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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[1]

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Abstract—C and O isotope composition of Middle-Upper Miocene and Lower Pliocene carbonates from Kerch-Taman Region (Eastern Paratethys) have been studied in order to reconstruct palaeoenvironmental variability and post-sedimentation changes. The $\delta^{13}C$ and $\delta^{18}O$ values of the Upper Sarmatian to Lower Pliocene organogenic carbonates reflect the desalinization of paleobasins, global Late Miocene Cooling, and increase in seasonal temperature fluctuations. Isotopic composition of the Middle Sarmatian organogenic carbonates was strongly influenced by evaporation processes, high bioproductivity, and local submarine methane emissions. Warm climate and low bioproductivity together with unstable hydrological regime during the Late Chokrakian and the Karaganian times influenced the isotope composition of primary carbonates. Calcite shell of *Spiratella sp.* ($\delta^{13}C = -0.4‰$ and $\delta^{18}O = -0.4‰$) from Tarkhanian sediments was formed in warm marine environment. Dolomitization prevails over other secondary mineralization in the studied carbonate rocks. Two groups of secondary dolomites that are characterized by negative and positive $\delta^{13}C$ values have been recognized. Lowe $\delta^{13}C$ values (up to $-31.4‰$) in dolomites indicate the influence of both dissolved inorganic carbon (DIC) from oxidized organic matter (C_{org}) and methane. Dolomites with positive $\delta^{13}C$ values (7.0 and 7.8‰) associat with migration of CO_2- and CH_4-containing saline groundwater.

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Palaeogeographic environments of the Eastern Paratethys (Ponto-Caspian part of the Paratethys) changed many times in the Late Neogene (Nevesskaya et al., 1986). Conditions of sedimentation in basin depended on several factors as such as development of transgressions and regressions (regional and eustatic), tectonic movements, desalinization and isolation (partial or total) of the basin as well as climate change. It is well known that sedimentary conditions are fixed in rock sequences and in the isotope composition of sediments. Influence of the post-sedimentary alterations reflected on the isotope geochemistry of rocks too.

The purposes of this paper are: study of the isotope composition of Middle-Upper Miocene and Lower Pliocene carbonates (from the Tarkhanian to the Kimmerian inclusively) of the Eastern Paratethys; revealing the dependence of variation in $\delta^{13}C$ and $\delta^{18}O$ values and palaeogeographic changes; and identification of influence of secondary alterations on the isotope composition of calcareous sediments. We studied C and O isotope composition of carbonates of Middle-Upper Miocene and Lower Pliocene relatively deep- and shallow-water deposits which were sampled in coastal outcrops of Kerch and Taman Peninsulas. The isotope data on some stratigraphic units of the Ponto-Caspian Neogene were published at the present time (Kiyashko, Paramonova, 1987; Peryt et al, 2004, etc.). This paper represents new carbon and oxygen isotope data for carbonates from all regional stages of the Middle-Upper Miocene (Tarkhanian, Chokrakian, Karaganian, Konkian, Sarmatian, Maeotian, Pontian) and the Lower Pliocene (Kimmerian) of studied area of the Paratethys.

GEOLOGICAL SETTING AND STRATIGRAPHY

The Middle-Upper Miocene sediments of the Kerch-Taman Region were accumulated in relatively deep- and shallow-water environments (at depths ranging from 30–50 to 150–250 m). These deposits

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are exposed in coastal outcrops and mainly consist of clays that contain beds of carbonate rocks, diatomites, and single volcanic-ash horizons. The Lower Pliocene (Kimmerian) sediments consist of clays of the Azovian layers and oolitic irons ores of the Kamyshburunian layers. These deposits were formed in shallow-water environments (at depths of 30–50 m). The Middle-Upper Miocene and Lower Pliocene sediments are exposed in coastal outcrops of Kerch and Taman Peninsulas.

The Skelya, Kop-Takyl and Janish-Takyl sections were studied in the Kerch Peninsula while Zelenskiy Mount, Taman, and Zhelezniy Rog sections—in the Taman Peninsula (Fig. 1). The Tarkhanian, Chokrakian and Karaganian sediments are traced in Skelya and Kop-Takyl sections. Zelenskiy Mount section is represented by succession from the Upper Chokrakian to the Upper Maeotian. The Upper Sarmatian, Maeotian, Pontian and Kimmerian sediments are observed in Taman, Zhelezniy Rog and Janish-Takyl sections. The thickness of Middle-Upper Miocene sediments is about 1000 m and of Lower Pliocene sediments it varies from 15 to 25 m.

Bryozoan bioherms are located in the base of the Lower Chokrakian and the Lower Maeotian. Planar and cone-shaped microbialites (stromatolites and thrombolites) occur in the Upper Chokrakian, the Karaganian and Middle Sarmatian clays. The beds of carbonates rich in coprolites are observed in the upper part of the Middle Sarmatian as well as in the Upper Sarmatian. Detailed descriptions of these sections are given in numerous publications (Andrusov, 1890, 1903; Gubkin, 1915; Zhizhchenko, 1940; Kolesnikov, 1940; Merklin, 1950; Nevesskaya and Stevanovich, 1985; Goncharova, 1989; Popov and Zastrozhnov, 1998; Rostovtseva and Goncharova, 2006; Rostovtseva, 2009a, 2009b, 2009c; Radionova et al., 2012). Maikop Series clays underlay Middle-Upper Miocene sediments.

The Chokrakian, the Karaganian and the Konkian regional stages of the Eastern Paratethys correlate to the Middle Miocene and correspond to the Badenian of the Central Paratethys, as well as to the Langhian and the lower part of the Serravallian of the Mediterranean (Nevesskaya et al., 2003) (Fig. 1). Lower boundary of the Sarmatian is estimated as 13 Ma for the Central Paratethys (Rögl, 1998) and 13.6–13.7 Ma for the Eastern Paratethys (Chumakov, 1993). The Maeotian and Pontian correspond to the Upper Miocene (Nevesskaya et al., 2003).

According to general stratigraphic scale the Miocene-Pliocene (Messinian-Zanclean) boundary is dated 5.3 Ma. According to some researchers this boundary in the Eastern Paratethys coincides with the Pontian-Kimmerian transition (Chumakov, 2000) while others suppose it is within the Kimmerian stage (Semenenko et al., 2009).

DEPOSITIONAL SETTING

Water of the Eastern Paratethys had salinity about 30–32‰ in the Early Tarkhanian (the end of the Early Miocene and the beginning of the Middle Miocene) (Nevesskaya et al., 1986, 2003, 2005) (Table 1). Climate was subtropical (Akhmet'ev, 1993). It is correlated with the global warming that lasted from 17 to 15 Ma and is known as the Middle Miocene Climatic Optimum (Zachos et al., 2001).

Activation of tectonic processes in the Early Chokrakian caused a considerable shoaling of the Eastern Paratethys which area spreaded to north and east (Nevesskaya et al., 2003). The Early Chokrakian basin had a salinity of not less than 28‰ (Bagdasaryan, 1959; Goncharova, 1989). The isolation of the Eastern Paratethys from adjacent marine basins was increased in the Late Chokrakian. At the time, specific hydrological conditions with unstable water salinity occurred and consequently caused disappearance of most mollusk fauna species. There is an evidence of insignificant aridization of climate at the Late Chokrakian (Goncharova et al., 2001).

