Marine phreatic cements in the Triassic limestones from the Western Balkanides

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Abstract. Five major types of marine phreatic cements are established in winnowed and semi-winnowed limestone textures from the Triassic section of the Western Balkanides: radial fibrous, bladed, radiaxial bladed, cryptocrystalline and syntaxial. They were precipitated mainly in the inner and middle parts of a carbonate ramp in the active zone of the marine phreatic diagenetic environment. The radial fibrous and bladed cement types are markedly predominant. Evidence is found that at least a part of the syntaxial overgrowths upon crinoid fragments were generated during the early marine phreatic diagenesis.

The primary mineralogy of the cement phases has been mainly high-Mg calcite with only limited precipitation of acicular aragonite. However, the later diagenetic events as well as the nature of the sedimentation do not allow to infer specific cyclicity pattern in the Triassic section with respect to the abiogenic carbonate precipitation. The factors controlling the original mineral composition are assumed to have been mostly the saturation state of seawater with respect to calcite and aragonite as well as kinetic factors. The predominance of primary high-Mg calcite marine cements differs from the prevailing aragonite primary mineralogy of the associated ooids in the Spathian-Anisian limestones. The former has been probably predetermined by the lower rate of carbonate anion supply in the interallochem space of the grainstones.


Key words: cement, marine, phreatic, limestones, Triassic, Western Balkanides

Introduction

The results from sedimentological investigations on the carbonate rocks of Spathian-Anisian age in the Western Balkanides have been recently published (Chatalov, 1994; 1996; 1997a; 1997b; 1998; 1999a; 1999b). They threw light on different aspects of the depositional environments and diagenesis of the sediments. Meanwhile field observations were made and sample material was also collected during these investigations from younger carbonate Triassic rocks in the mentioned area.
The newly obtained data from the study of this material can be interpreted in order to arrive at more comprehensive conclusions about the evolution of the overall Triassic carbonate sedimentogenesis.

The present paper is concentrated on the marine phreatic cementation pattern in mainly winnowed textures from the Triassic carbonate rocks of the Western Balkanides. The beginning of this specific study was initiated in a previous work (Чаталов, 1997) but referred only to the rocks of the Mogila Formation (Spathian - Anisian) (Ассепето и др., 1983) whereas the newly obtained data embrace the whole cross section of the Iskar Carbonate Group (Spathian - Carnian) (Тронков, 1981). Different marine phreatic cement types are described and classified on the basis of their petrographical features as special attention is paid to the controversial origin of the available syntaxial cement. Some geochemical characteristics were investigated resulting, along with the petrographic features, in an attempt to evaluate the primary mineralogy of the cement types. The obtained data are used to elucidate the general abiotic carbonate precipitation during most of the Triassic period for the territory of present northwestern Bulgaria. In order to arrive at more precise conclusions a comparison is made with respect to other abiotic phases (ooids) in the rocks of Spathian - Anisian age. Finally, the factors controlling both composition and morphology of the cement phases are discussed.

Various cement types from ancient carbonate rocks have been described in the Bulgarian sedimentological literature based on their petrographic features with the exclusive application of transmitted light microscopy. However, genetic interpretations (including recognition of marine cement precipitation) have been rarely put forward (Колева-Рекалова, 1996) although morphological evidence, for example fibrous morphology, was clearly presented in some studies. Besides, no conclusions have been drawn about the primary mineralogy of the respective cements and the controlling factors over the abiotic marine precipitation.

Lithostratigraphic notes

Most of the carbonate sediments from the Balkanide type of Triassic (Ганев, 1974) belong to the Iskar Carbonate Group. The latter comprises several formal lithostratigraphic units in the Western Balkanides (s. s.) (Боенчев, 1986) which were introduced by several authors: Babino Formation (Anisian), Milanovo Formation (Ladinian) and Ruznovdel Formation (Ladinian - Carnian) (Тронков, 1968), Belimel Formation (Ladinian) and Mitrovo Formation (Ladinian - Carnian) (Тронков и Мохов, 1971), Edivetar Formation (Anisian), Toshkovdol Formation (Anisian - Ladinian) and Cheshmichka Formation (Carnian) (Тронков, 1973), Mogila Formation (Spathian - Anisian). Meanwhile the presence of the Svidol Formation (Spathian) (Чаталов, 1974) was also established in the framework of the Western Balkanides with its type area being situated in the Central Balkanides. According to newly presented data, the lower part of the holostratotype of the Godec Formation (Anisian - Ladinian) (Тронков, 1992) was referred to the Milanovo Formation and its upper part - to the Rusinovdel Formation (Чаталов и Бенатов, 2000). The Belimel Formation, Mitrovo Formation and Cheshmichka Formation were regarded by Ганев и др. (1986) as members of the Vasiliov Formation (Ladinian - Carnian) (Чаталов, 1984).

Materials and methods

The investigated sample material was collected basically from ten cross sections of the Iskar Carbonate Group (Fig. 1) plus a number of other outcrops. Only sampling of macroscopically distinguished allochemic limestones was carried out in the field in order to select exclusively grainstone textures. Representatives of the latter were eventually found in the following lithostratigraphic units: Mogila Formation, Edivetar Formation, Babino Formation, Toshkovdol Formation, Milanovo Formation and Belimel Formation.

Thin sections were prepared from about two hundred rock samples and a great part of them were subjected to staining using the technique of Dickson (1966) in order to differentiate the relative ferrous iron content in the calcite phases. Scanning electron microscopy (JEOL JSM - T300 и Philips SEM 515 apparatus) was applied to reveal the nature of the cement crystals, and particularly, the presence of microdolomite inclusions and the shape of crystal terminations. For this purpose polished rock slices were used which were prior to that etched in 10% solution of HCl for 5 seconds and then vacuum-coated with carbon. Electron microprobe analysis was applied to record the Mg and Sr content in those cement types showing fibrous morphology. Uncovered double polished thin sections were prepared and investigated by means of EDS Tracor Northern TN-2000 analyzer operating in the following regime: 20 kV voltage, 2.10+ A beam current and 2 mm spot size. Celestite and diopside were used as standards for strontium and magnesium respectively. Leitz-lu-
minoscope was used on a minor scale to reveal the cathodoluminescence behaviour of some marine cement phases. For this purpose the same double-polished thin sections were investigated applying 15 kV and 500 mA current regime of the apparatus (exposure time was 7-8 minutes).

