



TRIASSIC LIME MICRITES FROM THE WESTERN BALKANIDES: EVIDENCE FOR PREVAILING ABIOTIC PRECIPITATION OF THE ORIGINAL LIME MUDS

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Micritic matrix in limestones is considered as less reliable indicator for primary abiotic carbonate mineralogy compared to ooids and penecontemporaneous cements. The main reason is related to the possibility that precursor lime muds may be partly or entirely not a result of physicochemical precipitation. The latter is still challenged for modern occurrences of marine muds despite certain evidence favouring this particular mechanism. Meanwhile, the lack of standard criteria to precisely prove the origin of most ancient micrites is a major problem concerning their interpretation. Nevertheless, the possibility that part of the fine-grained matrix in marine limestones was precipitated as cement should not be precluded (Reid et al., 1990). If such nature is inferred for particular lime mudstones, they may appear as the only source of information on the primary abiotic mineralogy for those stratigraphic intervals where oolitic and winnowed textures are absent.

Triassic micrites from the Western Balkanides were sampled in the field and studied by laboratory techniques to reveal their mineral precursors. The collected 44 samples cover discontinuously a stratigraphic interval extending from the Upper Olenekian to the Lower Carnian substage. The applied methods comprise SEM observations, electron microdiffraction determinations and bulk rock chemical analysis. The obtained petrographic data enable to distinguish two contrasting varieties of micrites. The first one is built up predominantly of "microspar" crystals with platy-like morphology on fracture surfaces, curvilinear boundaries and pitted faces on polished, etched sections. In some cases, the calcite crystals contain mineral inclusions with mostly needle habit, which were recognized as aragonitic by their microdiffraction pattern. The second variety is composed of blocky, truly "micrite" crystals (as observed on fracture surfaces), which display smooth faces and are inclusion-free on polished, etched sections. In terms of chemical composition the "microsparites" show distinctly higher mean Sr value compared to the "micrites".

Following the standard criteria proposed by Lasemi and Sandberg (1993) enables to infer aragonite-dominated precursor (ADP) for the "microsparites" and

(high-Mg) calcite-dominated precursor (CDP) for the "micrites", respectively. The fundamental differentiation between both rock varieties is based on the positive correlation of their microfabrics and geochemistry. Also, microtextural resemblance is established with respect to experimentally consolidated lime muds of differing primary mineralogy (Papenguth, 1991), as well as with respect to stabilized monomineralic aragonite or high-Mg calcite allochems and orthochems.

The geochemical characteristics of the recognized ADP and CDP micrites reveal similar modification style of the initial lime muds. Thus, Fe and Mn enrichment plus Sr depletion in the neomorphic calcite are established for both mineralogical varieties. These relationships together with variations in the Mg concentrations (enrichment in the ADP micrites and depletion in the CDP micrites) testify to stabilization in semi-closed diagenetic system either with the participation of meteoric water, or during marine burial. Meanwhile, certain deviations from the linear relationship on the scatter plots might be explained with different magnitude in the alteration of the initial elemental concentrations. In particular, the absence of distinct relationship between Sr and Mg may be a result from: mixed primary mineralogy (e. g. aragonite plus calcite), variable amounts of low- and high-Mg calcite in the former lime muds, presence of some pelitomorphous low-Sr aragonite from desintegration of mollusk shells, variable ratio between high-Mg calcite constituents with contrasting abiotic and biotic origin, or syndimentary alterations in the concentrations of the chemical elements controlled by the pore fluids. In summary, the Ca/Sr vs Mn scatter plot (Brand, Veizer, 1980) appears as most indicative for the particular diagenetic modification of all micrites (Fig. 1).

Stabilization of the aragonite-dominated muds must have proceeded through transformation of the original particles and their concurrent cementation by low-Mg calcite. Such mechanism could explain the preservation of relatively few aragonite relics in the newly formed calcite crystals in comparison with the sus-

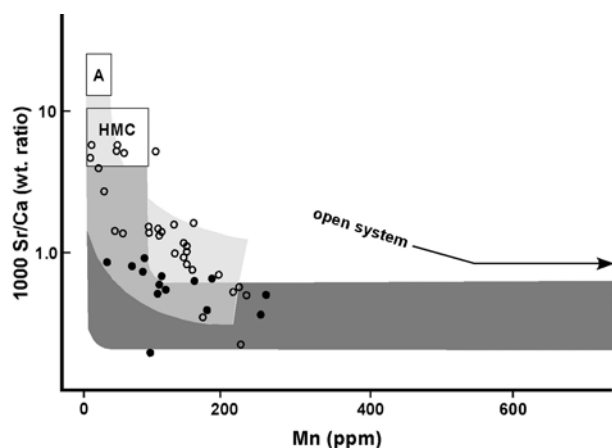


Fig. 1. Ca/Sr vs. Mn scatter plot for the studied micrites. Notes: The A and HMC fields outline the theoretical possible ranges of aragonite and high-Mg calcite in equilibrium with present-day seawater. Diagenetic trends for both phases (aragonite in light grey and high-Mg calcite in dark grey) with stabilization by meteoric water, as well as the “open system” field are from Brand and Veizer (1980).

pected abundance of aragonite needles in the precursor lime muds. Furthermore, this conclusion rules out the hypothesis for consolidation through aggrading neomorphism of already stabilized calcite micrites by means of multiple events of dissolution-precipitation. In this sense, solid evidence is the positive correlation between Sr content and mean crystal size for the respectively interpreted ADP and CDP micrites. In turn, the (high-Mg) calcite-dominated muds were most probably consolidated through incongruent dissolution and overgrowth cementation of the original grains, resulting in good preservation of the primary microfabric.