Depositional environments in the Karaganian were similar to the Late Chokrakian. The first signs of the beginning of the global cooling are noted at the end of the Karaganian (Basov, 1999). This is in good agreement with the data on rapid growth of the East Antarctic ice sheet and cooling of the ocean bottom waters identified from 14.8–14.5 Ma (Flower, Kennett, 1993a). A cooling trend at about 14 Ma is obvious from the macrofloral and palynological data of the Ukrainian Miocene (Syabryaj et al., 2007).

Marine transgression at the beginning of the Konkian led to increased salinity of water to 30‰. The Eastern Paratethys in the Early Sarmatian was a part of a vast basin that extended from the Alps to the Aral Sea. Salinity at that time was about 14–15‰ and could reach 16–18‰ (Nevesskaya et al., 2003).

Conditions of sedimentation in the Early Sarmatian basin were similar to those of the first half of the Middle Sarmatian. Abrupt environmental changes occurred in the second half of the Middle Sarmatian. Intense orogenic movements caused the shoaling of the Eastern Paratethys and consequently reducing its size. Salinity was below 15‰.

The basin area at the end of the Sarmatian reduced and salinity of water decreased down to 4–9‰. In the Early Maeotian, salinity increased (up to 18‰) in the East Paratethys as a result of marine transgression.

In the Late Maeotian and Pontian, the Eastern Paratethys represented a brackish-water basin[2] that

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[2] Brackish-water basin had a salinity of 0.5 to 5–8‰ with a marine ionic composition of salts and could reach a 16‰ salinity with a Caspian salt composition (domination of Ca^{2+} and SO_4^{2-} and a lesser content of K^+ and Cl^- ions) (Nevesskaya et al., 2005).

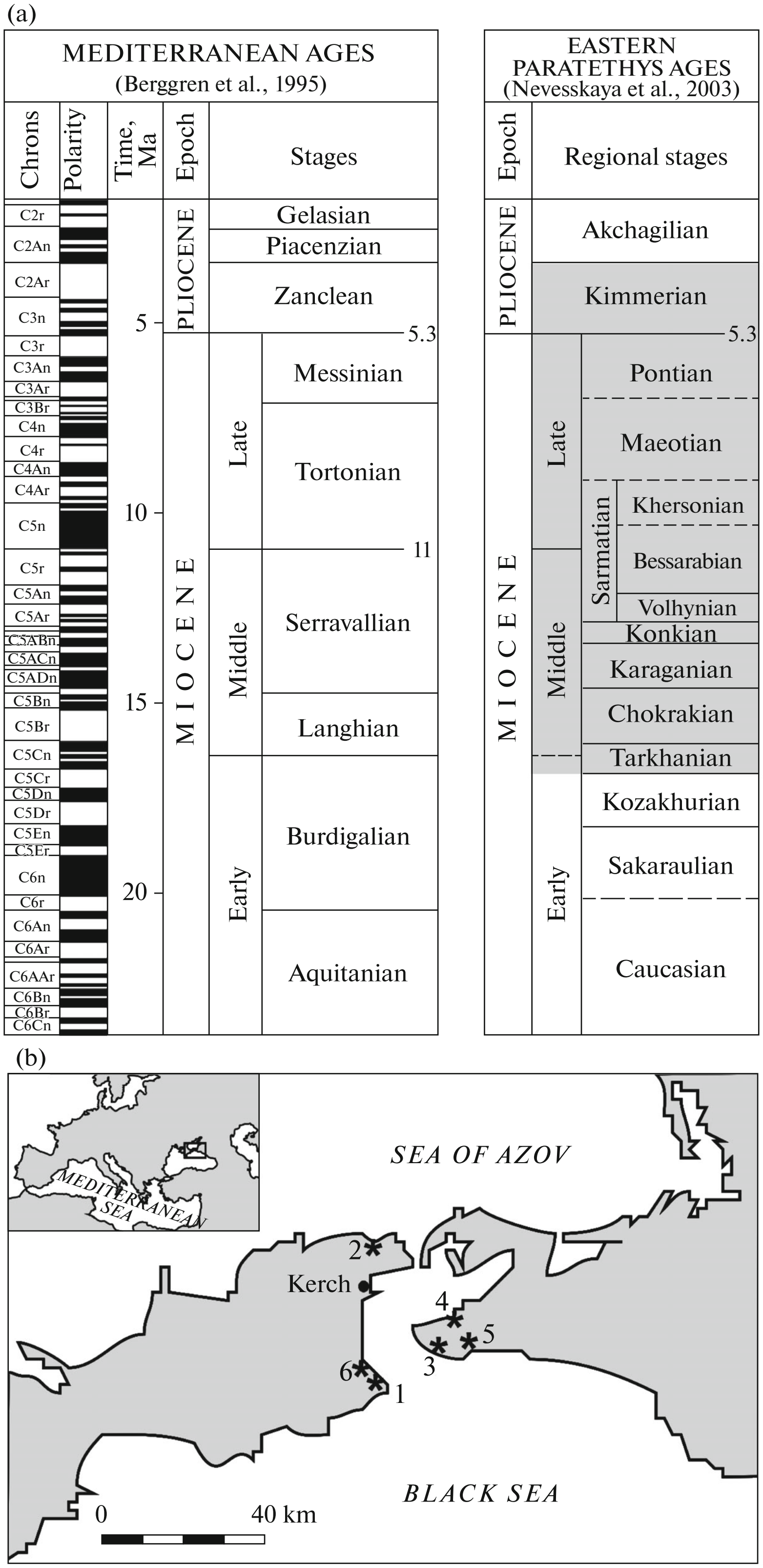

Fig. 1. Stratigraphy (a) and location of the studied sediments (b).
1—Cop-Takyl, 2—Skelya, 3—Zhelenskiy Mount, 4—Taman, 5—Zhelezniy Rog, 6—Janish-Takyl.

Table 1. Feature palaeoenvironments of the Ukraine Plain and Eastern Paratethys in the Middle and Late Miocene (by Syabryaj et al., 2007; Nevesskaya et al., 2005)

Eastern Paratethys		(Syabryaj et al., 2007)		(Nevesskaya et al., 2005)	
Regiostages	Beds	MATn, °C	MAPn, mm	SMM, %	S, ‰
Kimmerian	Kamyshburunian	–	–	0	–
	Azovian	–	–		–
Pontian	Bosphorian	13.8	897	0	–
	Portaferian				–
	Novorossian			1.3	5–10
Maeotian	Akmanaian			3	9–10
	Bagerovian	5.2 4.9	735 389	6.5	18
Sarmatian	Khersonian			1.6	9
	Bessarabian	4.6	735	9	<15
	Volhynian			11.5	15
Konkian	Veseljanian	15.6	1304	18	20
	Sartaganian			35	>30
Karaganian	Kartvelian	15.2	1146	1.0	?
	Varnean			–	–
	Arkhashenian			0.5	?
Chokrakian	Brykian	16.4	1217	3	?
	Zukian			29	>28
Tarkhanian	Argunian	17	1146	27	30–32
	Terskian			27	30–32
	Kuvinian			32	32

MATn—minimum mean annual temperature, MAPn—minimum mean annual precipitation, SMM—percentage of marine bivalve genera among genera of bivalves basins with normal salinity, S—salinity.

had not more 10‰ salinity during the Akmanaian and Novorossian.