General petrography and origin of the grainstones

The studied grainstones are built up of both allochems and cements. The relative amount of the former constituents varies between 40% and 85%
with all major allochem types being represented. Thus intraclastic, ooid, bioclastic, peloid and ooid grainstones were established with numerous intermediate subvarieties. Some of these textures occur preferentially in one or a few of the lithostratigraphic units. For example, bioclastic grainstones prevail in the Babino Formation whereas ooid grainstones are a major rock type in the Toshkovdol Formation.

The great majority of the grainstones contain marine cements as fringes around the allochems. Locally only micrite envelopes have developed around the latter indicating that micritization was another diagenetic process having taken place in marine conditions. The rest interallochem space in the fully winnowed textures is occupied by equant calcite cement (mostly showing drusy fabric) which may be interpreted to be either of meteoric phreatic and/or deep burial origin (Plate I, 1, 3, 4). Few grainstone samples lack marine cements at all but contain only equant drusy calcite.

Apart from the fully winnowed textures few packstones/grainstones were established among the collected material. The orthospar/micrite ratio in these semi-winnowed textures is variable (from 20/80% to 70/30%) and two varieties were differentiated. In the first one both marine cement fringes and equant cement are observed in the winnowed sectors of the rock, whereas micrite matrix is the groundmass in the rest of its volume. In the subordinate second variety marine cement phases have grown everywhere upon the allochem substrate but the rest pore space has been later occupied by sedimentary micrite (Plate I, 6).

All of the mentioned carbonate sediments are supposed to have been deposited in the range of a shallow carbonate platform which was interpreted by Catalov (1988) to be of the ramp model. The great bulk of the sediments were generated in the subtidal zone - much more in its shallower parts and less on the deeper ramp. A negligible part of the grainstones was deposited also in intertidal channels which were a constructive element of the Spathian - Anisian peritidal complex (Чatalов, 1997; Chatalov, 1998)

Marine phreatic cement types - petrography and origin

General features and recognition of marine phreatic cements

Cementation is a major isochemical diagenetic process contributing to the lithification of carbonate sediments. The knowledge about marine cements is of special importance because they reflect significant changes in the geochemistry of seawater on a global and local level being themselves a product of abiotic marine precipitation. Revealing the primary nature of ancient carbonate cements, however, is a special and sometimes difficult task. Different modern methods have been applied in the last decades to prove the primary mineralogy of cements including electron microprobe analysis, cathodoluminescence microscopy, isotopic determinations, etc.

Some common features testifying to the marine phreatic origin of carbonate cements may be outlined in brief. For example, marine cements always constitute the first cement generation, and when elongated crystals occur, they are normally oriented towards the substrate. A common feature is the isopachous character of the cement fringes. Yet this is not an absolute evidence for marine phreatic origin since isopachitic bladed crusts are also generated in the meteoric phreatic diagenetic environment (Longman, 1980; Heckel, 1983). If the pore space is completely occluded by marine phreatic cements characteristic polygonal sutures (Shinn, 1969) appear between the competitively grown cement fringes. This feature itself is especially diagnostic when combined with the fibrous morphology of the cements (Shinn, 1975). Undoubtedly convincing for marine origin is the presence of micritic internal sediment overlying or being interlayered with marine cements. The same holds true for boring traces which crosscut both the allochems and their cement fringes. Indicative is also the fact that marine cements always predate compaction features. In respect to composition marine cements are generated almost entirely in the form of metastable carbonate phases (aragonite or Mg-calcite) and geochemical indications for such mineralogy are frequently found in ancient, low-Mg calcitic at present, limestones. Additional characteristic is the low iron and manganese content, and finally, isotopic signatures may confirm the seawater-derived nature of the precipitated carbonate phases.

Beside the listed common features there are also conspicuous differences between the various marine cement types mainly resulting from morphological and, as mentioned above, mineralogical variations. The factors controlling this variability are discussed below concerning particularly the marine phreatic cement types of this study.

Types of marine phreatic cements in the studied grainstones

In spite of the widely accepted definition for the specific diagenetic process called "cementation" (Ba-thurst, 1975) a lot of controversies still exist in the designation of the cement types themselves. Terms like "fibrous", "palisade", "columnar", "acicular", "bladed", "prismatic" or "radiaxial" have been loosely used to denote marine cements. To escape this, the
simple and logical terminology suggested by Tucker & Wright (1990) is used in the present study. Thus the following marine phreatic cement types were differentiated in the studied rocks (grainstones and packstones/grainstones): radial fibrous, bladed, radiaxial bladed, cryptocrystalline and syntaxial (Fig. 2). In particular, the latter type is additionally discussed below with respect to its marine origin.

The established marine phreatic cement types build up between 15% and 30% (not including the syntaxial overgrowths) of the rock volume and locally may be predominant with respect to the later equant calcite (Plate I, 1, 3). This is mainly the case when close textural packing is available or mechanical compaction has taken place more intensely to leave little interallochem space. However, the progressive process of recrystallization is the reason for which marine phreatic cements are not always distinctively recognized in the rocks. Meanwhile, the separate cement types show most of the common diagnostic features of marine phreatic cementation. Other characteristics are the lack of successive appearance of different marine phreatic cement types as well as multiple cementation phases in one and the same cement type. The latter is particularly confirmed by the lack of interlayered micrite, Cyanobacterial encrustations or skeletal debris inside the fringes. Also, no immediate intimate overgrowths by specific later cements of non-marine origin, such as prismatic calcite, were established to succeed the marine cementing phases.

