ISSN 0145-8752, Moscow University Geology Bulletin, 2015, Vol. 70, No. 2, pp. 113–130. © Allerton Press, Inc., 2015.
Original Russian Text © R.R. Gabdullin, E.N. Samarin, A.V. Ivanov, N.V. Badulina, M.A. Afonin, D.V. Igtisamov, E.Yu. Fomin, A.Yu. Yurchenko, 2015, published in Vestnik Moskovskogo Universiteta. Geologiya, 2015, No. 2, pp. 39–57.

The Lithological–Geochemical and Paleoecological Characteristics of Sedimentation Conditions in the Crimean Mountains in the Maastrichtian

R. R. Gabdullin[a], E. N. Samarin[a], A. V. Ivanov[b], N. V. Badulina[a], M. A. Afonin[a], D. V. Igtisamov[a], E. Yu. Fomin[a], and A. Yu. Yurchenko[a]

[a] *Department of Geology, Moscow State University, Moscow, 119991 Russia*

[b] *Department of Ecology and Service, Saratov State Technical University, Saratov, 410054 Russia*

e-mail: mosgorsun@rambler.ru, samarinen@mail.ru, yashkovia@mail.ru, nvbadulina@mail.ru, mihail282@gmail.com, dinar.igtisamov@rambler.ru, foma92@list.ru, annette1988@inbox.ru

Received October 8, 2014

Abstract—The sedimentation conditions of Maastrichtian cyclic deposits in the Crimean Mountains were studied in detail for the first time using a complex of lithological and geochemical methods. The models of variations in temperature, salinity, and depth for the Tethys Ocean margin in the Maastrichtian were developed. Summary curves of $\delta^{18}O$ and $\delta^{13}C$ variations in Maastrichtian deposits of the Crimean Mountains were compiled.

Keywords: Maastrichtian, cyclicity, geochemistry, chemostratigraphy, paleogeography, depth, salinity, temperature, Crimea, Tethys

DOI: 10.3103/S0145875215020039

INTRODUCTION

Prospecting and exploration works, and subsequent development of hydrocarbon fields in the Black Sea Region requires the integration of geological data on the Crimea, Caucasus, and Black Sea. In order to compile diverse information, it is necessary to reinterpret historical data and to make an additional appraisal of the geological structure with detailed study of sedimentation conditions and reconstruction of paleogeographic settings at the modern scientific level. Complex lithological and geochemical study of Maastrichtian sediments of the Crimean Mountains is topical in terms of stratigraphy, sedimentology, and paleogeography. In our opinion, the obtained results are of practical scientific and educational interest for geological field works of the students of Moscow State University and other universities, as well as for the geological survey in the Black Sea Region, construction, and infrastructure development in the Crimean Peninsula.

The Research Method

Our research works were mainly carried out in the Bakhchisaray area of the Crimean Peninsula (Fig. 1) within the Kacha uplift in the interfluve between the Kacha and Bodrak rivers. The study area is located within the geological practice ground of second-year students of the Department of Geology of Moscow State University and at the boundary between sheets L-36-XXVII and L-36-XXIX of the 1 : 200000 Geological Map of Russian Federation.

The training facilities of students of St. Petersburg State University (SPSU) and the Russian State Geological Prospecting University (RSGPU) are also within the study area.

Apart from the above training facilities of three universities within the educational and scientific ground of MSU and sheet L-36-XXIX there is a training facility of Sternberg State Astronomical Institute (SSAI MSU) in the Nauchny settlement.

As a locality for additional appraisal the Belbek river valley (Fig. 1, Sevastopol area), where the uppermost Maastrichtian sequence was previously studied, the vicinity of the villages of Maloe Sadovoe (Gabdullin, 2002) and Tankovoe (Gabdullin, 2008) was chosen.

The aim of our research is to study the upper deposits of the Kudrino Formation (K_2kd, Upper Santonian–Maastrichtian), which correspond to the Maastrichtian. The sheet L-36-XXVII includes sections of Staroselie (section no. 1, environs of the town of Bakhchisaray), plateau Besh-Kosh (section no. 2), the Chakh-Makhly ravine (section no. 3, environs of village Skalistoe, the left bank of the Bodrak river). Sheet L-36-XXIX includes the Tokma ravine section on the right bank of the Bodrak river in vicinity of village Skalistoe (section no. 4).