The Eastern Paratethys had largely shoaled at the end of the Early Pontian. The most part of its areas was drained and an erosion surface have been formed (Popov, Nevesskaya, 2007; Rostovtseva, 2009d).

At the beginning of the Late Pontian, the Caspian basin detached from the Euxine part of the Eastern Paratethys. Depositional conditions in the second half of the Late Pontian were stabilized. Water salinity became low due to inflow of river waters.

The Pontian is correlated with the Messinian Salinity Crisis of the Mediterranean (Gillet et al., 2007; Popov, Nevesskaya, 2007; Rostovtseva, 2009d). Ice sheet in the East Antarctic was in the increase in this time (Zachos et al., 2001).

In the Kimmerian, salinity was below that in the Pontian probably. During the second half of the Kimmerian, when the Kamyshburunian iron ores were formed, the climate was warm (perhaps subtropical) (Semenenko, 1987).

MATERIALS AND METODS

Carbonate shells of marker mollusk were used for stable isotope study. Other types of calcareous fossils (bryozoans, stromatolite, nannoplankton etc.) were analyzed if preservation of shells was bad. Isotope composition of shell of *Anadara* sp. from recent coastal sediments of the Kerch Strait was studied for the comparison.

Samples of carbonate rocks of the Chokrakian, Karaganian, Sarmatian and Maeotian sediments (Skelya, Zelenskiy Mount, Taman sections) were studied to define the relation between post-sedimentation changes and isotopic composition of sediments. The samples were taken from layers of rocks with and without traces of secondary alterations (mainly dolomitization traces).

These carbonate rock samples were treated with orthophosphoric acid in vacuum at 25°C for an hour, following the standard method (McCrea, 1950). CO_2 obtained was considered as the product of calcite dissolution (Walters et al., 1972). Further, the samples continued decomposing at 100°C for 1.5 hour. Here, CO_2 obtained is the product of decomposition of lowsolubility carbonates (in this case dolomite) (Rosenbaum, Sheppard, 1986). A MI-1201V mass spectrometer was used to perform measurements. A Delta V Advantage mass spectrometer and a Gas-Bench-II system were applied to determine carbon and oxygen isotopes composition in calcareous fossils (shell, etc.). These samples were not pre-treated.

$\delta^{13}C$ and $\delta^{18}O$ values are given against VPDB; accuracy is ±0.2‰. Isotopic measurements were carried out at the Geological Institute of the Russian Academy of Sciences (Moscow).

X-ray diffraction method was applied to define mineral composition of carbonates (LMSU, analyst V.L. Kosorukov). A part of samples was studied using a Camscan-4 scanning electron microscope (LMSU, analyst V.O. Yupaskurt).

ISOTOPE GEOCHEMISTRY

Different genetic types of carbonates were analyzed. Carbonates represented by calcareous fossils (shells, etc.) are considered as primary organogenic sediments. $\delta^{13}C$ and $\delta^{18}O$ values reflect mainly depositional conditions. Carbonates with traces of post-sedimentation alterations (further named as secondary) are discussed as result of diagenetic transformations.

Primary Organogenic Carbonates and Palaeoenvironments

All isotope data for primary organogenic carbonates (shells of bivalves, etc.) are given in Table 2 and shown in Figs. 2 and 3. It is established that isotope values vary from –36.8 to 3.0‰ for $\delta^{13}C$ (PDB) and from –7.2 to 2.4‰ for $\delta^{18}O$ (PDB). Isotope data reflect existence of different depositional conditions. The isotope composition of a part of primary carbonates corresponds to marine environments of sedimentation (Fig. 2, field I).

Notable are carbonates with high $\delta^{13}C$ values. They were formed perhaps due to the increased bioproductivity of paleobasin and intensity organic matter accumulation (Fig. 2, field II).

Low $\delta^{13}C$ values determined by the degree of participation in their formation of oxidized organic matter carbon (TOC).

Thrombolite from the low part of the Middle Sarmatian deposits is characterized by extraordinary negative value of $\delta^{13}C$ (–36.8‰). These data show that CO_2 (DIC) was formed due to methane oxidation (Fig. 2, field III).

Low $\delta^{18}O$ values could be explained mainly by desalinisation and warming (e.g. Pliocene Kamyshburunian layers). More intense evaporation processes and some other factors caused to increase $\delta^{18}O$ values.

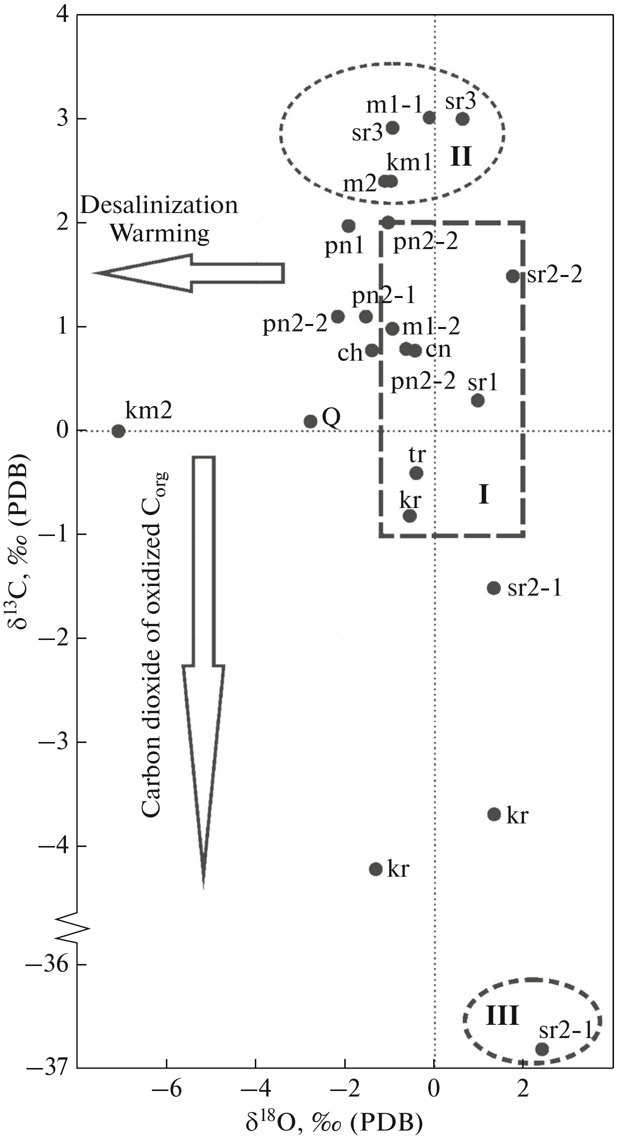

Fig. 2. The isotope composition of the primary organogenic carbonates.
Age of carbonates: Tarkhanian (tr), Chokrakian (ch), Karaganian (kr), Konkian (kn), Lower Sarmatian (sr1), the lower part of the Middle Sarmatian (sr2-1), the upper part of the Middle Sarmatian (sr2-2), Upper Sarmatian (sr3), lower part of the Lower Maeotian (m1-1), upper part of the Lower Maeotian (m1-2), Upper Maeotian (m2), Lower Pontian (pn1), the lower part of the Upper Pontian (pn2-1), the upper part of the Upper Pontian (pn2-2), Lower Kimmerian (km-1), Upper Kimmerian (km-2), Quaternary (Q).
Fields of carbonates deals with: I—high bioproductivity and evaporation, II—marine conditions, III—oxidized methane.