The investigated by means of cathodoluminescence microscopy marine phreatic cements (only from the Mogila Formation) displayed dull luminescence conditioned by the low Fe and Mn content (Чацалов, 1997). Thus the oxygenated nature of the marine phreatic diagenetic environment is reflected as well as the negligible amounts of these trace elements in seawater. Sporadically, however, isopachous bladed crusts composed of ferroan calcite (stained reactions applied) were observed in some grainstones and these may be interpreted as possibly precipitated in reducing conditions of the meteoric phreatic diagenetic environment. Alternatively, the presence of incorporated ferrous iron might indicate just a specific primary mineralogy of the bladed cements (see below).

Other typical marine phreatic cement types such as peloidal and botryoidal ones were not established in the studied grainstones. Also, no evidence was found to confirm the presence of marine vadose cementation (microstalactitic or meniscus forms of cements) in the rocks. Indeed, such phases might have been obliterated by later diagenetic processes.

Radial fibrous cement. This is the most relatively abundant marine phreatic cement type as it occurs in grainstones from all the mentioned lithostratigraphic units. Its fibrous character is conditioned by the length/width ratio of the crystals which is greater than 6:1 (Folk, 1965). Two important features of the discrete crystals are to be mentioned: their unit extinction and the locally dis-

![Fig. 2. Sketch drawings of the established marine phreatic cement types. Notes: the continuous lines inside the radiaxial bladed crystals designate curved twin planes; the crossed straight lines transecting both the echinoderm substrate and its syntaxial overgrowth indicate their common optical continuity at crossed polars](image-url)
played straight twin planes. The radial fibrous fringes around the allochems are principally isopachitic and form palisades (all crystals are parallel) (Fig. 2). These show maximum development in larger free pore spaces, and on the contrary, may be quite thin if close packing of the allochems was available in the original sedimentary texture. When such close packing is not observed the thin fringes might be an indication of slow rate of mineral nucleation and limited ion volumes available for precipitation. Very specific for the radial fibrous cement is the development of polygonal boundaries (sutures) between contacting adjacent cement fringes (Plate I, 3). In these cases their isopachitic character is disturbed resulting from the competitive growth of the fringes surrounding the neighbouring allochems. In some ooid grainstones only fringes with polygonal sutures have occupied the whole interallochem space.

Apart from the described common characteristics of the radial fibrous cement two morphological varieties with respect to the specific crystal width were established - columnar and acicular ones (Fig. 2). The latter is represented on a larger scale in the studied rocks and this is typical of grainstones compared to bioclastic limestones (Tucker & Wright, 1990). The width of the columnar variety is characterized by values of more than 10 μm (up to 30 μm) with their maximum size reaching up to 0.4 mm (Plate I, 5). When surrounding ooid allochems with radial fabric of the cortices the columnar cement may show an optical continuity with the substrate. The columnar variety is composed of constantly clear crystals when observed in plane light. Most crystals of the acicular variety are also clear but have width of less than 10 μm (commonly a few μm) and their length reaches up to 0.2 mm. Unlike the columnar form, the acicular crystals constitute sometimes dense isopachitic rinds where the discrete crystals are almost indistinguishable in plane light but are well outlined at crossed polars (Plate I, 1). Sporadically the acicular variety is represented by ghost crystals in pseudospar mosaics (Plate I, 4). The size of the equant pseudospar crystals ranges between 0.06 mm and 0.3 mm, and their boundaries are crosscut by the delineations of the original acicular cement crystals whereupon the latter are only vaguely outlined in the form of minute inclusions. The composition of these inclusions was not determined in this study but on the analogy of other occurrences (Mazzullo, 1980; Sandberg, 1985; Tucker, 1985) it is suggested that they represent relics from minerals, fluid phases and possibly organics. The acicular variety of the radial fibrous cement which is observed as ghosts in pseudospar mosaics was established only in some intraclastic grainstones from the Toshkovdol Formation.

The observations with SEM revealed the steep-sided terminations of those clear (both columnar and acicular) radial fibrous cement crystals which have not been strongly affected by recrystallization (Plate I, 2). This can be evident even in transmitted light especially where the fringes bound on micritic groundmass (i.e. in packstones/grainstones) (Plate I, 1, 5). Besides, in most of the clear crystals numerous microdolomite inclusions (Lohmann & Meyers, 1977) were detected during the SEM observations. These represent euhedral dolomite crystals sized up to 10 μm which have the same optical orientation as the host calcite.

The microprobe analyses on radial fibrous crystals showed a specific bilateral trend. The Sr content of the clear cements remain below the detection limit of the apparatus - 0.1 weight % SrO. Respectively, their Mg values are principally elevated although varying in a broad interval - an average of 0.88 ± 0.58 mole % MgCO₃. Contrasting, all analyses accomplished on the ghost acicular variety in the pseudospar mosaics display elevated Sr content of the calcite - an average of 1800 ± 300 ppm while the Mg values remain comparatively low - from 0.24 to 0.34 mole % MgCO₃.

The majority of marine phreatic cements in ancient limestones have fibrous morphology (Wilkinson & Given, 1986) and the present study confirms this regularity. However, it is well known from the literature that Holocene fibrous cements occur in nature both of primary aragonitic and high-Mg calcitic composition (Shinn, 1969; Alexandersson, 1972; Marshall & Davies, 1981). On the analogy of ancient radial fibrous cements, which have been interpreted as originally calcitic, it is suggested that the clear varieties of this study have also a calcite precursor. On the one hand, the good preservation of the crystals along with the lack of replacement fabrics is a solid evidence as well as the steep-sided crystal terminations (Longman, 1980). The optical continuity of the cement phases and the radial ooid cortices, which also are to be interpreted as former calcitic (Chatalov, unpubl. data), should analogously testify to their common primary calcitic nature (Moore, 1989). Finally, very convincing are the constant low Sr values in the present low-Mg calcite. A special problem is to prove the primary Mg content of the precipitated calcite, i.e. whether it was either low-Mg (0-4 mole % MgCO₃) or high-Mg (11-19 mole % MgCO₃) phase. It is well known that all magnesian calcites lose Mg²⁺ during diagenesis by incongruent dissolution (Bathurst, 1975). Yet, they may still retain sufficient Mg in their crystal lattice to indicate originally high levels (so called "Mg memory") and microscopic dolomite crystals may be precipitated during the stabilization of the former metastable phase within the newly formed calcite crystals. It is assumed that contents of more than 0.5 mole % MgCO₃, with most of the obtained data in this
study being above that threshold, rather indicate a former high-Mg calcite precursor (Lohnmann & Meyers, 1977; Prezbindowski, 1985; Tucker & Wright, 1990). In particular, such values testify to a closed diagenetic system (low water/rock ratio) and the presence of microdolomite inclusions is another evidence. Therefore most of the studied clear radial fibrous cements show evidence for original high-Mg calcite composition. On the other hand, the availability of open diagenetic system should be the explanation for the occasional lack of microdolomite inclusions and the recorded lower Mg content.

