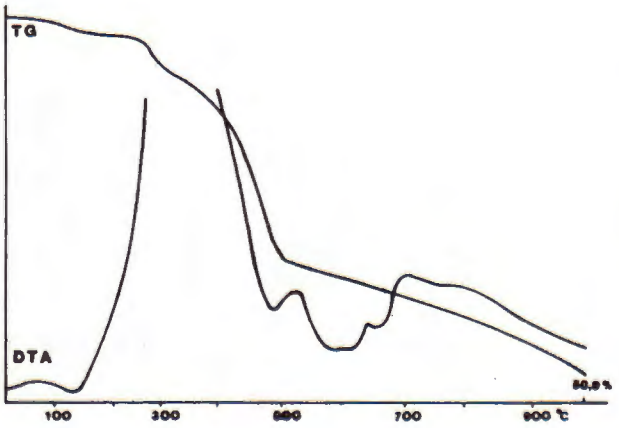

Fig. 4. Thermoanalytical curves of indissolved residue of kerogenous calcite dolomite sample (Vrdovo–Golo Brdo, occurrence No. 2). With TG curve there is also a loss of mass expressed in percent. X-ray diffraction powder pattern of natural sample is shown in fig. 2.

Sl. 4. Termoanalitičke krivulje neotopljenog ostatka uzorka kerogenog kalcitnog dolomita (Vrdovo–Golo Brdo, pojava 2). Uz TG krivulju označen je gubitak mase u postocima. Rendgenska difrakcijska slika praha prirodnog uzorka prikazana je na sl. 2.

Taking into account the assessed concentration of this mineral and the adequate glowing loss, the difference of total glowing loss of mass is expressed as an approximate concentration of organic component in the undissolved residue.

By the described procedures it was found out that kerogenous dolomitized limestones of Golo Brdo (occurrence No. 1) contain approximately 75% of calcite, 5% of dolomite, 1% of aragonite, 7% of illite, 3% of quartz, a small quantity of potassium feldspar and approx. 7% of organic component. Kerogenous calcitic dolomites of Golo Brdo (occurrences 2 and 3) contain 14–38% of calcite, 38–70% of dolomite, 2–8% of aragonite, 1–3% of illite, 1–4% of quartz (and in chert nodules in the occurrence No. 3 even more than 50% of quartz), a small quantity of potassium feldspar and 8–11% of organic component.

Kerogenous calcitic dolomite of Briščić contains approx. 40% of calcite, 56% of dolomite, traces of aragonite, a small quantity of illite and quartz, and approx. 2% of organic component.

Kerogenous dolomitized limestone of Bitelić contains approx. 85% of calcite, 3% of dolomite, 3% of aragonite, a small quantity of illite, quartz and potassium feldspar, and approx. 6% of organic component.

In three samples from Vrdovo after selective dissolution of calcite and aragonite (1 M sodium acetate buffer with acetic acid at pH 5), parts of strontium have been determined in the filtrate by means of atomic spectrophotometry. The obtained values quoted in table 1 represent the concentrations of strontium in calcium carbonates (calcite + aragonite). In table 1 data about dolomite, calcite and aragonite parts, and parts of organic component in the samples are contained, too.

Table 1. The approximate weight fractions of carbonates and organic component in the samples of Vrdovo and concentrations of strontium (ppm) in calcium carbonates (calcite + aragonite) in corresponding samples

Tablica 1. Orijentacijski udjeli karbonata i organske komponente (mas. %) u uzorcima Vrdova i koncentracije Sr (ppm) u kalcijskim karbonatima (kalcit + aragonit) odgovarajućih uzoraka

Sample uzorak	dolomite dolomit	calcite kalcit	aragonite aragonit	organic component organska komp.	strontium stroncij
Golo Brdo Occurr. No. 2 Pojava 2	38	38	8	11	2060
Golo Brdo Occurr. No. 3 Pojava 3	70	14	2	8	1250
Briščić	56	40	trace trag	2	530

From the data in Table 1 the content of strontium in aragonite cannot be determined, though aragonite surely contains essentially more strontium than calcite. Nevertheless, the comparison of calcite and aragonite concentration with the corresponding strontium concentrations in Table 1, indicate that the strontium concentration in aragonite is about several thousands of ppm. This concentration of strontium surely accounts for the stabilization of the aragonite structure (Füchtbauer, 1974).

