GEOLOŠKI ANALI BALKANSKOGA POLUOSTRVA
Volume 85 (1), July 2024, 117–128
–
https://doi.org/10.2298/GABP240218006R
Original scientific paper
Оригинални научни рада

Upper Miocene aragonite sediments of the Eastern Paratethys (Zheleznyi Rog section): whiting events or not?

Yuliana V. Rostovtseva[1]

Abstract. The upper Sarmatian and lower Maeotian unlithified aragonite sediments of the Zheleznyi Rog section (Taman Peninsula, Eastern Paratethys, Russia) were investigated by field observations and laboratory methods, including scanning electron microscopy, X-ray diffraction and isotope analyses. Aragonite sediments occur at separate intervals of the studied section, forming thin (millimeter-sized) interlayers with clays. These carbonate sediments consist almost entirely of crystals (individuals and twins) and aggregates of aragonite, ranging in size from 5 to 23 µm. It is assumed that the isotopic composition ($\delta^{13}C$ = 5.7 and 5.3‰, $\delta^{18}O$ = –2.4 and –2.8‰ for upper Sarmatian and lower Maeotian aragonites, respectively) reflects the sedimentation conditions, characterized by reduced basin salinity, increased surface water bioproductivity, and periods of aridization. Abiotic precipitation of these aragonites most likely occurred due to the action of triggering mechanisms, which could include planktonic algae blooms (e.g. diatoms). The obtained results do not contradict the hypothesis that the studied aragonites may be considered as sediments of whiting phenomenon.

Key words: *Aragonite sediments, upper Sarmatian, lower Maeotian, Zheleznyi Rog section, Eastern Paratethys.*

Апстракт. Горњосарматски и доњомеотски нелитификовани арагонитски седименти на профилу Железни Рог (Полуострво Таман, источни Паратетис, Русија) истраживани су теренским осматрањима и лабораторијским методама, укључујући скенирајућу електронску микроскопију, дифракцију X-зрака и анализу изотопа. Арагонитски седименти се на проучаваном профилу јављају у одвојеним интервалима, формирајући танке (милиметарске) прослојке са глинама. Ови карбонатни седименти се готово у потпуности састоје од кристала (индивидуалних и близанаца) и агрегата арагонита, величине од 5 до 23 µm. Претпоставља се да изотопски састав ($\delta^{13}C$ = 5.7 и 5.3‰, $\delta^{18}O$ = –2.4 и –2.8‰ за горњосарматске и доњомеотске арагоните, респективно) одражава услове седиментације, које карактерише смањен салинитет басена, повећана биопродуктивност површинских вода и аридни периоди. Абиотичко излучивање ових арагонита највероватније је настало услед деловања покретачких механизама, који би могли да укључују цветање планктонских алги (нпр. дијатомеја). Добијени резултати нису у супротности са хипотезом да се проучавани арагонити могу сматрати седиментима „белог феномена“.

Кључне речи: *Арагонитски седименти, горњи сармат, доњи меот, профил Железни Рог, источни Паратетис.*

[1] Geophysical Center of the Russian Academy of Sciences (GC RAS), Molodezhnaya Street 3, 119296 Moscow, Russia

Introduction

Whiting as a carbonate precipitation phenomenon refers to mysterious clouds of fine-grained calcium carbonate particles that drift in the water column and appear suddenly (Larson & Mylroie, 2014). These clouds can form patches, ranging in size from meters to kilometers (Dierssen et al., 2009) and extending up to tens of meters to a depth. The duration of these clouds can be from days to weeks (Shinn et al., 1989). It is assumed that whiting can start from a point source and expand over time to cover large areas due to tides and currents. Whiting events can occur in tropical and temperate waters, as well as in marine and lacustrine environments. Whiting events have been reported widely in lakes, including North America's Great Lakes (Barbiero et al., 2006; Watkins et al., 2013; Binding et al., 2015), Fayetteville Green Lake (Brunskill & Ludlam, 1969; Stanton et al., 2023), Otisco Lake (Effler & Johnson, 1987), and Lake Geneva (Many et al., 2022). In the marine environment, such events have been found in the waters of the Bahama Banks (Black, 1933; Shinn et al., 1989; Boss & Neumann, 1993; Bustos-Serrano et al., 2009; Larson & Mylroie, 2014; Yao et al., 2023), Florida coastal waters (Long et al., 2014, 2018), Adriatic Sea (Sondi & Juračić, 2010), and Persian (Arabian) Gulf (Wells & Illing, 1964; Morse & He, 1993; Shanableh et al., 2019, 2021). Whitings may consist of suspended carbonate minerals such as low- and high-magnesium calcite, and aragonite. The triggering mechanisms of whitings have continuously been debated. For example, three hypotheses have been proposed for whiting events in the Bahamas (Black, 1933; Shinn et al., 1989; Friedman et al., 1993): (1) resuspension of bottom sediments due to turbulent tidal flow or bottom-feeding fish, (2) abiotic precipitation from bank water, and (3) precipitation due to planktonic algal blooms. Whitings in modern environments are described in numerous publications; however, descriptions of the ancient sediments formed as a result of these events are still scarce. According to Turpin et al. (2011), the Middle Miocene sediments on the margin of the Great Bahama Bank contain aragonite needles associated with whiting phenomena.

In the Upper Miocene sediments of the Zheleznyi Rog section (Taman Peninsula, Eastern Paratethys, Russia), a series of thin layers (up to 2–3 mm thick) consisting of aragonite was identified (Rostovtseva, 2012; Popov et al., 2016). The aim of the current study is to investigate these aragonite sediments and to determine their origin, taking into account the possible influence of whiting events on their precipitation. Thin layers of aragonite, similar to the sediments studied here, were found in the Sarmatian Topola Formation of Northeastern Bulgaria (Koleva-Rekalova, 1994, (packet 2); Yaneva et al., 2019), as well as in the upper Sarmatian of the Northwestern Bulgaria and the Maeotian of the Eastern Serbia (Petrović & Koleva-Rekalova, 2009).

Material and methods

Geological setting of the study area and sampling sites

The Zheleznyi Rog section is located on the Black Sea coast of Taman Peninsula (N45°11'06.1" E36°74'48.4") and comprises well-exposed upper Sarmatian-Kimmerian sediments. Since its first description by Andrusov (1903), this geological section has been studied by palaeontological, paleomagnetic and lithological methods (Trubikhin, 1989; Filippova, 2002; Krijgsman et al., 2010; Vasiliev et al., 2011; Radionova & Golovina, 2011; Radionova et al., 2012; Rostovtseva, 2012; Chang et al., 2014; Popov et al., 2016).

In the Zheleznyi Rog section, thin layers of aragonite were found in the upper Sarmatian (Khersonian Substage) and the lower Maeotian (Bagerovian Substage, Fig. 1).