On the analogy of some modern acicular marine phreatic cements it is suggested that the described acicular variety showing elevated Sr and depleted Mg content must have had an aragonite precursor. Although Sr is depleted during diagenesis in the same way that Mg\(^{2+}\) is lost, in a closed system its relative enrichment is preserved (James & Choquette, 1983). Thus the recorded values of this study could reflect an aragonite precursor analogously to the data presented in other studies (Scherer, 1977; Wardlaw et al., 1978; Mazullo, 1980; Tucker, 1985). Major petrographical evidence for this conclusion should be the manner of preservation of the original crystals. On the analogy of the formation of neomorphic pseudospar showing relics from the original fabrics of mollusk shells (Sandberg & Hudson, 1983), ooids (Tucker, 1985; Chatalov, 1996) and cements (Heckel, 1983; Sandberg, 1985) it is assumed that the observed cements have been precipitated as aragonite. Their transformation to low-Mg calcite must have taken place through thin film in the framework of the carbonate grains (Wardlaw et al., 1978).

All of the established varieties of radial fibrous cements, irrespective of their primary mineral composition, have been precipitated in the marine phreatic realm. Indeed, fibrous low-Mg calcite cement is known also from the meteoric vadose diagenetic environment (Longman, 1980) but, as it was mentioned above, evidence for vadose diagenesis was not established in the studied rocks.

**Bladed cement.** The second relatively abundant marine phreatic cement type in the studied grainstones shows bladed morphology, i.e. its length/width ratio ranges from 2:1 to 6:1 (Folk, 1965). James et al. (1976) named such crystals of shorter length “bladed spar”. Similarly to the radial fibrous cement type the bladed one was established in the studied grainstones from all lithostratigraphic units. The crystal length ranges from 50 to 100 μm (Fig. 2). The separate crystals have homogeneous extinction and form commonly isopachitic fringes around the allochems with rarely manifested polygonal boundaries between them (Plate I, 6; Plate II, 1). Frequently the delineations of the bladed cements are obliterated as they have been succeed-ed by the later formation of drusy equant calcite mosaic, or alternatively, by neomorphic processes. On the contrary, the bladed morphology is best observed in semi-winnowed textures where internal sediment or cryptocrystalline (micritic) cement (?) have been formed after the bladed cement precipitation (Plate I, 6). In most cases the steep-sided terminations of the crystals can be seen even under the transmitted light microscope (Plate II, 1) and by means of SEM investigations the presence of microdolomite inclusions was established in most of the crystals (Plate II, 2). The present composition of the bladed cement is mostly non-ferroan calcite and sporadically ferroan calcite.

Bladed marine cements of primary magnesian calcite composition are widely known from modern sediments (James & Ginsburg, 1979). The specific morphology of their crystals (particularly the steep-sided crystal terminations) is considered indicative of the mineral precursor of similar ancient cements. Such cement phases were designated by Pierson & Shinn (1985) directly as “bladed Mg-calcite”. Another diagnostic feature in ancient examples is the presence of microdolomite inclusions. Thus considering the observed characteristics of the bladed cement from the studied grainstones a primary Mg-calcite precursor should be assumed. Meanwhile, the ferroan composition of some cements may represent a dilemma: either precipitation in a reducing, most probably meteoric, diagenetic environment, or taking up of the iron from the pore fluids at the time of diagenetic stabilization thus indicating former Mg-calcite mineralogy (Richter & Füchtbauer, 1978). Although bladed cements are known also from the meteoric phreatic-diagenetic environment (Longman, 1980) these are composed originally of low-Mg calcite and it is obviously not the case with most of the studied marine phreatic bladed cements.

**Radiaxial bladed cement.** Radiaxial bladed cement is a rarely observed type of marine phreatic origin in the studied Triassic limestones. It was established only locally in the grainstones of the Toshkovdol Formation. The cement crystals form isopachitic fringes around the allochems as the above described two cement types (Fig. 2) with their size reaching up to a length 0.5 mm and a width of 0.1 mm. The crystals have undulose extinction in crossed polars, and also turbid appearance and curved twin planes in plain light (Plate II, 3). They show irregular intercrystalline boundaries and are composed of constituting subcrystals which diverge away from the substrate (Fig. 3). This specific cement type is determined as radiaxial calcite because the undulose extinction of each crystal is a result of distally convergent fast vibration directions (optic axes) of the subcrystals. As a consequence the direction of the extinction swing in each crystal is the same as the turning of the
microscope stage and the adjacent subcrystals differ in extinction by 5-10°. Microdolomite inclusions were observed on a large scale in the radiaxial crystals applying SEM investigation.

The recorded Sr content of the calcite remains under the mentioned detection limit of the apparatus whereas the Mg values are variable - an average of 0.74±0.46 mole % MgCO₃.