The studied micrites with inferred differing precursor mineralogy do not show specific relation to the particular depositional environments, which marked the evolution of the Triassic carbonate ramp. However, their stratigraphic distribution follows a well outlined trend. Thus, the ADP micrites occur in rocks of Late Olenekian to Middle Anisian age, while the CDP micrites are found only sporadically through this stratigraphic interval, but are autonomously represented in the Upper Anisian - Lower Carnian sequence. The mentioned trend closely follows the distribution of isochronic ooids in the same rocks (Chatalov, 2005). Such relationship makes the prevailing abiotic origin of the precursor lime muds quite probable. Evidence comes also from the Sr/Mg ratio of the CDP micrites, which plot closely around the line of abiotic calcite (Carpenter, Lohmann, 1992). In third place, the lime mudstones are devoid of fossils, including calcareous

algae, and also, they were deposited in shelf environments dominated by ooid formation, i. e. generally unsuitable for such organisms. Finally, internal micrite cement was found in some limestones from the same carbonate sequence. In this context, Knoll (2003) pointed out that lime mudstones were generated worldwide at least partly by whittings during the Early Triassic epoch as a result from the slow biota recovery after the Permian-Triassic mass extinction, which continued until Middle Triassic time.

If chemogenic deposition of lime mud is assumed as a major mechanism it must have been directly influenced by factors that control abiotic carbonate precipitation. In this connection, there are two basic hypotheses explaining the secular oscillations in the primary composition of abiotic carbonates during the Phanerozoic. One of them postulates that the major ion chemistry of seawater (i. e. the Mg/Ca ratio) was the leading factor (Hardie, 1996), while the second hypothesis speculates that most important were variable levels of atmospheric and oceanic $p\text{CO}_2$, which influenced the degree of seawater carbonate saturation (Mackenzie, Pigott, 1981). The obtained data on the primary mineralogy of Triassic marine micrites and ooids from the Western Balkanides conform to the secular trend of abiotic marine carbonate mineralogy during the Phanerozoic (Mackenzie, Pigott, 1981 and others). In particular, the Triassic period was a time of global “aragonite sea”, which according to the predicted model of Hardie (1996) extended from Early Permian to Middle Jurassic times. Non-skeletal carbonates were precipitated largely as aragonite and high-Mg calcite during this interval, i. e. similarly to the modern “aragonite sea”. According to Stanley et al. (2002) at ambient Mg/Ca mole ratios between 2 and slightly above 5, aragonite precipitates along with high-Mg calcite, but at ratios between ≈ 1 and ≈ 2 high-Mg calcite precipitates alone. Therefore, the established irreversible change from predominant aragonite to solely high-Mg calcite precipitation during the Middle Triassic epoch might be ascribed to the progressive decrease of seawater Mg/Ca ratio. Such decrease during the Triassic period is predicted (although being of different magnitude) by most modeled Phanerozoic curves (cf. Horita et al., 2002). The alternative critical control of $p\text{CO}_2$ is less probable at least for two reasons: lack of distinct trend for the whole Triassic period, which is compatible with the obtained results, and inconsistency between the different reconstructions of paleo- $p\text{CO}_2$ levels. However, the degree of sea-

water carbonate saturation might have been reduced by the global decrease of sea surface temperature during the Triassic period (Veizer et al., 2000). The same effect could have been caused by the change from elevated to normal salinity during Middle Anisian time in the epicontinental Triassic sea that existed in the present territory of NW Bulgaria (Chatalov, 2005). The intermittent precipitation of (high-Mg) calcite-dominated muds and ooids during the Late Olenekian - Middle Anisian interval might be explained with short-term changes either in the ambient Mg/Ca ratio, or the degree of seawater carbonate saturation. These mineralogical transitions were probably controlled by temperature and/or salinity fluctuations, but kinetic factors promoting or inhibiting the precipitation of one mineral should not be precluded, too. An alternative possibility is related to temporal and/or local variability in the supply of skeletal fine-grained material.