The thickness of the upper Sarmatian sediments exposed in the Zheleznyi Rog section is about 120–130 m. In the lower part of these sediments, an alternation of clayey and carbonate layers 0.1–0.2 m thick occurs. In the upper part of the upper Sarmatian, weakly diatomaceous, weakly calcareous and non-calcareous clays containing thin layers of silt are observed. At 75–80 m below the Sarmatian/Maeotian boundary, these clays contain a 5-meter-thick layer with several horizons (up to 1–1.5 m) of thin (millimeter-sized) alternation of dark gray clayey and whitish aragonite sediments. The first batch of

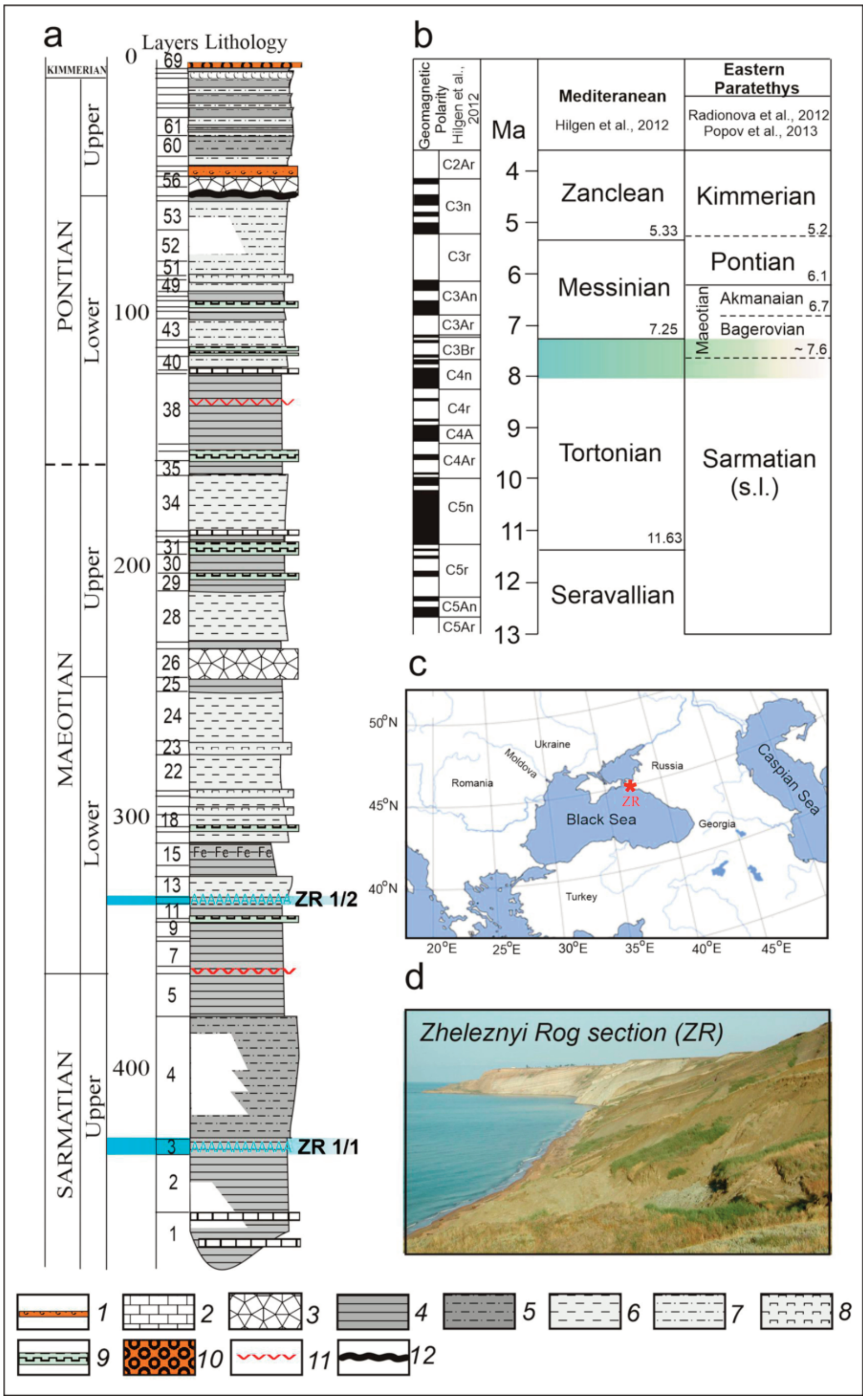

*Fig. 1. The Zheleznyi Rog (ZR) section: **a)** stratigraphic column with intervals of aragonite sediments (ZR 1/1 and ZR 1/2), **b)** correlation scheme of the Eastern Paratethys and the Mediterranean, with the position of the mapped interval, **c)** geographical position and **d)** panoramic view of the study area. Lithology: (1) detrital limestones with Congeria subrhomboidea, (2) carbonates, (3) clay breccia, (4–7) clay: (4) slightly diatomaceous, (5) silty, (6) calcareous, and (7) calcareous and silty, (8) clayey diatomite, (9) diatomite, (10) iron ore, (11) volcanic ash, (12) eroded boundary. Layer-by-layer description of the Zheleznyi Rog section according to Rostovtseva (2012) and Popov et al. (2016).*

samples (ZR1/1, about 10 samples) was collected from this level. The upper Sarmatian clays, overlying the layer with aragonite sediments, contain diatom assemblage with *Achnanthes brevipes, A. longipes*, brackish-water *Actinocyclus krasskei, A. gorbunovii, Rhopalodia, Surirella* and some marine species of the genus *Actinoptychus* and *Thalassiosira decipiens* (Popov et al., 2016). These clays accumulated in the basin under the influence of the input of deltaic distal suspended load due to the fluvial runoff of river paleo-Donets or paleo-Don (Popov et al., 2004 (map 8); Popov et al., 2016).

The thickness of lower Maeotian sediments in the Zheleznyi Rog section is about 105–119 m. These sediments are mainly clays, with sporadic diatomites. At 13–14 m above the Sarmatian/Maeotian boundary, these clays contain a 2-meter-thick layer with thin (millimeter-sized) alternation of dark gray clayey and whitish aragonite sediments. The second batch of samples (ZR1/2, about 8 samples) was collected from this layer.

In the lower Maeotian clays located below and above the layer with aragonite sediments (Layers 11 and 14-16 of the Zheleznyi Rog section, respectively), the following associations of brackish-water and marine diatoms were found: *Paralia sulcata*, *Thalassiosira baltica*, *Grammatophora marina*, *Actinocyclus octonarius* and *Achnanthes brevipes*, *Surirella maeotica*, *Diploneis bombus* (Popov et al., 2016). These sediments were formed during marine transgression that began in early Maeotian.

According to Popov et al. (2016, 2019), the upper Sarmatian and lower Maeotian sediments of the Zheleznyi Rog section accumulated in relatively deep-water conditions (at least 75–100 m) in the axial part of the Kerch–Taman trough. The studied aragonite layers of the upper Sarmatian and the lower Maeotian are represented by unlithified sediments. These layers were first found in 1996, during the layer-by-layer description of the Zheleznyi Rog section (Rostovtseva, 2012).