This is one of the controversial cement types which has been principally considered to be of marine origin. It has been mostly described as having fibrous morphology and hence termed radiaxial fibrous calcite (RFC) (Bathurst, 1959). Meanwhile, some workers considered it to be a product of neomorphosed originally fibrous aragonite cement (Kendall & Tucker, 1973; Tucker & Hollingworth, 1986), and others assumed that RFC was a primary (high-Mg) calcite precipitate (Kendall, 1985; Sandberg, 1985; Zeeh et al., 1995). Bechstädt (1974) and Heinrich & Zankl (1986) suggested primary marine origin succeeded by alteration in meteoric waters. Finally, Prezbindowski (1985) and Videtich (1985) proposed a genuine meteoric origin. A solid actualistic evidence for a primary marine origin came from the discovery of marine radiaxial calcite in Miocene limestones from the Enewetak Atoll in the Pacific Ocean (Saller, 1986) and in the Pleistocene sediments of Japan (Sandberg, 1985). The primary mineralogy of these occurrences ranges from calcite to high-Mg calcite, and in particular, Saller (1986) assumed that the low-Mg RFC was precipitated by deep cool marine waters. The virtual absence of RFC from Quaternary limestones and its abundance in the past, especially in Paleozoic reefs and mounds, does suggest some change in the seawater chemistry. From the Enewetak occurrence it appears that a seawater undersaturated with respect to aragonite, active circulation of seawater during shallow burial and perhaps fluctuations in the degree of calcite supersaturation and crystal growth rate could be the factors controlling RFC precipitation (Saller, 1986). According to Kendall (1985) and Sandberg (1985) the characteristic fabric of convergent fast vibration directions in RFC is produced by a process of asymmetric growth as the calcite crystals were undergoing split-growth. The resulting composite crystals reflect the attempt of the crystals to assume a spherulitic growth form in a diageneric environment that favours the growth of length-slow calcite.

The absence of any dissolution effects or replacement textures in the observed radiaxial bladed cement suggests an original calcite mineralogy. This is also supported by the recorded low Sr content similarly to the clear radial fibrous cements. On the other hand, the principally elevated Mg content and the established microdolomite inclusions may testify strongly to a high-Mg calcite precursor as interpreted in other studies (Lohnmann & Meyers, 1977; Kendall, 1985). It is suggested that variations in the Mg concentration may be due to precipitation at variable rates caused by changes in the degree of seawater supersaturation (Saller, 1986). An alternative assumption should be related to the openness of the diageneric system.

Cryptocrystalline cement. This cement type was established sporadically in grainstones only from the Edivetar Formation. It is observed as thin micritic coatings around the allochems which display almost constant thickness reaching up to 0.1 mm (Fig. 2). The cementing character of this sedimentary material was recognized on the basis of its isopachitic character, as suggested by Meyers (1978), and the lack of geopetal infilling of the interallochem space. Especially important are the available micritic coatings around the coexisting siliclastic grains which preclude that their development resulted from diageneric micritization (Plate II, 4). Indeed, on account of the local merging with the available micrite envelopes around some lime allochems, the cryptocrystalline cement may look thicker than its real thickness.

Former terms to designate this specific cement type were “micrite” (Friedman, 1964; Purser, 1969) and “submicrocrystalline” (MacIntyre, 1967) but following the remarks of Friedman (1985) it seems reasonable to use “micrite” only to denote mechanically deposited lime mud. Recently, Reid et al. (1990) attempted to distinguish between different varieties of micrite in carbonate sediments and proposed to term attached nonskeletal precipitates in cavities as “internal micrite cement.”
Although cryptocrystalline cement has been described on a large scale in Recent sediments its recognition in ancient ones is comparatively rare. Occurrences have been reported from modern both subtidal marine-phreatic (MacIntyre, 1967; Alexandersson, 1972; James et al., 1976; Marshall & Davies, 1981) and intertidal marine-vadose (Gavish & Friedman, 1969; Meyers, 1987) environments. Purser (1969) was the first sedimentologist to establish cryptocrystalline cement in ancient rocks and after that such cement has been recognized mainly in reef limestones (Prezbindowski, 1985; Tucker & Hollingworth, 1986).

On the analogy of modern counterparts (James et al., 1976; Marshall & Davies, 1981; Meyers, 1987) it is suggested that the described cryptocrystalline cement has had a high-Mg calcite precursor. Its formation is believed to have taken place in the marine phreatic diagenetic environment as neither meniscus nor pendant distribution of its coatings was observed. One important fact must be also considered and it is that not absolute criteria have been pointed out so far to prove that a part of the available micrite groundmass in ancient packstones is not sedimentary micrite but cryptocrystalline (micritic) marine cement (James & Choquette, 1983). In other words, it is quite possible that a part of the micrite matrix in the studied packstones/grainstones represents actually cryptocrystalline marine phreatic cement.

The problematic nature of syntaxial cement

Clear syntaxial overgrowths occur on a largest scale around the observed echinoderm fragments (in optical continuity with them) although some of the described above cement types may show circumgranular development of fringes (Fig. 2). Syntaxial overgrowths are the only cementing phase in some crinoidal grainstones. In a number of cases micritization process has either predated or postdated the precipitation of syntaxial overgrowths (Plate II, 5). When stained the syntaxial cements proved to be mostly composed of ferroan calcite but zoned character in respect to the contained ferrous iron is more characteristic.

Syntaxial cement has been for long considered to be of meteoric (both phreatic and vadose) origin (Bathurst, 1975; James & Choquette, 1984; Kaufman et al., 1988). Longman (1980) mentioned also possible deep burial genesis whereas Meyers & Lohmann (1978) assumed formation in the mixed marine-meteoric diagenetic environment. A basic evidence for non-marine origin is considered to be the mere absence of syntaxial overgrowths on echinoderm fragments in Holocene sediments as well as the lack of fibrous cements forming upon echinoderm shells in the meteoric diagenetic environment. However, several workers convincingly demonstrated that syntaxial cements can be of marine phreatic origin (Gorur, 1979; McGill & Walker, 1982; Walker et al., 1990). Finally, Perkins (1985) found syntaxial overgrowths upon crinoids in the modern sediments of Bermuda. Alternatively to the enumerated hypotheses, Walkden & Berry (1984) assumed probable multi-phase formation in the mentioned above diagenetic environments and the same view was shared by Tucker & Wright (1990). The primary mineralogy of all ancient syntaxial cements is assumed to be high-Mg calcite and the frequent ferroan character of the present low-Mg calcite is considered indicative namely for that (Richter & Fiechtbauer, 1978).