Conclusion

Aragonite has been determined in some samples of profiled younger Lower Cretaceous kerogenous dolomites and dolomitized and/or recrystallized limestones from Mt. Dinara. In the area of Vrdovo there

are kerogenous carbonate rocks (dolomites and dolomitized limestones) as lens shaped parts of dolomite zone, whereas in Bitelić there are prevalently lenses of kerogenous limestones. Aragonite has been observed in some places in stromatolitic laminae and seldom in algal fragments. Its share of aragonite in rocks varies from small quantities to 8%.

In all Lower Cretaceous carbonate rocks of Mt. Dinara, which have been analyzed and in which aragonite has been found, contain also organic components. The share of aragonite is usually increased with the share of the organic component. The largest quantity of aragonite, i.e. approximately 8% has a rock in which the part of the organic component is largest, i.e. approx. 11%. The share of the clay component in the analyzed rocks is small. The connection between the share of aragonite and clay has not been observed. Aragonite in our samples contains strontium in the concentration of several thousands of ppm. According to what has been said and to generally known examples from literature, it can be concluded, that aragonite has been sporadically preserved in Dinara rocks owing to the presence of the organic matter which prevented the contact of aragonite and meteoric waters, and thus its conversion into calcite. Significant concentration of strontium in aragonite could have contributed to the preservation of aragonite.

The existence of aragonite in our examples indicates that it has primarily been precipitated together with the organic matter in very shallow sea environment, and according to sedimentologic characteristics in intertidal (-shallow subtidal). On the basis of sporadic findings of aragonite in kerogenous carbonate rocks it can be concluded that in younger Lower Cretaceous in the area of Mt. Dinara conditions have been very favourable for precipitation of aragonite and for its protection. With regard to the fact that only parts of studied kerogenous carbonate sediments are built of aragonite, it can be supposed, that calcite could have originated from aragonite and that the diagenetic transition of aragonite to calcite could have been homotaxial.

At present, nothing definitive can be said about the effect of dolomitization and recrystallization, except that this effect whether supporting or preventing the transition of aragonite into calcite, has not been significant.

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Aragonit u kerogenim donjokrednim karbonatnim stijenama Dinare

B. Šebečić i D. Slovenec

U mlađim donjokrednim karbonatnim stijenama Vrdova (Brišćić i Golo Brdo) i Bitelića (Dubravica) na Dinari (sl. 1 i 2) primjenom rendgenske difrakcije na prahu (sl. 3) i mikroskopski nakon bojenja nepokrivenih izbrusaka Feiglovom otopinom, determiniran je aragonit. Udio aragonita u desetak ispitanih uzoraka stijena variva od tragova do 8%. Aragonit se nalazi u stromatolitnim laminama, a rjeđe u algalnim fragmentima kako u kerogenim dolomitima tako i u kerogenim dolomitiziranim vapnencima: biomikritima (w), biointramikritima (w), fosilifernim intramikritima (w) i u rekristaliziranom vapnencu – fosilifernom pseudomikrosparitu.

U stijenama koje sadrže aragonit dominantni minerali su dolomit i kalcit. Udjeli kvarca, ilita i kalijskog feldspata su mali. Međutim, udio organske komponente je znatan (2–11%) s tim što se udio aragonita u uzorcima u pravilu povećava s udjelom organske komponente. Aragonit sadrži i Sr u koncentraciji nekoliko tisuća ppm, što slijedi nakon usporedbe podataka za udjele kalcita i aragonita i koncentracije Sr u kalcijevim karbonatima (Tablica 1).

Aragonit u analiziranim pojavama mjestimično je očuvan zbog prisustva organske tvari koja je sprečavala kontakt aragonita i meteorskih voda, a time i njegov prijelaz u kalcit. Očuvanju aragonita doprinijela je značajna koncentracija Sr u njegovoj strukturi. Prijelaz aragonita u kalcit bio je parcijalan i homoaksijalan. Pojave aragonitnog cementa nisu opažene. Kerogeni dolomiti su porijeklom (kasno) dijagenetski, a stromatolitna gradnja im je LLH–S tipa. Stromatoliti u kojima je interstratificirana organska tvar su nastali u sredini sa slabom cirkulacijom i nešto povećanim salinitetom vode, tj. u intertidalu (– plitkom subtidalu).