Methods

In study of aragonite sediments of the upper Sarmatian and lower Maeotianin Zheleznyi Rog section, field observations (layer-by-layer description of sediments, collection of macrofaunal remains to determine age, sampling of the rocks, photographing of the studied layers and section) were used.

The most representative 8–10 samples were analyzed by laboratory methods. The samples were analyzed using a Rigaku MiniFlex 600 X-ray diffractometer with Cu Kα (1.5406 Å) radiation, in order to determine their mineralogical composition and crystal structure. Continuous scan was conducted, typically for 2θ angles from 3.00 up to 70.00°, with a speed of 4.00°/min. The quantitative mineral composition was obtained by comparing the intensities of the corresponding reflections. The samples were further examined using a scanning electron microscope (SEM). The SEM used in this study was a JEOL JSM IT-500 with the Oxford Instrument INCA (v21) software.

The stable isotopes study of carbon and oxygen in aragonites was performed using a Thermo Scientific Delta V Advantage Isotope Ratio Mass Spectrometer. Dried ground samples were treated with polyphosphoric acid (105% H_3PO_4 basis) on a Thermo Scientific Gas Bench II sample preparation line, connected directly to the mass spectrometer. The abundance of stable isotopes of carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) in carbon dioxide released as a result of the reaction of carbonates with the acid was analyzed. The measurement accuracy was controlled using the international standard NBS-19. The $\delta^{13}C$ and $\delta^{18}O$ values are given against Vienna Peedee Belemnite (VPDB) standard; the accuracy was ±0.1‰. Each sample was analyzed twice.

All these laboratory studies were carried out at the Geological Faculty of the Lomonosov Moscow State University (MSU).

Results

In the Zheleznyi Rog section, the studied aragonite layers are characterized by predominantly sharply defined, more or less planar bottom and top surfaces and are traced along the strike. These layers are generally about 1–3 mm thick and can be considered as laminae. Aragonite laminae are whitish and form intervals of rhythmic alternation with mm-thick layers of clay.

According to the X-ray diffraction analysis, the studied upper Sarmatian aragonite laminae (sample ZR 1/1) contain aragonite (87%), calcite (5%) and quartz (8%). Aragonite (62%), quartz (15%), plagioclase (8%) and jarosite (15%) were identified in the studied lower Maeotian aragonite laminae (sample ZR 1/2), with quartz and plagioclase being clastic components and jarosite as a secondary mineral.

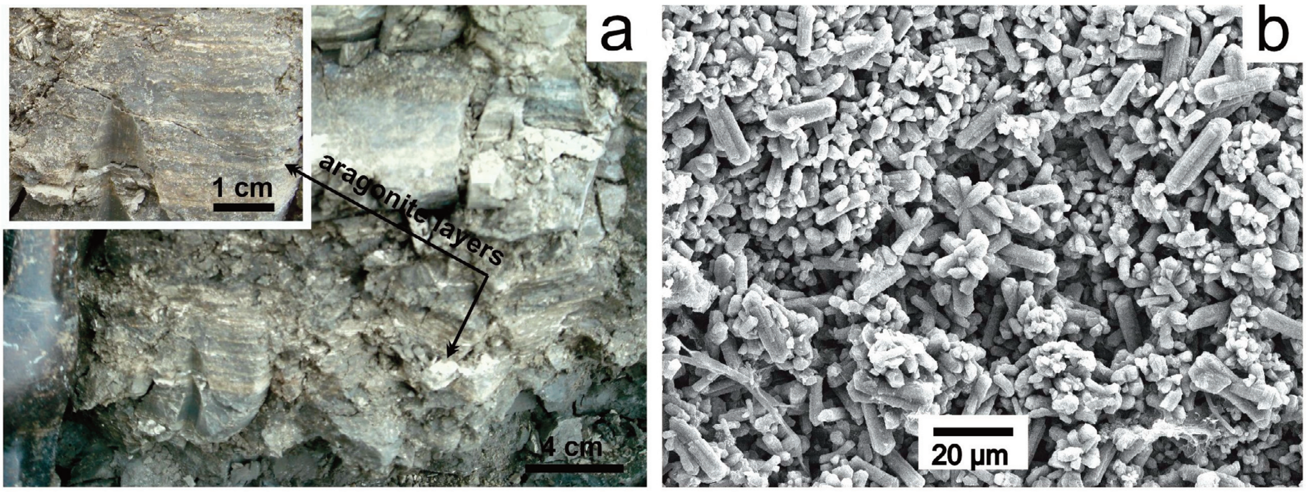

Fig. 2. *Upper Sarmatian aragonite sediments of the Zheleznyi Rog section:* ***a)*** *layers of aragonite sediments,* ***b)*** *SEM image of aragonite crystals.*