Considering the available petrographic evidence it can be concluded that at least a part of the observed syntaxial overgrowths should be interpreted as marine phreatic products. For example, on a local scale bladed or radial fibrous marine phreatic cements display limited development where they encounter adjacent thin syntaxial overgrowths (Plate II, 5). These textural relations may be indicative of competitive growth in the marine phreatic realm between two different cement types. The regular appearance of only thin overgrowths (< 0.25 mm) of almost isopachitic distribution probably indicates a limited time for their formation, e.g. possibly during the early marine diagenesis. Although being a minor phenomenon the observed micritization which has affected the surface of some syntaxial overgrowths brings to the same conclusion. Finally, the spired shapes (Evamy & Shearman, 1969) of some earliest overgrowths (Plate II, 6), also may be interpreted as possible marine precipitates (Walkden & Berry, 1984). In the rest cases, where none of the presented petrographic evidence is available, a marine phreatic origin cannot be proved convincingly so that meteoric or deep burial genesis, as well as multiphase precipitation, are also and maybe more probable hypotheses. In particular, the zoned character of most syntaxial cements may be diagnostic namely of multiphase precipitation.

Controlling factors on the marine cementation

General prerequisites

It is known from ancient and recent objects of investigation that the most intensive marine cement precipitation occurs in reefs, platform-margin shoals and strandline carbonate sands (Tucker & Wright, 1990). However, marine cementation is not uncommon also in inner and middle shelf depositional environments which is the case with the studied grainstones. Wherever the marine cementation takes place the general factors controlling it
are almost the same. The major prerequisite for marine cementation is the supersaturation of the marine waters with respect to calcium carbonate. This takes place principally in the active zone (Longman, 1980) of the marine phreatic diagenetic environment (Heckel, 1983). The circulating marine waters are flushed through the sediments by waves, tides and storms. On the other hand, it is possible that the cements in sediments deposited in the deeper parts of the mentioned carbonate ramp, as for example are the rocks of the Babino Formation, have been precipitated in the stagnant zone of the marine phreatic diagenetic environment. However, little cementation takes place in such conditions and this is well confirmed by the minor relative presence of marine cements in these limestones. The mentioned above rare occurrence of grainstones which do not show any evidence for marine cementation is the supersaturation of the water are required to fill one pore volume with a 10% precipitation efficiency which is roughly realistic for a natural pore system. Of course, a necessary prerequisite for the effective flushing of the fluids through the sediments is their good porosity and permeability combined with a stable pumping mechanism. Other workers assumed that a possible inhibition of marine cementation is aided by organics such as humic acids (Berner et al., 1978) although the opposite role of specific types of organic matter has been also contested (Mitterer & Cunningham, 1985). The inhibitory effects of magnesium, phosphate and sulphate ions have also been considered as important factors (Berner, 1975; Reeder, 1983) despite the fact that they affect in a different way the precipitation of aragonite, and respectively calcite (see below).

Factors controlling morphology and mineralogy

As far as cement crystal morphology is concerned, Folk (1974) considered that precipitation from seawater of high Mg/Ca ratio tends to generate elongate shapes of the abiotic carbonate phases. Alternatively, Lahann (1978) suggested that the crystal surface charge exerts the leading control over morphology. According to him, in case of cation excess over anions for the CaCO₃ system in seawater, the highest charge density is on the c-axis faces of the calcite crystals, and by attracting the largest number of carbonate anions this results in the fastest growth in the c-axis direction. Given & Wilkinson (1985) assumed that where carbonate ions are abundant and/or rates of fluid flow are high, c-axis growth is enhanced and therefore elongate shape is favoured. For the cryptocrystalline cements in particular, the nucleation rates are very high compared to the rate of crystal growth. Thus many nuclei are formed but they do not have the chance to grow to any substantial size or reach prevailing orientation.

It seems that precipitation of specific carbonate minerals as cements is controlled in some cases by the nature of the substrate carbonate mineralogy (i.e. allochems or “in situ” growing skeletons). However, in other cases aragonite allochems have calcite cement fringes, and vice versa. Moreover, some authors have even described radial fibrous cements of both mineralogies in one and the same pore space (Marshal & Davies, 1981) thus testifying to the possible rapid change of abiotic mineralogy in seawater. The lack of dependence between primary mineral composition of the cements and the substrate is well confirmed by the present investigation, for example by the presence of former aragonite ooids or mollusk shells with fringes of various types of primarily calcitic marine cement. Consequently, other factors must have influenced...
more the precipitation of the studied marine cements and they are to be related to two general controls: saturation state of seawater with respect to calcite and aragonite, and kinetic factors that promote or inhibit the precipitation of one mineral relative to the other.

At lower levels of seawater carbonate saturation the abiotic marine carbonates are composed of calcite and at higher saturation - of aragonite (Burton & Walter, 1987). Meanwhile, the degree of seawater carbonate saturation is influenced by numerous factors including temperature, salinity and CO₂ levels. Increasing temperature and salinity and decreasing CO₂ levels lead to higher saturation, thus favouring the precipitation of aragonite over calcite for kinetic reasons. In particular, the increase of temperature over the 5-37 °C interval causes an increase in the amount of Mg²⁺ in the calcite (Tucker & Wright, 1990).