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The accomplished investigation confirms the conclusion that fine-grained lime sediments might preserve their relative differences (i. e. with respect to original composition) for a long time period due to their low permeability and probably due to their early lithification. Moreover, they could provide information on the primary abiotic carbonate mineralogy for those stratigraphic intervals lacking oolitic and winnowed sediments. Also, the mentioned evidence for predominant aragonite precursor of the “microsparites” testifies against their formation through aggrading neomorphism of already stabilized calcite micrites. Finally, it is demonstrated, similarly to other studies, that data on the Sr concentrations in ancient micrites should be interpreted with some caution when attempting to recognize their precursor mineralogy, and instead, microfabric features should be used as leading criterion.

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ТРИАСКИ МИКРИТИ ОТ ЗАПАДНИТЕ БАЛКАНИДИ: ДОКАЗАТЕЛСТВА ЗА ДОМИНИРАЩО АБИОГЕННО УТАЯВАНЕ НА ПЪРВИЧНИТЕ ВАРОВИТИ ТИНИ

Атанас Чаталов

Микритният матрикс във варовиците обикновено се разглежда като по-слабо надежден индикатор за първичната абиогенна карбонатна минералогия в сравнение с ооидите и ранните спойки. Въпреки това при наличието на достатъчно доказателства

подкрепящи физикохимично утаяване на първичната варовита тиня, древните микрити могат да се окажат единствения източник на такава информация при отсъствието на оолити и промити структури в даден стратиграфски интервал.

Триаски микрити от Западните Балканиди бяха детайлно изследвани чрез комбинирана лабораторна методика с цел доказване на техния първичен минерален състав. Вземите проби покриват стратиграфски интервал простиращ се от горнооленекския до долнокарнския подетаж. Получените петрографски данни показват наличието на две разновидности микрити. Първата е изградена от преобладаващи “микроспаритни” кристали с извити граници, надупчени стени и редки арагонитни включения. Втората разновидност е изградена почти изцяло от същински “микритни” кристали, с гладки стени и без включения. В химично отношение, “микроспаритите” се отличават със значително по-високо средно съдържание на стронций в сравнение с “микритите”. На базата на критериите предложени от Lasemi and Sandberg (1993), съответните две разновидности бяха интерпретирани като имащи арагонитно- и (магнезиално)калцитно-доминиран предшественик. Освен това те показват голямо сходство спрямо експериментално консолидирани варовити тини и стабилизирани мономинерални алохеми и ортохеми с първично арагонитен или магнезиалнокалцитен състав.

Геохимичните характеристики на микритите са показателни за стабилизация на първичните тинести утайки в полузатворена диагенетична система най-вероятно с участието на метеорни води (Фиг.1). Същевременно, отклонения от линейната зависимост на някои от диаграмите, съпоставящи съдържанията на стронций, магнезий, желязо и манган, могат да се обяснят с различна магнитуда в промяната на съответните елементи, както и редица допълнителни фактори (например, смесен минерален състав на бившите тини, променливо участие на първичен нискомагнезиален калцит, и други). Допуска се, че самата стабилизация е протекла едновременно чрез процеси на трансформация на метастабилните карбонатни фази и спояване на първичните пелитоморфни зърна посредством нискомагнезиален калцит. Важно доказателство в тази посока е позитивната корелация между стронциевото съдържание и средния кристален размер за съвкупността от двата типа микрити.

Стратиграфското разпределение на “микроспаритите” е ограничено до долнооленекско-средно-анизкия интервал. За разлика от тях, микритите с калцитно-доминиран предшественик присъстват там само спорадично, но са представени самостоятелно сред горноанизко-долнокарнските скали. Същевременно този тренд изцяло съответства на вертикалното разпределение на изохронните ооиди в разреза. Подобна корелация е възможен индикатор за абиогенен произход на първичните тини, като тази хипотеза се подкрепя и от други данни: съотношението Sr/Mg при микритите с калцитно-доминиран предшественик, липсата на фосилни (и в частност водораслови) останки в скалите, наличието на микритна спойка в някои асоцииращи промити структури, и други. Като косвено доказателство може да се разглежда и заключението на Knoll (1993), че вероятното масово физикохимично утаяване на варовити тини през ранно- и среднотриаската епоха е било свързано с бавното възстановяване на организмовия свят след масовото измиране в края на пермския период.

Един възможен контролиращ фактор върху установената темпорална смяна в минералния състав на абиогенните утайки се свежда до съотношението Mg/Ca в морската вода, чието постепенно намаляване през целия триаски период е отразено на повечето моделирани криви за фанерозоя. От друга страна, подобна промяна в съществуващото тогава глобално “арагонитно море” може да е била повлияна от устойчивия спад на планетарната температура, както и от локалната нормализация на солеността през средния аниз в епиконтиненталното море простиращо се на днешната територия на СЗ България. Следователно е допустимо тези два фактора да са предизвикали съответно намаляване в степента на карбонатно насищане на морската вода, което на свой ред е благоприятствало отлагането на магнезиален калцит вместо арагонит. На свой ред установените минераложки вариации през къснооленекско-средноанизкия интервал могат да се отдадат на флуктуации в температурата или солеността, без да се изключва критичното влияние на някои кинетични параметри, или дори временната и/или локална промяна в доставката на финозърнест материал с биогенен произход.