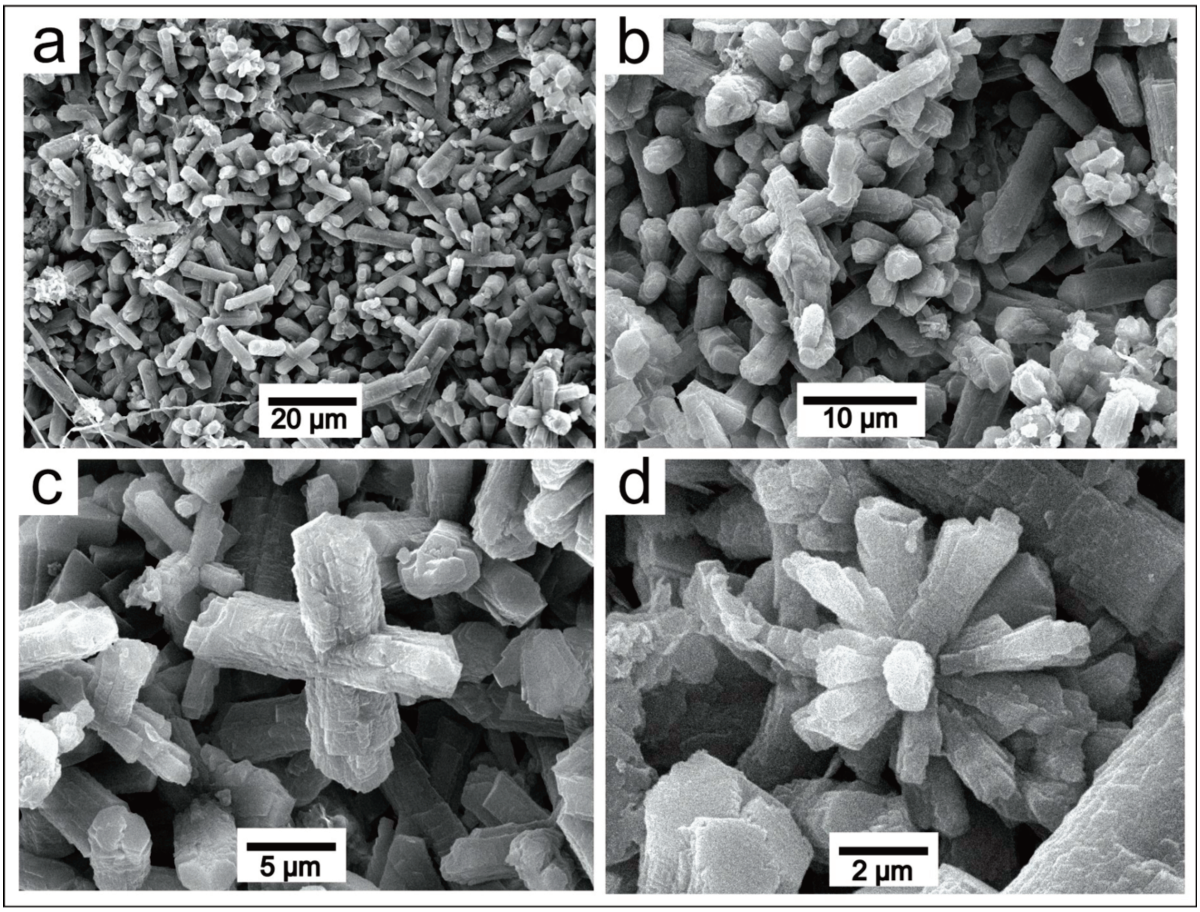

Fig. 3. *SEM images of the upper Sarmatian aragonite sediments of the Zheleznyi Rog section:* ***a)*** *aragonite needles,* ***b)*** *needle and twinned aragonite crystals,* ***c)*** *simple twinned aragonite crystal,* ***d)*** *aragonite crystal cluster.*

The SEM data show that the studied aragonites of the upper Sarmatian (ZR 1/1) consist of needle-shaped and twinned aragonite crystals, as well as aragonite clusters (Figs. 2, 3). The size of these crystals varies from 5–6 to 23 μm. The studied aragonites of the lower Maeotian (ZR 1/2) consist of aggregates and crystals (individuals and clusters)

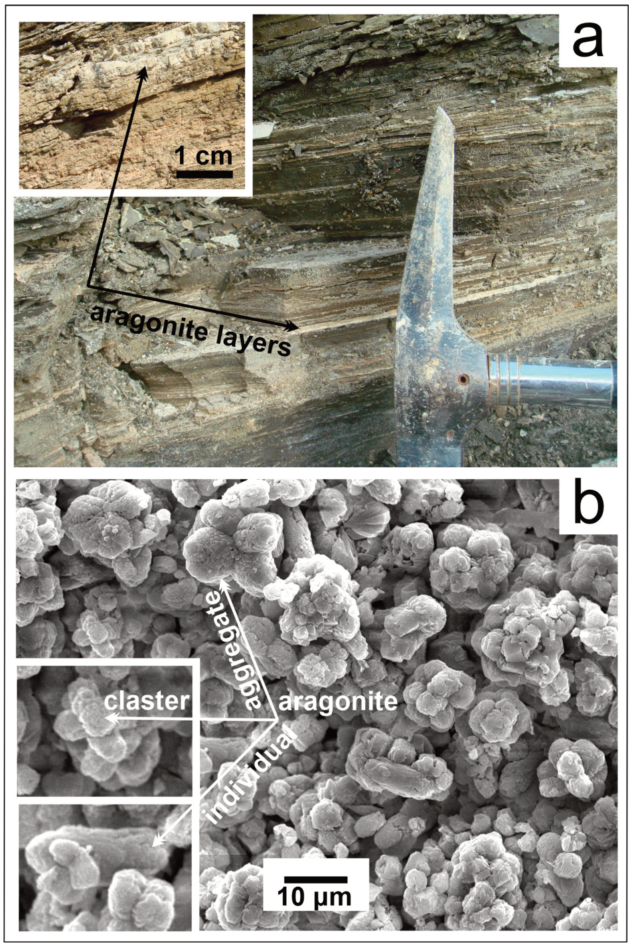

*Fig. 4. Lower Maeotian aragonite sediments of the Zheleznyi Rog section: **a)** layers of aragonite sediments, **b)** SEM image of aragonite sediments.*

of aragonite (Fig. 4). Needle-shaped aragonite crystals are less common in these sediments. Aragonite crystals and aggregates typically range in size from 5–6 to 15 μm. No obvious signs of mechanical redeposition or biogenic origin of the studied aragonite crystals were found. The crystals are distributed chaotically, with no preferred orientation. Biogenic components (diatoms, nannoplankton etc.) were not identified in these sediments. Aragonites from the upper Sarmatian (ZR 1/1) and the lower Maeotian (ZR 1/2) show values $\delta^{13}C$ = 5.7 ‰, $\delta^{18}O$ = –2.4‰ and $\delta^{13}C$ = 5.3 ‰, $\delta^{18}O$ = –2.8 ‰, respectively.

Discussions

Initially, the following main mechanisms of formation of the studied aragonite layers can be considered: 1) mechanical redeposition, 2) biogenic processes, 3) diagenetic origin and 4) abiogenic precipitation.

The idiomorphic forms of aragonite and the absence of signs of mechanical transport of these particles (i.e. no clasts of aragonite crystals) in the studied layers do not allow them to be classified as mechanically redeposited sediments. Also, no biogenic processes could be identified in the genesis of these sediments, since no particles of aragonite with biogenic morphology were found. The absence of oriented crystal growth, extent of aragonite layers along the strike, and the sporadic development in the studied sedimentary succession do not confirm a possible initial diagenetic origin of this carbonate mineral. The abiotic precipitation of the studied aragonite crystals due to the action of triggering mechanisms appears to be the most likely. Triggering mechanisms could include planktonic algae blooms and/or sudden changes in water geochemistry.

At the beginning of the Sarmatian, Eastern Paratethys was part of a vast basin that extended from the Alps to the Aral Sea. This basin was characterized by marine conditions in the early Sarmatian with a salinity about 14–18‰ (Illjina et al., 1976; Nevesskaya et al., 1986, 2003, 2005; Popov et al., 2004). A regression caused an exposure of marginal parts of the basin, as well as a significant decrease of salinity down to 4–9‰ at the end of the Sarmatian (Iljina et al., 1976; Nevesskaya et al., 1986, 2003, 2005). In the late Sarmatian, the Eastern Paratethys was mainly isolated. Associations of the most euryhaline groups of mollusks, foraminifera and ostracods were widespread during this period. In the Taman upper Sarmatian, phytoplankton has many freshwater species, but the occasional presence of marine taxa indicates incomplete closure of the basin (Radionova et al., 2012).

In some places, including of the Zheleznyi Rog section, water stratification was observed in this paleobasin (Popov et al., 2019). Clays containing freshwater organic-walled phytoplankton and diatom algae, as well as with admixture of sand and silt grains related to the fluvial runoff from the East European Platform, were accumulated in the depressions of the Taman region (Fig. 5). In this part of the Eastern Paratethys, the basin became distinctly shallow and progradation of deltaic systems occurred (Rostovtseva, 2012). The influence of diatom sedimentation became more noticeable. According to Popov et al. (2016), in the late Sarmatian, benthos probably did no tinhabit this part of the basin due to the unfavorable gas regime.