$\delta^{13}C$ and $\delta^{18}O$ ratios distributed within the studied sequence irregularly (Fig. 3). These values tend to increase from the Tarkhanian to the Middle Sarmatian and to decrease from the Upper Sarmatian to the Kimmerian. The $\delta^{13}C$ excursions in carbonates of

Table 2. The isotope composition of the primary organogenic carbonates

Age deposits		Samples	Mineral composition, %			δ^{13}C (PDB), ‰	δ^{18}O (PDB), ‰	L
Sub-regiostages	Beds		A	C	D			
recent beach sediments		*Anadara sp.*	100	0	0	0.1	–2.8	7
Kimmerian regiostage								
Upper	Kamyshburunian	*Pontalmyra crassatellata*	100	0	0	0.0	–7.2	6
Lower	Azovian	*Congeria* sp.	100	0	0	2.4	–0.9	4
Pontian regiostage								
Upper	Bosphorian	*Dreissena (Pontodreissena) rostriformis (l/clay)*	100	0	0	0.8	–0.7	5
		Dreissena (Pontodreissena) rostriformis (Desh.)(d/clay)	100	0	0	2.0	–1.1	5
		Paradacna abichi	100	0	0	1.1	–2.1	4
	Portaferian	*Congeria subrhomboidea*	100	0	0	1.1	–1.5	4
Lower	Novorossian	*Paradacna abichi*	100	0	0	2.0	–1.9	4
Maeotian regiostage								
Upper	Akmanaian	*Caspiohydrobia tamanensis*	0	100	0	2.4	–1.1	4
Lower	Bagerovian	*Abra tellinoides*	94	6	0	1.0	–0.9	4
		Bryozoans	0	100	0	3.0	–0.1	3
Sarmatian regiostage								
Upper	Khersonian	Coprolite	0	100	0	2.9	–0.9	3
		Mactra cf. caspia	0	100	0	3.0	0.7	3
Middle	Bessarabian	Shell fragments	97	3	0	1.5	1.8	3
		Cryptomactra pesanseris	96	4	0	–1.5	1.3	3
		Thrombolite deep water**	15	85	0	–36.8	2.4	3
Lower	Volhynian	*Musculus sarmaticus*	0	100	0	0.3	1.0	3
Konkian regiostage								
		*Reticulofenestra umbilica**	0	93	7	0.8	–0.4	3
Karaganian regiostage								
		Spaniodontella gentilis	100	0	0	–4.2	–1.3	3
		Thrombolite deep water**	0	100	0	–3.7	1.3	3
Upper Chokrakian–Karaganian		Stromatolite	0	100	0	–0.8	–0.5	2
Chokrakian regiostage								
Lower	Zukian	Oncolite	0	100	0	0.8	–1.4	2
Tarkhanian regiostage								
Upper	Argunian	*Spiratella**	10	83	7	–0.4	–0.4	1

A—aragonite, C—calcite, D—dolomite, L—location of samples (1—Cop-Takyl, 2—Skelya, 3—Zhelenskiy Mount, 4—Taman, 5—Zhelezniy Rog, 6—Janish-Takyl, 7—beach Kerch Strait). *—planktonic species, **—relatively deep-water formations. Clays: dark gray slightly calcareous (d/clay) and light gray calcareous (l/clay). The key values are highlighted.

some stratigraphic units are at inverse relation to δ^{18}O values.

Thus, variations of the isotopic composition reflect palaeoenvironmental changes and are influenced by a number of factors, namely: seawater inflows, desalinisation, intensity of evaporation processes, increase and decrease bioproductivity, fluctuations paleotemperatures, submarine gas emissions, etc. (Fig. 3).

Tarkhanian. Calcite of *Spiratella* shell from the top of Tarkhanian sediments shows values δ^{13}C = –0.4‰

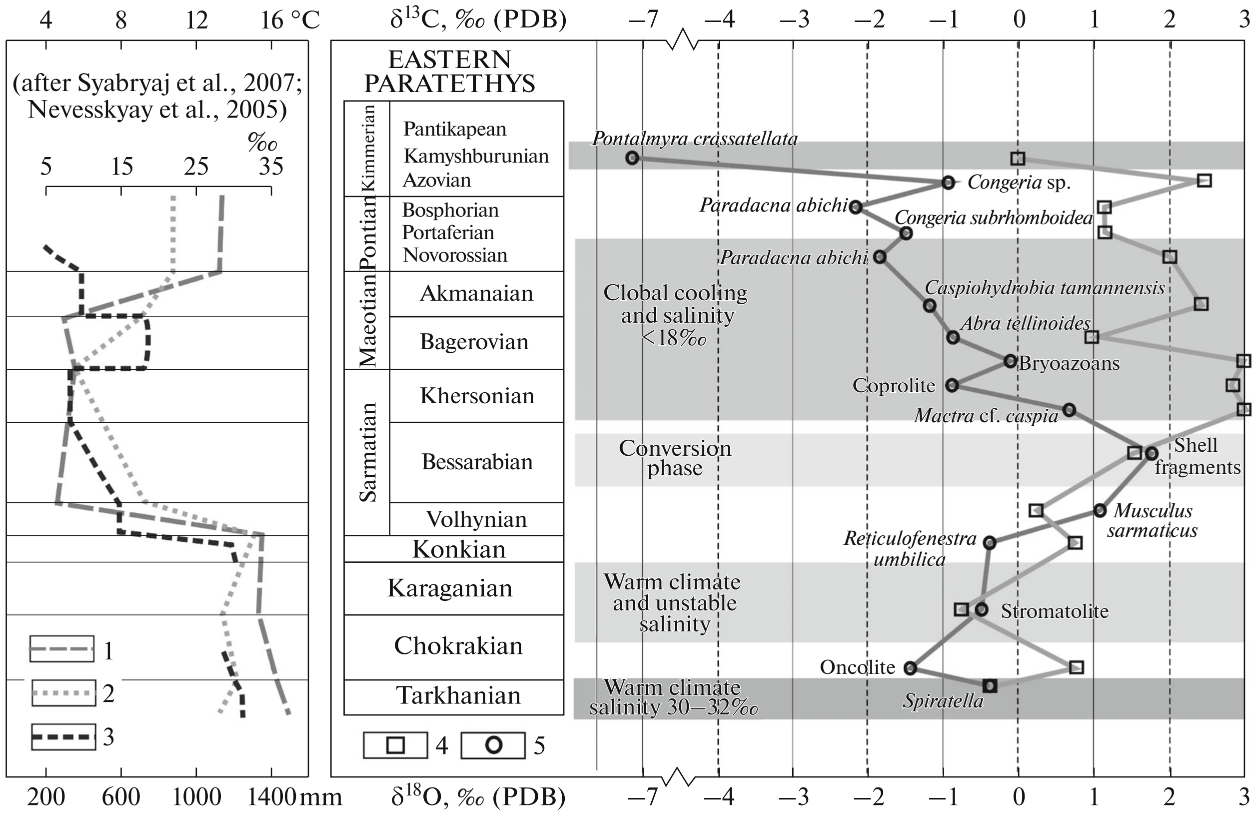

Fig. 3. Change in isotope composition of the primary organogenic carbonates and palaeoenvironments of Black Sea Region in the Miocene (key values are used (see Table 2), palaeoenvironments by Syabryaj et al., 2007; Nevesskaya et al., 2005). 1—minimum mean annual temperature, 2—minimum mean annual precipitation, 3—salinity, 4—values $\delta^{13}C$, 5—values $\delta^{18}O$.

and $\delta^{18}O = -0.4‰$ which are typical for carbonates formed in warm marine environments. This agrees with the conception that the climate was subtropical at that time and depositional conditions in the East Paratethys were close to the ordinary marine environments. Enrichment in ^{18}O isotope *Spiratella* shell indicates that pteropods lived at a high temperature of water. Water paleotemperature according to equation T (°C) = 16.0 – 4.14 ($\delta^{18}O_{calcite} - \delta^{18}O_{water}$) + 0.13 ($\delta^{18}O_{calcite} - \delta^{18}O_{water})^2$ (Leng and Marshall, 2004) could be ~25°C (at the $\delta^{18}O_{water} = 1.6‰$ PDB of surface waters of the eastern Mediterranean Sea (Gat et al., 1996)).