Factors related to the reaction kinetics of carbonate precipitation include Mg/Ca ratio, relative presence of carbonate, sulphate and phosphate anions, and organics. Berner (1975) and Mucci & Morse (1983) suggested that the Mg/Ca ratio of water is the primary factor that controls the mineralogy of the abiotic carbonate phases. The increase of the Mg/Ca ratio causes a kinetic advantage for aragonite precipitation, and in particular, the precipitation of low-Mg calcite is inhibited by the presence of Mg cations (Berner, 1975; Reddy & Wang, 1980). Sulphate and phosphate ions inhibit more the precipitation of calcite than that of aragonite (Mucci et al., 1989; Burton & Walter, 1990). Given & Wilkinson (1985) suggested that primary mineralogy is largely controlled by the kinetics of surface nucleation and the amount of reactants, principally carbonate ions, at growth rates. As a consequence, at high rate of CO₂²⁻ supply aragonite precipitation is favoured. They also suggested that the faster is the growth rate, the higher is the Mg²⁺ content in the crystals. In particular, the rapid crystal growth rate accounts for the high Mg²⁺ content of cryptocrystalline high-Mg calcite. However, Morse (1985) regarded the hypothesis of Given & Wilkinson (1985) as rather incorrect and unsustained by experimental and observational data. Organics are also believed to influence aragonite precipitation and experiments have been carried out in that direction (Berner et al., 1978). Finally, on the analogy of ooids, the degree of agitation may possibly favour the precipitation of one mineral over another (Davies et al., 1978). The rates of sedimentation have been also considered as important factor although this has been proved mainly for reefs (Lighty, 1985). According to Burton (1993) no single fluid parameter can be isolated as a primary or sole dominant control on changes in cement mineralogy unless the effects of other solution parameters are proven relatively insignificant.

To summarize the discussion, it should be pointed out that most probably numerous factors have influenced the primary mineralogy of the studied marine phreatic cements. Of special importance must have been the combined operation of both thermodynamic and kinetic factors. In terms of the established predominant primary mineralogy (high-Mg calcite), it may be suggested that the decreased fluid flow rates in the interallochem space of the grainstones have favoured the preferential precipitation of high-Mg calcite cements. However, as it was pointed out by Tucker & Wright (1990) the controls on the precipitation of abiotic marine carbonates obviously remain a substantial problem even regarding modern cement precipitation.

Comparison with other abiotic phases in the Triassic limestones

On the basis of previous investigations on the carbonate rocks of Spathian-Anisian age in the Western Balkanides (Chatalov, 1996; 1997a; Chatalov, 1997; Chatalov, 1999b) the presence of both primary aragonitic and calcitic abiotic phases in the form of ooid cortices was established. The obtained data for their vertical and lateral distribution allowed to assume predominance of aragonite primary mineralogy. The new results which are based on the study of marine cements refer already to nearly the whole Triassic period and confirm only the general trend, i.e. the presence of binary aragonite/calcite abiotic precipitation. These bilateral variations represent certain specific deviation from the general trend of 1st order global cyclicity according to which the Triassic period is a part of much longer time interval from the Phanerozoic history of the Earth dominated by aragonite abiotic precipitation (Sandberg, 1983). The relative prevalence of primary high-Mg calcite as marine cement phase was interpreted above in the light of factors controlling the primary mineralogy of the cements. Meanwhile, this opposes in some way the general Phanerozoic trend of marine cements outlined by Wilkinson & Given (1986) (Fig. 4). According to these authors fibrous calcite cement was precipitated during all geological epochs of the Phanerozoic while aragonite was attached to separate intervals of lowstand. In particular, the aragonitic cements are typical of the mentioned 1st order global cycle extending from the mid-Carboniferous to the Early Jurassic (Sandberg, 1985) and occur mainly in Upper Paleozoic and Triassic reefs (Scherer, 1977; Tucker & Hollingworth, 1986). It appears, however, from the obtained results that the aragonite precipitation in the form of marine cements during the Triassic period on the territory of present northwestern Bulgaria was subordinate. It is obvious that the longer intervals of
Fig. 4. Secular Phanerozoic trend in the mineralogy of marine carbonate cements after Wilkinson & Given (1986)

predominant high-Mg calcite marine cementation were interrupted by shorter time intervals when transition towards aragonite precipitation took place. Such variations in the seawater geochemistry have been sometimes very rapid which is illustrated well by the occurrence of primarily biminer- 
calic-aragonitic ooid cortices of Spathian-Anisian age (Chatalov, 1997a). Unfortunately, 
from the obtained data there cannot be inferred any specific cyclical trend or lateral distribution 
regularity concerning the established calcitic and 
aronitic cements mostly on account of the inten-
sive later processes of recrystallization, dolomiti-
zation and dedolomitization which prevent at 
present the detailed study of the possible varia-
tions. Especially oblitative with respect to the 
primary limestone textures have been the dolomiti-
zation events affecting the Ladianian and Carnian 
sediments (the Milanovo and Rusinovdel Forma-
tion). Besides, the investigated high-energy grain-
stones associate in the sections with non-win-
nowed (e.g. without marine cements) lime sedi-
ments as well as non-carbonate sediments both of 
which build up large vertical intervals. In the first 
case illustrative examples are the Babino Forma-
tion and the Cheshmichka Formation whereas in 
the second one - the Mitrovo Formation.

The possible explanation of the discrepancy be-
tween the established predominant cement and 
ooid primary mineralogy in the Spathian-Anisian 
rocks must be that, unlike ooids, marine cements 
are principally precipitated in narrow interal-
lochem space where the amount of carbonate an-
ions is reduced and therefore predetermines their 
high-Mg calcite composition (Given & Wilkinson, 
1985). Additional illustration for such a depend-
dence are the limestones containing relics of fi-
brous cements which were interpreted above as 
primary aragonitic. Actually these cements have 
been precipitated in comparatively large pore 
spaces - between coarse anisometric intraclasts.

Conclusions

The following general conclusions can be made on 
the basis of the accomplished investigation on ma-
rine phreatic cement types in the Triassic lime-
stones of the Western Balkanides:

1. Marine phreatic cements are established 
mainly in grainstones but also packstones/grain-
stones belonging to six lithostratigraphic units. The 
sediments were deposited prevalently in the high-
energy inner and middle parts of a carbonate 
ramp. The cements were precipitated principally 
in the active zone of the marine phreatic diagenet-
ic environment. No evidence is found in the rocks 
indicating marine-vadose cementation.