Maeotian in the Zheleznyi Rog section, the mollusks represented by imprints of ribs of *Cerastoderma* were found only in a 2-meter layer of the clays located 11 m below the studied lower Maeotian aragonites. According to Popov et al. (2016), the poorly aerated grounds were occasionally occupied by *Cerastoderma* sp. in the Eastern Paratethys. Marine diatom species *Thalassiosira coronifera* and *T. baltica* appear at the base of the Zheleznyi Rog Maeotian (Popov et al., 2016). Diatom sedimentation occurred in this part of the paleobasin. According to the ratio of marine and brackish-water taxa of bivalves, the late Sarmatian and early Maeotian basins belong to mixo-mesohaline (semi-marine) type seas of the Eastern Paratethys (Nevesskaya et al., 2005).

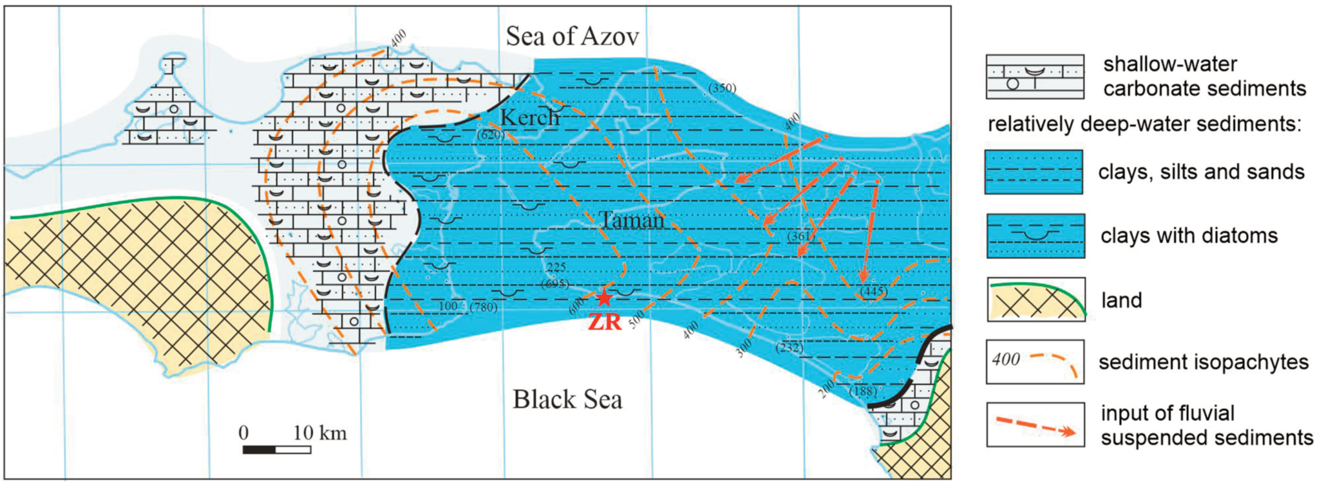

Fig. 5. *Late Sarmatian depositional environments in the Taman Region (according to Rostovtseva, 2012; ZR - Zheleznyi Rog section).*

The Maeotian started with a marine transgression, which increased salinity back to 18‰ and flooded marginal areas. In the early Maeotian, relatively deep-water conditions existed especially in the axial part of the Kerch–Taman trough located within the Taman Peninsula. In the Zheleznyi Rog section, the action of the Maeotian transgression was accompanied by the accumulation of clays and diatomaceous sediments. Taman depressions with large depths were characterized by oxygen-depleted conditions due to the stable stratification of the waters (Popov et al., 2019). At the beginning of the Maeotian, ecological conditions remained unfavorable for macrobenthic mollusk fauna in the Zheleznyi Rog section (Popov et al., 2016). In the lower part of the lower

Based on these data, it is suggested that the presence of geochemical barriers, changes in salinity (mixing of sea and fresh waters), water stratification, and planktonic algae blooms (e.g. diatoms) could be the triggers for the appearance of fine-grained suspension of carbonate particles in the water column and episodic abiogenic precipitation of aragonite during the late Sarmatian and early Maeotian in the studied part of the Eastern Paratethys. Intense planktonic algae blooms can contribute to a decrease in the dissolved carbon dioxide content in water, which is favorable for carbonate precipitation (Stanton et al., 2023).

The stable isotopes values of carbon ($\delta^{13}C$ = 5.7 and 5.3‰) and oxygen ($\delta^{18}O$ = -2.4 and -2.8‰) of the studied aragonites in the upper Sarmatian and lower Maeotian sediments are close, indicating the similarity in the genesis of these minerals. According to Koleva-Rekalova & Georgiev (2013), unlithified aragonite sediments of the Sarmatian Topola Formation of the Northeastern Bulgaria shows values $\delta^{13}C$ = 4.41‰, $\delta^{18}O$ = –2.92‰ (sample 217), $\delta^{13}C$ = 3.74‰, $\delta^{18}O$ = –1.49‰ (sample 238) and $\delta^{13}C$ = 4.20‰, $\delta^{18}O$ = –0.28‰ (sample 250). These sediments, in the same manner as the studied aragonites, are characterized by positive values of $\delta^{13}C$ and negative values of $\delta^{18}O$. The Topola Formation corresponds to the upper part of the Bessarabian and the lower part of the Khersonian Substages of the Sarmatian (Kojumdgieva & Popov, 1988). The studied aragonites are comparable in $\delta^{13}C$ values to the whiting sediments of Great Bahama Bank, differing from them in lower $\delta^{18}O$ values (Bustos-Serrano et al., 2009; Fig. 6). The enrichment in the heavy carbon isotope of the studied aragonites may be associated with an increased surface water bioproductivity and/or an intensification of evaporitic processes. The negative values of $\delta^{18}O$ may reflect climate warming and/or decreased basin salinity due to the influence of freshwater inputs. During the late Miocene, there was a global cooling trend (known as the Late Miocene Cooling), which was reflected in the sedimentary environments of the Eastern Paratethys (Syabryaj et al., 2007; Rostovtseva & Kuleshov, 2016). A study of spores and pollen in the Zheleznyi Rog section showed that at the end of the Sarmatian and at the beginning of the Maeotian, the climate was warm-temperate with periodic aridization (Fillipova, 2002; Popov et al., 2016). Considering the climatic conditions and salinity of the Eastern Paratethys during the late Sarmatian and early Maeotian, the depletion of $\delta^{18}O$ in the studied aragonites may be explained by the low salinity of the paleobasin.

In the Black Sea, which belonged to the Euxine part of the Eastern Paratethys in the past, the Holocene organic-rich sediments (Holocene Unit 2) contain several aragonite laminae (Koleva-Rekalova et al., 2018). These laminae are composed of fine-grained (less than 0.02 mm) needle-shaped crystals and aggregates of aragonite. Aragonite aggregates have a center around which crystals are radially arranged. According to Koleva-Rekalova et al. (2018), these aragonite sediments were initially in situ precipitated in the shallow coastal and shelf settings as a result of the Black Sea Early Holocene regression and under arid conditions. The organic-rich sediments of the Holocene Unit 2 accumulated in the marine environment. These Holocene aragonite laminae are similar in particle shape and thickness to the studied Upper Miocene aragonite sediments. The whitings of the Great Bahama Bank also consist of a combination of micron-scale aragonite needles (with rectangular or hexagonal shape) and aggregations of these needles (Shinn et al., 1989; Dierssen et al., 2009).