Insignificant enrichment in the light carbon isotope *Spiratella* shell may be defined by the different factors. The principal ones are a slight decrease in water salinity of the Eastern Paratethys in the Later Tarkhanian, and an increase in terrigenous organic carbon contents. Supply of large volumes of eroded sediments containing terrestrial organic matter occurred at the end of the Tarkhanianwas a result of increasing the tectonic activity and basin shallowing.

Early Chokrakian. Oncolites of the Lower Chokrakian in contrast to the planktonic *Spiratella* of the Tarkhanian shows decrease oxygen isotope composition ($\delta^{18}O = -1.4‰$) and increase carbon isotope composition ($\delta^{13}C = 0.8‰$). The low $\delta^{18}O$ value can be explained by formation of oncolites in more warmed shallow waters.

In the Early Chokrakian, the climate was still subtropical, and the salinity remained relatively high (S > 28‰, which is favorable for echinoderms). Increase of bioproductivity of the basin and decrease volume of terrigenous organic matter supplied from the land could be the cause of an enrichment in heavy ^{13}C isotope. During this time, the area of the Eastern Paratethys was enlarged. The coastline was moved northward and eastward.

Late Chokrakian and Karaganian. The Upper Chokrakian-Karaganian stromatolites are characterized by negative $\delta^{13}C$ and $\delta^{18}O$ values. Such light isotope composition could be explained by mixing of freshwater and marine water. Climate was warm at that time and bioproductivity in the paleobasin was reduced.

The Karaganian deep-water shell of *Spaniodontella gentilis* and thrombolites are characterized by similar negative $\delta^{13}C$ values. In contrast to shell of *Spaniodontella gentilis*, thrombolites display a positive $\delta^{18}O$ value

(1.3‰). High ^{18}O content in trombolites is due to specificity isotope composition of interstitial water. In general, the isotope data obtained on carbonates of the Upper Chokrakian and Karaganian are similar to previously published geochemical data of the identical deposits (Peryt et al., 2004).

Konkian. Calcareous nannofossils *Reticulofenestra umbilica* from the top of Konkian sediments show δ^{13}C = 0.8‰ and δ^{18}O = –0.4‰ values that are typical for marine carbonates. It agrees well with the concept that the Eastern Paratethys had extensive connection with the world ocean at that time.

Early and Middle Sarmatian. The Lower and Middle Sarmatian calcareous fossils are characterized by high δ^{18}O values (from 1 to 2.4‰). Such oxygen isotope composition may be due the cooling of climate and aridisation. In Fig. 3 shown, the average annual minimum temperature decreases from the Konkian to the Lower Sarmatian, as well as the decreases of average annual minimum precipitation (Syabryaj et al., 2007) and salinity (Nevesskaya et al., 2005).

In comparison with the Lower Sarmatian shells, a higher δ^{18}O value in shell fragments of the upper part of the Middle Sarmatian could be explained by high evaporation rates occurred in hydrologically restricted settings. According to Latal et al. (2004), the highest δ^{18}O values for shells taken from the Sarmatian deposits of Eisenstadt-Sopron basin (“Mactra Zone” from 11.9 to 11.5 Ma, St. Margarethen section) are caused by evaporation, too.

Relatively deep-water thrombolite taken from the lower part of the Middle Sarmatian (Rostovtseva, Konovalova, 2005; Goncharova, Rostovtseva, 2009) exhibits the lightest δ^{13}C value (–36.8‰) that indicates influence of the isotopically light oxidized methane carbon. Thrombolites of this type can be considered as seep carbonates formed in the areas of sea floor where methane-rich fluid emissions occurs due to the reconstruction of the basin (Fig. 4). The results of isotope analysis are consistent with data of the biomarker analysis (Rostovtseva, Yurchenko, 2015). A homologous series of n-alkanes with chain lengths from C_{16} to C_{31} carbon atoms as well as pristane and phytane were identified in the nonpolar fraction of lipid extracts from thrombolites. The crocetane and pentamethylicosane (PMI) considering as markers of archaea and sulphate-reducing bacteria are determinated also. Thrombolites formed with influence of the bacterial oxidation of methane. The methane-rich fluid emissions took place at this time as a result of orogenic movements. Influence of the submarine methane emissions insignificantly reflected on δ^{13}C ratio in the aragonite of *Cryptomactra pesanseris* (δ^{13}C = –1.5‰) taken from the Middle Sarmatian relatively deep-water thrombolite.

Water salinity of basin at the end of the Middle Sarmatian was lower 15‰. Heavy oxygen isotope composition of carbonates could be explained as effect intensification of evaporation due to aridisation.

Shell fragments of the upper part of the Middle Sarmatian are rich of heavy carbon isotopes (δ^{13}C = 1.5‰). These isotope data could reflect the high bioproductivity due to mass development of diatoms. The high content of diatoms in the Middle and Upper Miocene sediments of the Kerch-Taman Region is detected from the second half of the Middle Sarmatian.

Diatom sedimentation is influenced by a multitude of factors, including climatic cooling. It is known that diatom-rich siliceous facies of the Monterey formation (Miocene) were formed from about 13.2 to 6 Ma by the global cooling and ocean hydrology changes (Flower, Kennett, 1993b). The cooling caused the decrease near-surface water temperature and consequently increase content of dissolved CO_2 (DIC), which might foster to higher diatom production.

According to Kürschner et al. (2008), decrease in the concentration of atmospheric CO_2 down to ≈280 ppmv about 12 Ma was caused by dramatic changes in terrestrial ecosystems and expansion of grasslands. The concentration of atmospheric CO_2 was equal to ≈550 ppmv during the Miocene Climatic Optimum about 16 Ma.

Late Sarmatian–Kimmerian. Carbonates from the Upper Sarmatian to Kimmerian sediments show a negative δ^{18}O values. But, the shell of *Mactra cf. caspia* from the base of the Upper Sarmatian yielded still a positive δ^{18}O values (δ^{18}O = 0.7‰). In contrast to the Middle Sarmatian shell fragments (δ^{18}O = 1.8‰), shell of *Mactra cf. caspia* is depleted in δ^{18}O that could be explained by increased desalinization of paleobasin. In the Late Sarmatian, salinity of the Eastern Paratethys decreased down to 4–9‰.