2. The established cement types are radial fi-
brous, bladed, radiaxial bladed, cryptocrystalline 
and syntaxial. Most of these types have not been 
described in the domestic literature so far. In par-
ticular, cryptocrystalline cement is rarely recog-
nized in ancient carbonate rocks and evidence for 
marine origin of syntaxial overgrowths on echino-
derm fragments is not common. The relative distri-
bution of the cement types is marked by the pre-
dominance of radial fibrous and bladed types. On 
the contrary, the radiaxial bladed and cryptocryst-
talline cements occur only on a minor scale in nar-
row vertical intervals.

3. The primary cement mineralogy was repre-
sented mainly by high-Mg calcite. Only locally the 
acicular variety of the radial fibrous type shows 
solid petrographical and geochemical evidence for 
an aragonite precursor. The primary mineralogy of 
the cement phases was controlled by the saturation 
state of seawater with respect to calcite and arago-
nite as well as kinetic factors, and possibly, by the 
mineral composition of the allochem substrate 
and other other factors.

4. Neither cyclical trend nor regularities in the 
lateral distribution of the former aragonitic and 
high-Mg calcitic cements can be inferred from the
obtained data. The major hindrances are the intensive recrystallisation and dolomitization events as well as the presence of thick vertical intervals represented by either limestones with non-winnedowed textures or non-carbonate sediments.

5. The relative predominance of high-Mg calcite primary cements differs from the prevailingly aragonite original composition of the ooid cortices in the Spathon-Anisian rocks. The main prerequisite for this discrepancy must have been the lower rate of carbonate anion supply for cement precipitation in the narrow interallochem space of the grainstones.

6. The obtained results should be considered as a concrete step in the investigation on abiogenic carbonate phases in the Triassic limestones. In this sense, a forthcoming study on the isochronous oolites from the study area might contribute to the knowledge about the stratigraphical and geographical variations of the primary abiogenic carbonate mineralogy.

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PLATE I

1. Clear radial fibrous acicular cement forming isopachous fringes around blocky ooid (centre of the photo) and other allochems. The steep-sided terminations of the crystals (arrows) indicate primary (high-Mg) calcite mineralogy. Bioclastic-ooid grainstone, Belimel Formation, cross section VIII. Plain light, ×50.

2. Radial fibrous cement having grown upon micritic ooid and succeeded by later drusy cement. Although the rock has undergone certain recrystallization locally steep-sided crystal terminations are still preserved (arrows) indicating former (high-Mg) calcite mineralogy. Ooid grainstone, Toshkovdol Formation, cross section VIII. SEM microphotograph, ×480 (scale bar is 100 mm).

3. Polygonal sutures (arrow) between radial fibrous acicular cement fringes surrounding adjacent allochems. The fringes are not isopachous in some places on account of their competitive growth. Only locally free pore space has remained after the marine cementation and has been later occupied by drusy cement (dc). Intraclastic-ooid grainstone, Toshkovdol Formation, cross section VIII. Plain light, ×50.

4. Relic ghosts of radial fibrous acicular cement in pseudospar mosaic lining coarse intraclast allochems. The textural features of this cement is one evidence for its primary aragonite composition. Toshkovdol Formation, cross section VIII. Plain light, ×50.

5. Clear radial fibrous columnar cement forming isopachous fringes around micritic intraclasts. The lack of replacement fabrics and the steep-sided crystal terminations (arrow) testify to former (high-Mg) calcite mineralogy. Note the planar intercrystalline boundaries in the fringes. Intraclastic-bioclastic grainstone, Mogila Formation, cross section VI. Crossed polars, ×50.

6. Bladed isopachitic fringes around ooid allochems whose precipitation has predated the deposition of sedimentary micrite. The latter may be internal sediment or possibly cryptocrystalline cement. Ooid packstone/grainstone, Mogila Formation, cross section IV. Plain light, ×50.

PLATE II

1. Bladed cement fringes around ooid allochems and bivalve shell showing well outlined steep-sided terminations of their crystals (arrow) and thus indicating primary (high-Mg) calcite mineralogy. Bioclastic-ooid grainstone, Mogila Formation, cross section II. Plain light, ×50.


3. Radial bladed cement precipitated upon a bivalve shell substrate. Major diagnostic features are the curved twin planes and undulose extinction within each crystal. The latter is conditioned by the distally convergent optic axes of the subcrystals diverging themselves away from the substrate. Unlike the palisades of the radial fibrous cement the intercrystalline boundaries in the radial bladed cement are irregular. Bioclastic grainstone, Toshkovdol Formation, cross section VIII. Crossed polars, ×50.

4. Cryptocrystalline cement forming thin isopachous coatings (arrow) around fossil allochems and clastic quartz grains (Q). The fact that the micritic coatings surround non-carbonate grains precludes their origin as resulting from early diagenetic micritization. Sandy bioclastic grainstone, Edivetar Formation, cross section X. Plain light, ×50.

5. Coarse crinoid allochem (C) overgrown by syntaxial cement (s) bounds on ooid individual surrounded in its turn by radial fibrous cement fringe (f). Where both cement types encounter (arrow) they show limited development obviously depending on the opposite cement type growth. The conclusion from this textural relation may be that the syntaxial overgrowth was generated at least partly in the marine phreatic diagenetic environment simultaneously with the radial fibrous cement. Ooid-bioclastic grainstone, Mogila Formation, cross section I. Plain light, ×50.

6. Crinoid fragment overgrown by syntaxial cement with spired shapes of the earliest overgrowth (Evamy & Shearman, 1969) being observed (arrow). The latter may be interpreted as possible marine precipitate (Walkden & Berry, 1984), moreover, they surround isopachously the whole allochem. Bioclastic grainstone, Babino Formation, cross section VII. Crossed polars, ×50.