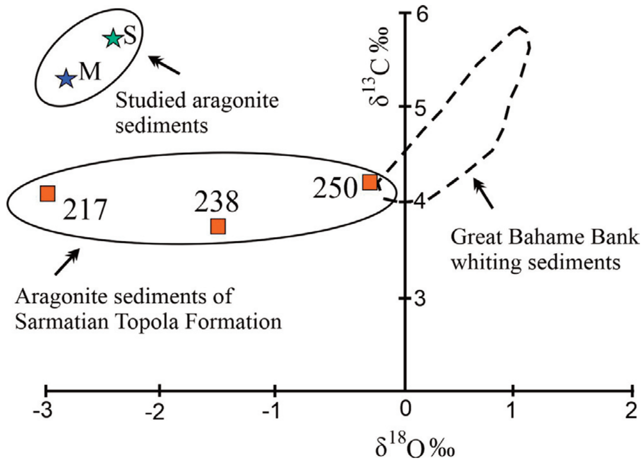

Fig. 6. *$\delta^{13}C$ versus $\delta^{18}O$, relative to the PDB standard, of the studied upper Sarmatian (S) and lower Maeotian (M) aragonite sediments, aragonite sediments of the Sarmatian Topola Formation (according to Koleva-Rekalova & Georgiev, 2013; № samples: 217, 238, 250) and Great Bahama Bank whiting sediments (according to Bustos-Serrano et al., 2009).*

Water stratification and oxygen depletion in bottom waters could have been favorable for preserving the studied aragonite laminae in the upper Sarmatian and lower Maeotian sediments of the Zheleznyi Rog section. In the late Sarmatian and the early Maeotian, benthos probably did not inhabit this part of the basin because of an unfavorable gas regime (Popov et al., 2016). The difference in the morphology of aragonite crystals/aggregates between ZR 1/1 and ZR 1/2 could arise from: (1) original differences in depositional environments (oxicity, salinity, stability of physicochemical parameters, etc.); (2) secondary transformation due to the weathering of pyrite in clayey laminae and formation of jarosite (in this case, aragonite laminae may serve as a geochemical barrier for acidic sulfate solutions).

Taking into account the peculiarities of crystal growth, it is assumed that idiomorphic aragonite crystals, predominant in the studied sediments of the upper Sarmatian, were formed at very low supersaturation. The lower Maeotian aragonite sediments containing predominantly aragonite aggregates were formed at higher supersaturation. The higher supersaturation of surface waters during the formation of lower Maeotian aragonites could be influenced by an increase in Mg/Ca ratio caused by the development of marine transgression at that time. In the studied part of the Zheleznyi Rog section, the rhythmic alternation of clays and aragonites indicates a periodicity in the accumulation of carbonate sediments, which may be associated with seasonal changes in depositional conditions. The accumulation of these aragonites most likely occurred due to a combination of several factors. These sediments are very important archive in the geological record for reconstructing paleogeographic conditions. Based on the obtained results, the studied aragonites of the Zheleznyi Rog section may be the products of phenomena known as whiting events.

Conclusions

In the study of aragonite sediments of the upper Sarmatian and lower Maeotian in the Zheleznyi Rog section (Taman Peninsula, Eastern Paratethys), field observations and laboratory methods (SEM, X-ray diffraction and isotope analyses) were used. These aragonite sediments are present at certain intervals of the section, characterized by thin (mm-sized) alternation of clayey and carbonate layers. These carbonate sediments consist almost entirely of crystals and aggregates of aragonite, ranging in size from 5 to 23 μm. Aragonites show positive values of $\delta^{13}C$ and negative values of $\delta^{18}O$, which reflects the conditions of accumulation of these sediments, characterized by reduced salinity of the basin, increased surface water bioproductivity and intensification of evaporitic processes. The stratification of the basin waters and the unstable gas regime of bottom conditions favored the preservation of aragonites, the precipitation of which was most likely controlled by periodic (seasonal) changes in sedimentary settings. The influence of the input of fresh water at the end of the Sarmatian (with salinity changing from 14–18‰ to 4–9‰) and the input of sea water at the beginning of the Maeotian (with salinity changing from 4–9‰ to 18‰) in the studied part of the Eastern Paratethys may have generally contributed to the conditions for aragonite precipitation. It is assumed that the aragonites are formed due to abiotic precipitation triggered by various mechanisms, including planktonic algal blooms and/or variability of geochemical conditions. It is suggested that the studied aragonites may represent sediments of mysterious whiting events, indicating a specific combination of various factors.

Acknowledgments

This work was funded by budgetary funding of the Geophysical Center of RAS, adopted by the Ministry of Science and Higher Education of the Russian Federation (project 075-00764-22-00). The author is grateful to E. Koleva-Rekalova for interesting research on Sarmatian rocks in Bulgaria, which served as an additional motivation for studying the aragonites of the Zheleznyi Rog section in the Taman region. The author would like to thank two anonymous reviewers whose suggestions helped to improve the manuscript.

References

Andrusov, N. 1903. Geological research at the Taman Peninsula. *Materials for Geology of Russia*, 21 (2): 257–383.

Barbiero, R.P., Tuchman, M.L. & Millard, E.S. 2006. Post-dreissenid increases in transparency during summer stratification in the offshore waters of Lake Ontario: Is a reduction in whiting events the cause? *Journal of Great Lakes Research*, 32 (1): 131–141.

Binding, C.E., Greenberg, T.A., Watson, S.B., Rastin, S. & Gould, J. 2015. Long term water clarity changes in

North America's Great Lakes from multi-sensor satellite observations. *Limnology and Oceanography*, 60 (6): 1976–1995.

Black, M. 1933. The precipitation of calcium carbonate on the Great Bahama Bank. *Geological Magazine*, 70 (10): 455–466.

Boss, S.K. & Neumann, A.C. 1993. Physical versus chemical processes of "whiting" formation in the Bahamas. *Carbonates and Evaporites*, 8 (2): 135–148.

Brunskill, G.J. & Ludlam, S.D. 1969. Fayetteville Green Lake, New York. I. Physical and Chemical Limnology. *Limnology and Oceanography*, 14 (6): 817–829.

Bustos-Serrano, H., Morse, J.W. & Millero, F.J. 2009. The formation of whitings on the Little Bahama Bank. *Marine Chemistry*, 113 (1-2): 1–8.

Chang, L., Vasiliev, I., van Baak, C., Krijgsman, W., Dekkers, M.J., Roberts, A.P., Fitz Gerald, J.D., van Hoesel, A. & Winklhofer, M. 2014. Identification and environmental interpretation of diagenetic and biogenic greigite in sediments: a lesson from the Messinian Black Sea. *Geochemistry, Geophysics, Geosystems*, 15 (9): 3612–3627.