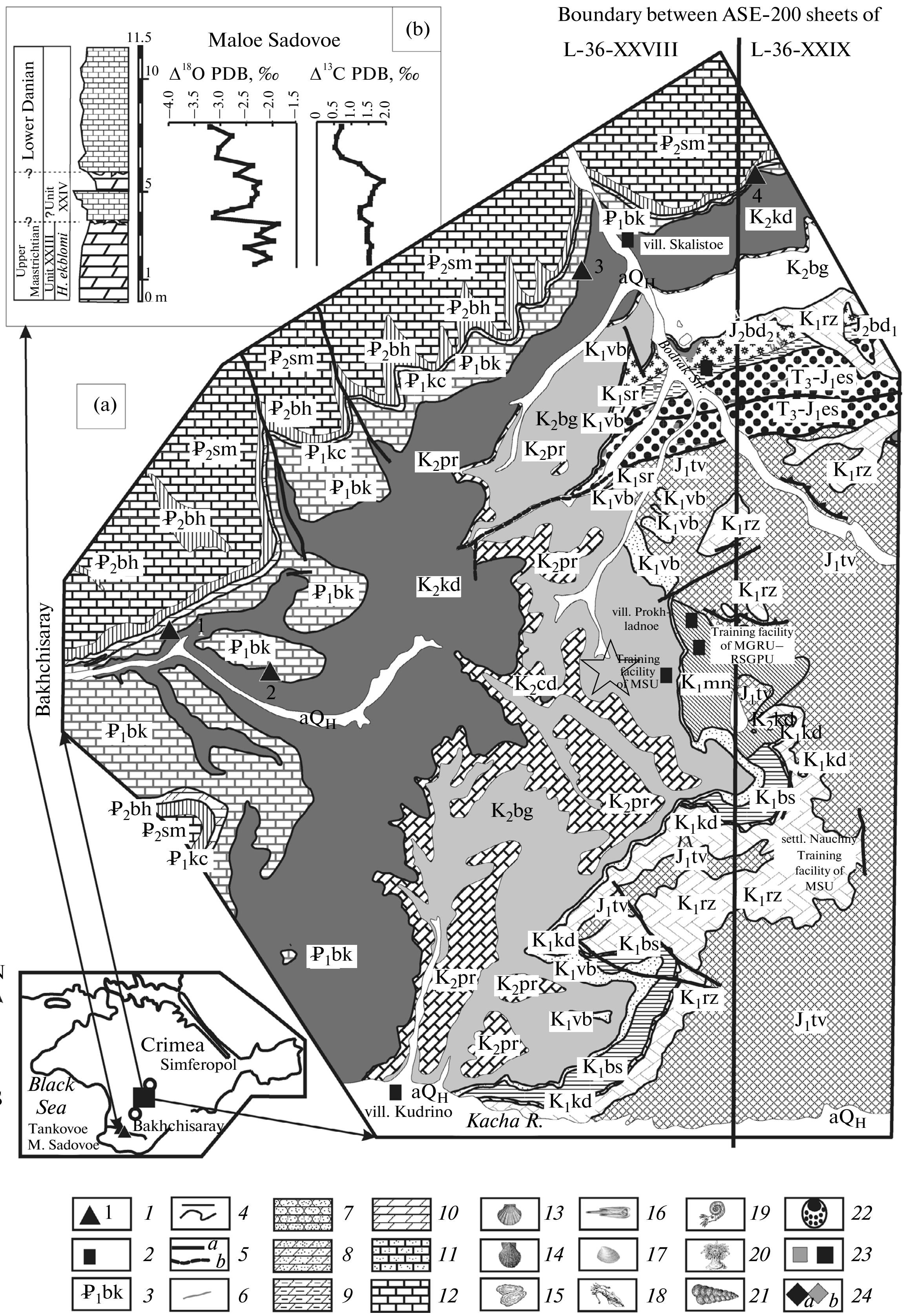
(b)
Maloe Sadovoe
Δ18O PDB, ‰
Δ13C PDB, ‰
Lower Danian
Upper Maastrichtian
Unit XXIII
?Unit XXIV
H. ekblomi
0 m
11.5
(a)
Boundary between ASE-200 sheets of
L-36-XXVIII
L-36-XXIX
Bakhchisaray
vill. Skalistoe
Bodrak Str.
vill. Prokhladnoe
Training facility of MGRU–RSGPU
Training facility of MSU
settl. Nauchny Training facility of MSU
vill. Kudrino
Kacha R.
N
S
Crimea
Simferopol
Black Sea
Tankovoe
M. Sadovoe
Bakhchisaray

Fig. 1. A geological map of the study area (a) and geochemical characteristics of the Maloe Sadovoe section (b): *1*, location of the section and its number; *2*, human settlements, training facilities; *3*, a stratigraphic index of a formation; *4*, geological boundaries; *5*, dislocations (*a*, proven, *b*, proposed); *6*, intrusions; *7*, sandstones; *8*, sandy marl; *9*, clayey marl; *10*, marl; *11*, *12*, arenaceus limestone; *13*, *Pecten*; *14*, *Chlamys*; *15*, *Ostrea*;*16*, *Pholadomya*; *17*, *Nucula*; *18*, *Belemnoidea*; *19*, *Ammonoidea*; *20*, *Anthozoa* (corals); *21*, *Textularia* (foraminifera); *22*, *Porifera* (Sponges); location of samples in the section, collected for: *23*, geochemical analysis, *24*, isotope paleothermometry (*a*, our data, *b*, archival data).