The global cooling continued in the Late Miocene and thus enriched oceanic sediments in heavy oxygen isotopes (Zachos et al., 2001). The studied Upper Miocene sediments, however, exhibit a trend of enriching carbonates with light oxygen isotopes due to a progressive desalinization of the Eastern Paratethys during the Late Miocene. Depletion in δ^{18}O values was largely connected to non-marine water influence. Variability in δ^{18}O ratios is explained by periodicity of marine water influx (e.g. Early Maeotian) and climatic fluctuations affecting the paleotemperature and precipitation.

Bioproductivity in the basin could be responsible for excursions of δ^{13}C values. Increased ^{13}C content in carbonates were resulted from the bioproductivity fostered by cooling. Such bioproductivity is confirmed by diatom algae abundant in the Upper Sarmatian, Maeotian and Lower Pontian sediments.

The Upper Pontian sediments are characterized by cyclic structure influenced by astronomical climatic fluctuations well known as the Milankovitch cycles. These fluctuations was reflected in oxygen isotope

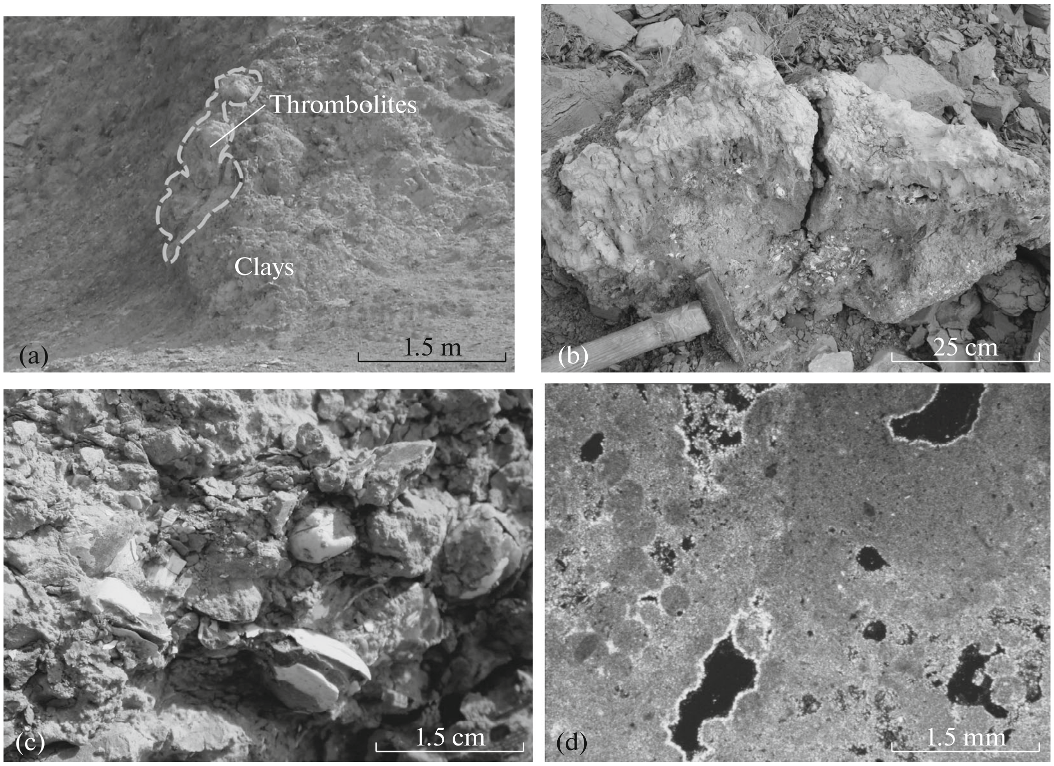

Fig. 4. Relatively deep-water thrombolites of the lower part of the Middle Sarmatian of the Taman peninsula (Zhelenskiy Mount section).
(a) thrombolites in clays, (b) thrombolite, (c) *Cryptomactra pesanseris* in thrombolite, (d) microbial structure of thrombolite.

composition of aragonite shell *Dreissena* (*Pontodreissena*) *rostriformis Desh.*). Carbonates characterized more heavy oxygen isotope composition were formed during colder and dryer climatic periods.

The Upper Kimmerian carbonates exhibit uneven variations in isotope composition. The fact that shell of *Pontalmyra crassatellata* taken from Kamyshburunian is appreciably rich in contents of light oxygen isotopes ($\delta^{18}O = -7.2‰$), can be explained by desalination of the water basin and significant warming of climate. As is well known, accumulation of Kamyshburunian sediments occurred in warm and humid climate (Semenenko, 1987).

Secondary Carbonates and Post-Sedimentation Changes

Authigenic dolomite and calcite in the studied carbonate rocks developed widely. Isotope data for secondary carbonates and for some layers of primary limestones (without any visible traces of post-sedimentation changes) are shown in Table 3. Wide variations of C and O isotope ratios ($\delta^{13}C$ varied from –31.4 to 7.8‰ and $\delta^{18}O$ varied from –2.6 to 3.1‰) indicate various conditions of secondary carbonatization and different sources of CO_2 (DIC) in this process. This is well seen in Fig. 5. Primary limestones vary within a narrow range of $\delta^{13}C$ and $\delta^{18}O$ values (–3.7 to 4.6‰ and –3.1 to 1.3‰, respectively).

Secondary dolomites and calcites occupy different isotope geochemical fields, differ sharply from sedimentary marine carbonates. It confirms that they were formed by diagenesis in presence dissolved inorganic carbon of various origin and isotopic composition.

Karaganian carbonates entirely replaced by secondary dolomites show the lowest $\delta^{13}C$ values (to –31.4‰), mainly due to the oxidation of methane carbon (Lein, 2004).

Karaganian authigenic dolomites with the lowest $\delta^{13}C$ values in contrast to secondary carbonates of other types characterized by the highest $\delta^{18}O$ values (Fig. 5). This testify to specific conditions in which dolomites were formed. One from them was precipitated in solutions enriched in ^{18}O, or dolomites were formed at lower temperatures in contrast to other carbonates (both, primary and secondary). The solutions enriched in ^{18}O may be as result of the illitization of smectite minerals occurred in deep-burial environments (Lavrushin, 2012).

Karaganian dolomites with lower $\delta^{13}C$ values are confined to lower part of carbonate beds (Figs. 6a, 6b). Upper parts of these beds are usually composed of calcite or calcite and dolomite of different forms (Fig. 6c). At

Table 3. The isotope composition of the studied carbonate rocks

Age deposits		Carbonate rocks	Mineral composition, %			Calcite		Dolomite		L
Sub-regiostages	Beds		A	C	D	$\delta^{13}C$ (PDB), ‰	$\delta^{18}O$ (PDB), ‰	$\delta^{13}C$ (PDB), ‰	$\delta^{18}O$ (PDB), ‰	
Maeotian regiostage										
Upper	Akmanaian	Oolitic	0	90	10	3.0	–0.6	–	–	4
Sarmatian regiostage										
Upper	Khersonian	Fine-grained	100	0	0	4.6	–3.1	–	–	3
Middle	Bessarabian	Coprolitic	0	18	82	–	–	7.8	–1.3	2
		Trombolite	0	29	71	–20.9	1.0	–3.7	–1.9	2
		Fine-grained	0	0	100	–	–	7.0	–0.5	2
Karaganian regiostage		Fine-grained	0	100	0	–3.6	0.04	–	–	2
		Fine-grained sample 23–48 (top)	0	45	55	–8.2	1.0	–6.5	–1.3	2
		Fine-grained sample 23–48 (base)	0	19	81	–15.8	1.1	–21.8	–1.1	2
		Fine-grained sample 20–10 (top)	0	100	0	–3.7	1.3	–	–	2
		Fine-grained sample 20–10 (base)	0	0	100	–	–	–31.4	2.9	2
		Fine-grained	0	0	100	–	–	–30.7	3.1	2
Chokrakian regiostage										
Upper	Brykian	Fine-grained	0	31	69	–4.4	–2.4	–7.2	–2.6	1
Lower	Zukian	Broazoan build-up	0	48	52	–2.6	–2.3	–17.0	–1.7	1