Dierssen, H.M., Zimmerman, R.C. & Burdige, D.J. 2009. Optics and remote sensing of Bahamian carbonate sediment whitings and potential relationship to wind-driven Langmuir circulation. *Biogeosciences*, 6 (3): 487–500.

Effler, S.W. & Johnson, D.L. 1987. Calcium carbonate precipitation and turbidity measurements in Otisco Lake, New York. *Journal of the American Water Resources Association*, 23 (1): 73–79.

Filippova, N.Yu. 2002. Spores, pollen, and organic-walled phytoplankton from Neogene deposits of the Zheleznyi Rog reference section (Taman' Peninsula). *Stratigraphy and Geological Correlation*, 10 (2): 176–188.

Friedman, G.M., Robbins, L.L. & Blackwelder, P.L. 1993. Biochemical and ultrastructural evidence for the origin of whitings: A biologically induced calcium carbonate precipitation mechanism: Comment and reply. *Geology*, 21 (3): 287–288.

Hilgen, F.J., Lourens, L.J. & Van Dam, J.A.2012. The Neogene Period. *In*: Gradstein, F., Ogg,J., Schmitz, M. & Ogg, G. (Eds.).*A Geological Time Scale 2012*- 2 volume book. Cambridge University Press, 923–979.

Iljina, L.B., Nevesskaya, L.A. & Paramonova, N.P. 1976. *Patterns of the mollusk development in brackish sea basins of Eurasia*. Paleontological Institute of the USSR Academy of Sciences, Nauka, 288 pp.

Kojumdgieva, E. & Popov, N. 1988. Lithostratigraphy of the Neogene sediments in Northwestern Bulgaria. *Palaeontology, stratigraphy and lithology,* 25: 3–25.

Koleva-Rekalova, E. 1994. Sarmatian aragonite sediments in Northeastern Bulgaria - origin and diagenesis. *Geologica Balcanica*, 24 (5): 47–64.

Koleva-Rekalova, E. & Georgiev, V. 2013. Isotope study ($\delta^{13}C$ and $\delta^{18}O$) of the Sarmatian aragonite sediments from Northeast Bulgaria. *In*: Ognjanova-Rumenova, N., Yaneva, M. & Nikolov, G. (Eds.). *The Fifth International Workshop on the Neogene from Central and South-Eastern Europe, 16–20 May, Varna, Bulgaria*, *Abstracts Volume*, Bulgarian Academy of Sciences, Sofia, 26–27.

Koleva-Rekalova, E., Genov, I. & Slavova, K. 2018. Aragonite in the Holocene sediments of cores EUXRo01-1 and EUXRo03-3 from the NW Black Sea slope. *Comptes rendus de l'Académie Bulgare des Sciences*, 71 (7): 930–936.

Krijgsman, W., Stoica, M., Vasiliev, I. & Popov, V.V. 2010. Rise and fall of the Paratethys Sea during the Messinian Salinity Crisis. *Earth and Planetary Science Letters*, 290: 183–191.

Larson, E.B. & Mylroie, J.E. 2014. A review of whiting formation in the Bahamas and new models. *Carbonates and Evaporites*, 29: 337–347.

Long, J., Hu, C. & Robbins, L. 2014. Whiting events in SW Florida coastal waters: A case study using MODIS medium-resolution data. *Remote Sensing Letters*, 5 (6): 539–547.

Long, J.S., Hu, C. & Wang, M. 2018. Long-term spatio-temporal variability of southwest Florida whiting events from MODIS observations. *International Journal of Remote Sensing*, 39 (3): 906–923.

Many, G., Escoffier, N., Ferrari, M., Jacquet, P., Odermatt, D., Mariethoz, G., Perolo, P. & Perga, M.-E. 2022. Long-term spatiotemporal variability of whitings in Lake Geneva from multispectral remote sensing and machine learning. Remote Sensing, 14 (23), 6175.

Morse, J.W. & He, S. 1993. Influences of T, S and PCO_2 on the pseudo-homogeneous precipitation of $CaCO_3$ from seawater: Implications for whiting formation. *Marine Chemistry*, 41 (4): 291–297.

Nevesskaya, L.A., Goncharova, I.A., Ilyina, L.B., Paramonova, N.P., Popov, S.V., Babak, E.V., Bagdasarian, K.G. & Voronina, A.A. 1986. *The history of the Neogene Paratethys mollusk*. Paleontological Institute of the USSR Academy of Sciences, Nauka, 208 pp.

NEVESSKAYA, L.A., GONCHAROVA, I.A., ILYINA, L.B., PARAMONOVA, N.P. & KHONDKARIAN, S.O. 2003. The Neogene stratigraphic scale of the Eastern Paratethys. *Stratigraphy and Geological Correlation*, 11 (2): 105–127.

NEVESSKAYA, L.A., GONCHAROVA, I.A. & ILYINA, L.B. 2005. Types of Neogene marine and nonmarine basins exemplified by the Eastern Paratethys. *Paleontological Journal*, 39 (3): 227–235.

PETROVIĆ, S. & KOLEVA-REKALOVA, E. 2009. Maeotian and Upper Sarmatian (Chersonian) laminated aragonite-clayey sediments: Examples from Eastern Serbia and Northwestern Bulgaria. *In*: NAKOV, R. (Ed.). *Proceedings of the National Conference with international participation "Geosciences 2009".* Bulgarian Geological Society, 71–72.

POPOV, S.V., AKHMETIEV, M.A., GOLOVINA, L.A., GONCHAROVA, I.A., RADIONOVA, E.P., FILIPPOVA, N.Y. & TRUBICHIN, V.M. 2013. Neogene regiostage stratigraphic scale of the South Russia: current state and perspectives. *In*: FEDONKIN, M.A. (Ed.). *General Stratigraphic Scale of Russia: Current State and Ways of Perfection*. Geological Institute of RAS, Moscow, 356–360.

POPOV, S.V., RÖGL, F., ROZANOV, A.Y., STEININGER, F.F., SHERBA, I.G. & KOVAC, M. 2004. *Lithological–Paleogeographic maps of Paratethys. 10 maps. Late Eocene to Pliocene*. Courier Forschungsinstitut Senckenberg, 1–46.

POPOV, S.V., ROSTOVTSEVA, YU.V., FILLIPPOVA, N.YU., GOLOVINA, L.A., RADIONOVA, E.P., GONCHAROVA, I.A., VERNYHOROVA, YU.V., DYKAN, N.I., PINCHUK, T.N., ILJINA, L.B., KOROMYSLOVA, A.V., KOZYRENKO, T.M., NIKOLAEVA, I.A. & VISKOVA, L.A. 2016. Paleontology and stratigraphy of the Middle–Upper Miocene of the Taman Peninsula: Part 1. Description of key-sections and benthic fossil groups. *Paleontological Journal*, 50 (10): 1039–1206.

POPOV, S.V., ROSTOVTSEVA, YU.V., PINCHUK, T.N., PATINA, I.S. & GONCHAROVA, I.A. 2019. Oligocene to Neogene paleogeography and depositional environments of the Euxinian part of Paratethys in Crimean-Caucasian junction. *Marine and Petroleum Geology*, 103: 163–175.