PLATE – TABLA I

Vrdovo – Briščić

Fig. 1. Platy and (slightly wavy) laminated kerogenous dolomitized limestones: fossiliferous micrites (M) and biomicrites (w) and calcitic sparse biodolomites (C) in the adit entrance. Aragonite has been registered in the dolomitized biomicrite layer (w) at the top of the adit.

Sl. 1. Pločasti i (blago-valovito) liminirani kerogeni dolomitizirani vapnenci: fosiliferni mikriti (M) i biomikriti (w), te kalcitni biodolomiti s razasutim alokemima (C) na ulazu u potkop. Aragonit je registriran u sloju dolomitiziranog biomikrita (w) pri vrhu potkopa.

Fig. 2. Fragment of kerogenous stromatolite in dolomitized biomicrite (w). 1N, 33x.

Sl. 2. Fragment kerogenog stromatolita u dolomitiziranom biomikritu (w). 1N, 33x.

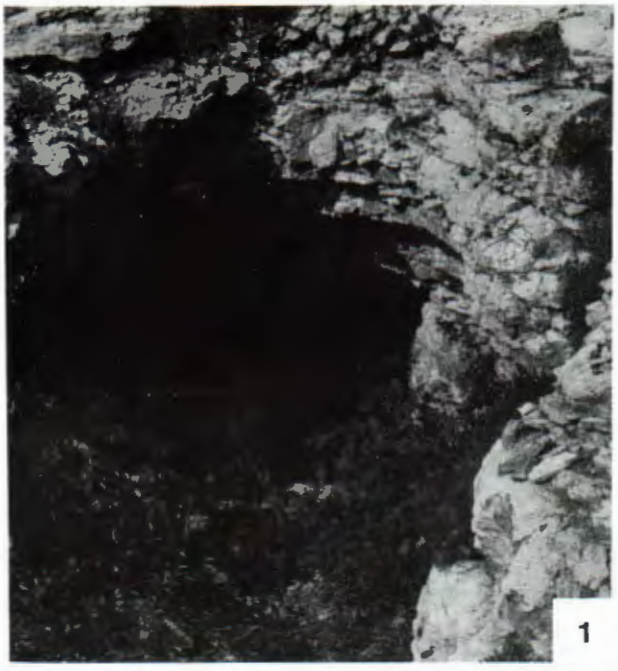
Vrdovo – Golo Brdo, occurrence No. 2, pojava 2

Fig. 3. on the left (a)
Kerogenous stromatolitic dolomitized limestone – dolomite.

Sl. 3. lijevo (a)
Kerogeni stromatolitni dolomitizirani vapnenac – dolomit.

Fig. 3, on the right (b) and fig. 4.
Kerogenous calcitic dolomite (fig. 3) with convoluted laminations (fig. 4). 1N, 33x.

Sl. 3, desno (b) i sl. 4.
Kerogeni kalcitni dolomit (sl. 3) s izuvijanim laminama (sl. 4). 1N, 33x.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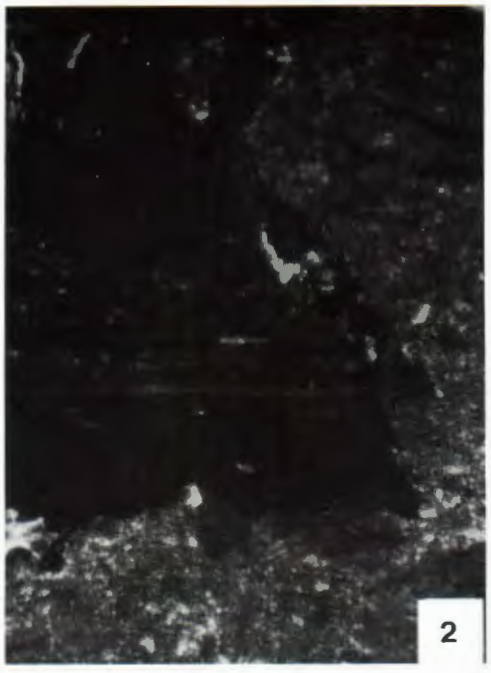
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a
b
3


4