A—aragonite, C—calcite, D—dolomite, L—location of samples (1—Skelya, 2—Zhelenskiy Mount, 3—Zhelezniy Rog, 4—Taman). The primary limestones values are highlighted.

the base of carbonate beds, dolomite crystals are characterized by non-planar fabrics forming homogeneous mass. Dolomite formed as a result of metasomatic replacement of the primary substance that caused the morphology of pre-existing carbonate crystals to degrade. The intensity of dolomitization process in the carbonate beds (up to 0.2–0.3 m thick) reduced upwards. Some carbonate beds (about 5–8 cm thick) are usually composed entirely of calcite.

Secondary dolomites from fine-grained and coprolitic carbonate layers which are totally or considerably dolomitized in the Middle Sarmatian sediments exhibit high $\delta^{13}C$ values (7.8 and 7‰) and negative $\delta^{18}O$ ratios (–0.5 and –1.3‰) and localized in the upper part of graph in Fig. 5. High $\delta^{13}C$ values testified probably about the slow oxidation of methane by approximate to equilibrium conditions in system: CH_4–CO_2. Oxygen isotope composition of such type of secondary dolomites is much lighter in comparison to dolomites with the lowest $\delta^{13}C$ values. Therefore, this indicates the separate phase of secondary dolomitization. During this phase, dissolved inorganic carbon could been formed by methane oxidation, but the oxygen isotope composition of mineralized solutions was 3–4‰ lighter, or dolomite-formation temperatures were higher by 12–15°C.

Electron microscopy allowed to establish that the Middle Sarmatian secondary carbonates are dolomitized within the whole rock groundmass. These carbonates have multiple pores with walls covered by sparite idiomorphic crystals of dolomite (Figs. 6d, 6e). The groundmass of carbonates consists of micritic dolomite with an almost rhombohedral shape of crystals. Idiomorphic shape of dolomites well-visible on sparite of cavity edges indicates formation of these minerals from solutions. Some pores are filled with gypsum crystals (Fig. 6f). Well-developed gypsum druses and veins are observed at the contact of carbonate and clay beds.

Thus, dolomitization of the Middle Sarmatian carbonates was influenced by CO_2- and CH_4-containing saline groundwater that caused secondary dolomites and sulphates precipitations. The solutions were enriched in sulphates and Mg^{2+} cations, which are

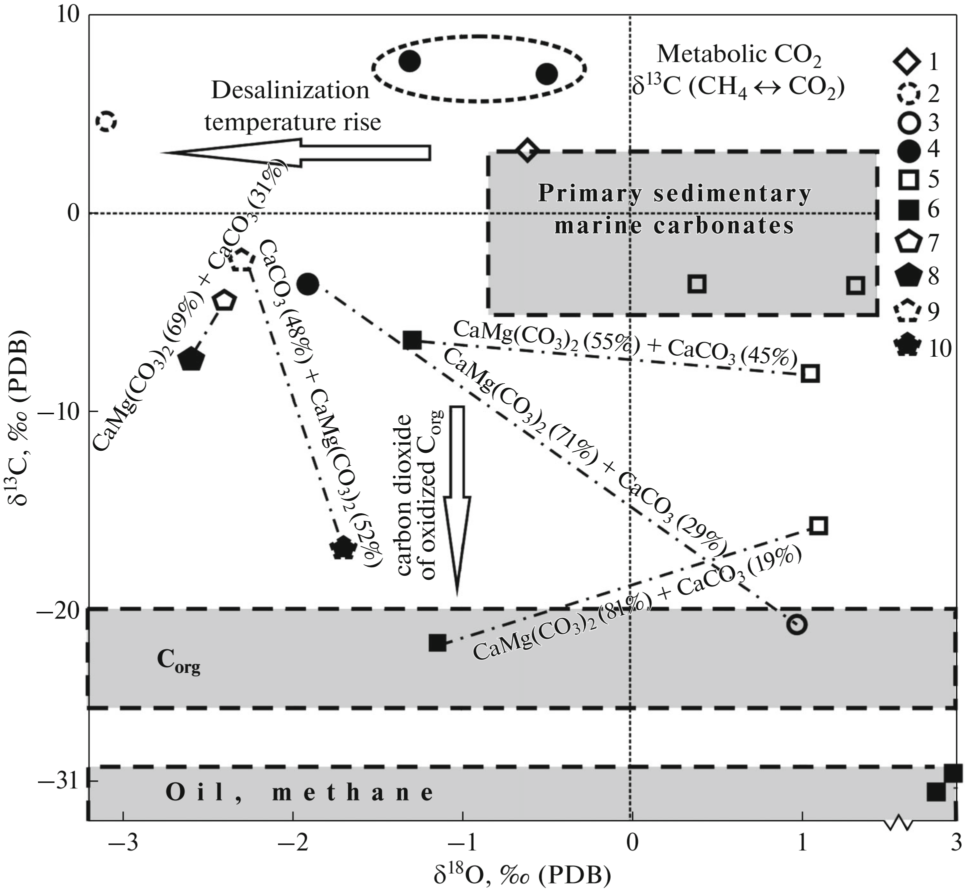

Fig. 5. The isotope composition of the studied carbonate rocks.
Age of carbonates: 1—Upper Maeotian, 2—Upper Sarmatian, 3, 4—Middle Sarmatian, 5, 6—Karaganian, 7, 8—Upper Chokrakian, 9, 10—Lower Chokrakian. 4, 6, 8, 10—dolomite, other—calcite or aragonite.

quite reasonable considering the widespread development of clays in the studied deposits. Note, the carbon dioxide enriched in ^{13}C ($\delta^{13}C$ up to 16‰) is revealed in gases of Taman mud volcanoes, containing mostly methane (from 70% and more) (Valyaev et al., 1985; Lavrushin, 2012). In Taman Region, the mud volcanic fluids with mineralization about 10–22 g/L are formed at the burial depths from 1 to 4 km (average 1.7–2.1 km) and temperatures about 68–85°C (Lavrushin, 2012). According to B.M. Valyaev et al. (1985), the enrichment in ^{13}C isotope CO_2 occurs with increasing content of the carbon dioxide in gases of Taman mud volcanoes.

Some authigenic carbonates were formed in an early diagenesis with active participation of carbon oxidized organic matter (C_{org}). Secondary calcites in this case are characterized by high ^{12}C content ($\delta^{13}C$ from −21 to −2.6‰) and also by both positive and negative $\delta^{18}O$ values appropriate for the diagenetic environment. Dolomites in such rocks are characterized usually different $\delta^{13}C$ and $\delta^{18}O$ values versus calcite that indicate a separate phase of dolomitization. Dolomite formation occurred in the presence of solutions having proximate and ^{16}O-rich isotopic composition or proceeded at similar and higher temperatures (up to 10–12°C), compared with the formation of coexisting calcites.