RADIONOVA, E.P. & GOLOVINA, L.A. 2011. Upper Maeotian-lower Pontian "transitional strata" in the Taman Peninsula: stratigraphic position and paleogeographic interpretation. *Geologica Carpathica*, 62 (1): 77–90.

RADIONOVA, E.P., GOLOVINA, L.A., FILIPPOVA, N.YU., TRUBIKHIN, V.M., POPOV, S.V., GONCHAROVA, I.A., VERNIGOROVA, YU.V. & PINCHUK, T.N. 2012. Middle-Upper Miocene stratigraphy of the Taman Peninsula, Eastern Paratethys. *Central European Journal of Geosciences*, 4 (1): 188–204.

ROSTOVTSEVA, YU.V. 2012. *Sedimentogenesis in the basins of the Middle and Late Miocene of the Eastern Paratethys (stratotype Kerch–Taman region)*. Unpubl. PhD Thesis, Faculty of Geology, Lomonosov Moscow State University, 371 pp.

ROSTOVTSEVA, YU.V. & KULESHOV, V.N. 2016. Carbon and oxygen stable isotopes in the Middle-Upper Miocene and Lower Pliocene carbonates of the Eastern Paratethys (Kerch-Taman Region): palaeoenvironments and post-sedimentation changes. *Lithology and Mineral Resources,* 51 (5): 333–346.

SHANABLEH, A., AL-RUZOUQ, R., GIBRIL, M.B.A., FLESIA, C. & AL-MANSOORI, S. 2019. Spatiotemporal mapping and monitoring of whiting in the semi-enclosed gulf using Moderate Resolution Imaging Spectroradiometer (MODIS) time series images and a generic ensemble tree-based model. *Remote Sensing*, 11 (10): 1193.

SHANABLEH, A., AL-RUZOUQ, R., GIBRIL, M.B.A., KHALIL, M.A., AL-MANSOORI, S., YILMAZ, A.G., IMTEAZ, M.A. & FLESIA, C. 2021. Potential factors that trigger the suspension of calcium carbonate sediments and whiting in a semi-enclosed gulf. *Remote Sensing*, 13 (23): 4795.

SHINN, E.A., STEINEN, R.P., LIDZ, B.H. & SWART, P.K. 1989. Whitings, a sedimentologic dilemma. *Journal of Sedimentary Research*, 59 (1): 147–161.

SONDI, I. & JURAČIĆ, M. 2010. Whiting events and the formation of aragonite in Mediterranean karstic marine lakes: New evidence on its biologically induced inorganic origin. *Sedimentology*, 57 (1): 85–95.

STANTON, C., BARNES, B.D., KUMP, L.R. & COSMIDIS, J. 2023. A re-examination of the mechanism of whiting events: A new role for diatoms in Fayetteville Green Lake (New York, USA). *Geobiology*, 21 (2): 210–228.

SYABRYAJ, S., UTESCHER, T., MOLCHANOFF, S. & BRUCH, A.A. 2007. Vegetation and palaeoclimate in the Miocene of Ukraine. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 253 (1-2): 153–168.

TRUBIKHIN, V.M. 1989. Paleomagnetic data for the Pontian. *In*: STEVANOVIĆ, P., NEVESSKAYA, L.A., MARINESCU, F., SOKAČ, A. & JÁMBOR, Á. (Eds.). *Chronostratigraphieand Neostratotypen. Neogen der Westlichen ("Zentrale") Paratethys, Bd. VIII, Pl1. Pontien*. Verlag der Jugoslawischen Akademie der Wissenschaften und Künste und der Serbischen Akademie der Wissenschaften und Künste, 76–79.

Turpin, M., Emmanuel, L., Reijmer, J.J.G. & Renard, M. 2011. Whiting-related sediment export along the Middle Miocene carbonate ramp of Great Bahama Bank. *International Journal of Earth Sciences*, 100 (8): 1875–1893.

Vasiliev, I., Iosifidi, A.G., Khramov, A.N., Krijgsman, W., Kuiper, K., Langereis, C.G., Popov, V.V., Stoica, M., Tomsha, V.A. & Yudin, S.V. 2011. Magnetostratigraphy and radioisotope dating of upper Miocene-lower Pliocene sedimentary successions of the Black Sea Basin (Taman Peninsula, Russia). *Palaeogeography, Palaeoclimatology, Palaeoecology*, 310 (3-4): 163–175.

Watkins, J.M., Rudstam, L.G., Crabtree, D.L. & Walsh, M.G. 2013. Is reduced benthic flux related to the Diporeia decline? Analysis of spring blooms and whiting events in Lake Ontario. *Journal of Great Lakes Research*, 39 (3): 395–403.

Wells, A.J. & Illing, L.V. 1964. Present-day precipitation of calcium carbonate in the Persian Gulf. *Developments in Sedimentology*, 1: 429–435.

Yao, Y., Hu, C. & Barnes, B.B. 2023. Mysterious increases of whiting events in the Bahama Banks. *Remote Sensing of Environment*, 285: 113389.

Yaneva, M., Koleva-Rekalova, E., Nikolov, P. & Ognjanova-Rumenova, N. 2019. Topola Formation, Northeastern Bulgaria – biostratigraphical and palaeoecological aspects. *Review of the Bulgarian Geological Society*, 80 (3): 133–135.

Резиме

Горњомиоценски арагонитски седименти источног Паратетиса (профил Железни Рог): периоди „белог феномена“ или не?

У изучавању арагонитских седимената горњег сармата и доњег меота на профилу Железног Рога (Полуострво Таман, источни Паратетис), примењена су теренска истраживања и лабораторијске методе (SEM, дифракција X- зрака и изотопска анализа). Арагонитски седименти се на проучаваном профилу јављају у одвојеним интервалима (до 2 m дебљине) и то у виду танких (mm реда величине) алтернација са глинама. Ови карбонатни седименти се готово у потпуности састоје од кристала и агрегата арагонита, величине од 5 до 23 μm. Горњосарматски и доњомеотски арагонити показују значајне вредности $\delta^{13}C = 5.7‰$, $\delta^{18}O = -2.4‰$ и $\delta^{13}C = 5.3‰$, $\delta^{18}O = -2.8‰$. Претпоставка је да изотопски састав арагонита одражава услове седиментације, које карактерише смањен салинитет басена, повећана биопродуктивност површинских вода и аридни периоди. Стратификација басенских вода и нестабилан гасни режим на дну басена погодовали су очувању ламина арагонита, чије је излучивање највероватније било контролисано периодичним (сезонским) променама у режиму седиментације. Арагонитске ламине су вероватно настале услед абиотског излучивања које је изазвано различитим механизмима, укључујући цветање планктонских алги и/или варијабилност геохемијских услова. На основу добијених резултата, претпоставља се да проучавани арагонити на профилу Железног Рога могу бити продукти феномена познатог као „бели феномен“.

Manuscript received February 18, 2024
Revised manuscript accepted April 26, 2024