CONCLUSIONS

Carbonates of the Upper Sarmatian to Lower Pliocene deposits exhibit mostly positive $\delta^{13}C$ values and negative $\delta^{18}O$ values. Isotope composition of sediments reflected the environmental conditions developed in the Eastern Paratethys during the global climatic cooling. The fact that carbonates were rich in light oxygen isotopes is mainly explained by desalinization of the basin waters and partly by temperature climate changes. Enrichment of carbonates in heavy carbon isotopes ^{13}C was a result of intensive bioproductivity of the paleobasin caused by climatic cooling. Periodic climatic fluctuations in the Late Pontian known as Milankovitch cycles were responsible for isotope composition variability observed for mollusk shells. The climate warming occurred in the second

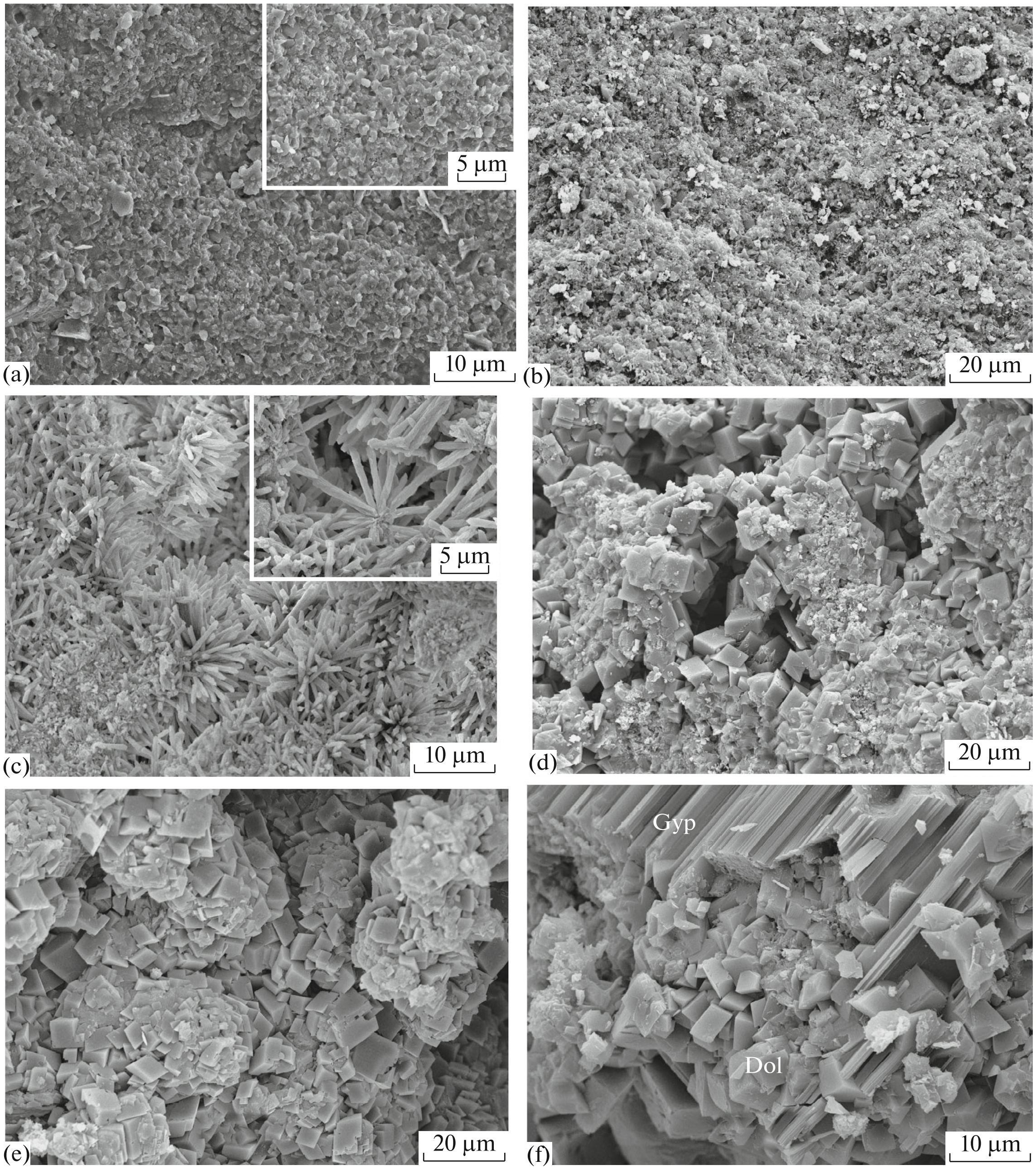

Fig. 6. Photos showing surfaces of carbonate rocks (Zhelenskiy Mount section) (SEM).
(a) dolomite (base layer, sample 20–10, Karaganian), (b) dolomite and calcite (base layer, sample 23–48, Karaganian), (c) calcite (top layer, sample 20–10, Karaganian), (d) dolomite (sample 23–36, the upper part of the Middle Sarmatian), (e) dolomite in marginal part of the cavern (sample 23–36, the upper part of the Middle Sarmatian), (f) dolomite and gypsum (sample 23–36, the upper part of the Middle Sarmatian). (Dol) dolomite, (Gyp) gypsum.

half of the Kimmerian caused an enrichment in ^{16}O isotopes of mollusk shells.

In the first half of the Middle Sarmatian tectonic activity and structural reorganization of the basin occurred. In that time organogenic carbonates with anomalously light carbon isotope composition were formed due to submarine methane emissions.

At the end of the Middle Sarmatian, intensive processes of evaporation led to the enrichment of mollusk shells aragonite by heavy oxygen isotopes ^{18}O. High biological productivity of water resulted in increased content of heavy carbon isotope ^{13}C.

Negative $\delta^{13}C$ values in the Upper Chokrakian-Karaganian and Karaganian calcareous fossils are most likely due to mixing of seawater and nonmarine water, and low bioproductivity of the basin. Climate was still warm at that time.

Shells of *Spiratella* from the Tarkhanian sediments show $\delta^{13}C$ and $\delta^{18}O$ values most close to zero that are associated with the marine environment of Middle Miocene climate optimum.

In the studied sediments, dolomitization prevailed against other secondary mineralization processes. There were several phases of authigenic formation of carbonates that occurred at various temperatures. Dissolved inorganic carbon (DIC) and waters of the mineralized solutions had different carbon and oxygen isotope composition.

CO_2 resulting from oxidation of organic carbon and methane was the main source of DIC in mineralized solutions. Karaganian dolomites showing abnormally low $\delta^{13}C$ values were formed by oxidation of methane carbon.

Formation of secondary dolomites was also influenced by CO_2- and CH_4-containing saline groundwaters. Dolomites of this type are presented in the Middle Sarmatian sediments. The inflow of additional Mg^{2+} into the layers of carbonates was carried out from clays widely developed in the studied sequences.

Various factors that led to formation of secondary dolomites in diagenesis depended upon the tectonic development of the Kerch-Taman Region related to the formation of the Crimean and Caucasian fold systems.

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