In section 1 (Staroselie) nine samples of upper Maastricht–lower Danian were collected. The results from studying four samples from this section are presented in this work, except for the greatest part of the Lower Danian deposits. In section 2 (Besh-Kosh) 9 samples (Maastrichtian–lower Danian) were collected. To interpret the results the literature data (Alekseev and Kopaevich, 1997; Gabdullin, 2002) on this section were used. In section 3 (the Chakh-Makhly ravine) the previously published data on 20 sampling sites (Gabdullin, Pervushov, and Tolstova, 2007) were not reinterpreted, but this section is necessary for layer-by-layer correlation with section 4 (Tokma ravine) and to clarify the sedimentation conditions of unit XXI (lower Maastrichtian). The previously studied Tokma ravine section (Sizanov, Rudakova, and Gabdullin, 2006) was a site of additional appraisal. As a result, the geochemical features of 62 samples of lower Maastrichtian deposits (unit XXI) were studied.

Sections 2–4 were previously studied to varying degrees with a complex of petrographic, chemical, physical, petromagnetic, and paleontological methods. A description of the methods and the results were given in (Alekseev and Kopaevich, 1997; Gabdullin, 2002; Sizanov, Rudakova, and Gabdullin, 2006; Gabdullin, Pervushov, and Tolstova, 2007).

The geochemical analysis of 80 samples (predominantly carbonate, and, to a lesser degree, terrigenous-carbonate rocks) was first made on the MARC.GV X-ray fluorescence spectroscan (NGO Spectron, St. Petersburg) at the Faculty of Engineering Geology, Department of Geology, Moscow State University (analyst E.N. Samarin). In total, 62 samples from section 4 (Tokma ravine), 9 samples from section 2 (plateau Besh-Kosh), and 9 samples from section 1 (Staroselie) were analyzed. In addition, the data on four samples from the Staroselie section (Maastrichtian and lower Danian) were taken into consideration.

The ratios of contents of several chemical elements that indicate variations in sedimentation conditions (a depth of the water, fluid dynamics, climate, etc.) were then calculated. The ratio values we obtained allowed us to clarify the previously formulated understanding of the sedimentation conditions in the study area.

Analysis of Oxygen and Carbon Isotopy in Carbonates and Paleothermometry

Oxygen- and carbon-isotope compositions were determined using a Thermo Delta V Advantage isotope-ratio mass spectrometer. Dried and ground samples were treated with 10.5% polyphosphoric acid using a GasBench II (GB) sample preparation device coupled to an isotope ratio mass spectrometer. We analyzed the oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) stable isotope compositions of carbon dioxide released as result of the acid–carbonate reaction. The measurement accuracy was controlled by the international NBS-19 standard. Isotope values are given in parts per million (ppm) relative to the VPDB.

All the samples were analyzed twice. The standard deviation did not exceed 0.1 ppm. Variations in $^{18}O/^{16}O$ ratio can be measured with a mass spectrometer with an accuracy of ±0.01%. However, due to fact that the sample preparation methods for the analysis did not allow one to achieve such a level of accuracy, the paleotemperature values were determined with an accuracy of up to 1°C, rarely up to 0.5° (Verzilin, 1979; Hefs, 1983).

If the carbonate skeletons of organisms (or chemogenic carbonate) formed in isotope equilibrium with the surrounding water at a constant isotope composition of the water in the carbonate substance, then the $^{18}O/^{16}O$ ratio depends greatly on the temperature variations, since the isotope equilibrium constant depends on the temperature. The dependence between the temperature and the $^{18}O/^{16}O$ ratio values for chemogenic and organogenic (shells of some marine invertebrates) calcites was experimentally determined.

The obtained equation of the paleotemperature scale is as follows:

$$t\,°C = 16.5 - 4.3(\delta^{18}O_c - \delta^{18}O_w) + 0.14(\delta^{18}O_c - \delta^{18}O_w)^2,$$

where, t °C is the temperature of the water where the calcium carbonate formed; $\delta^{18}O_c$ is the oxygen isotope composition in carbon dioxide released due to decomposition of calcium carbonate with 10.5% polyphosphoric acid and measured relative to the PDB standard, and $\delta^{18}O_w$ is the oxygen-isotope composition of carbon dioxide, equilibrated with water, from which $CaCO_3$ precipitates, and measured relative to SMOW (Faure, 1986; Kaplin and Yanina, 2010). However, when studying marine carbonates, there are a number of key tasks that must be achieved for a sufficient accuracy of paleotemperature determinations. First, one must know the $\delta^{18}O$ value of the sea water that is in equilibrium with a sample. Secondly, the $CaCO_3$ that is produced by some organisms is not in equilibrium with the water; therefore, the equation is unacceptable. Third, the oxygen-isotope fractionation is significantly influenced by the mineralogical composition.

The stratigraphic scheme of Maastrichtian deposits of the Bakhchisaray area, southwestern Crimea (after (Alekseev, 1989))

Stage	Sub-stage	Zone	Unit	Lithology
Maastrichtian	Upper	Neobelemnitella kazimiroviensis	XXIV	Marl, silty, glauconite-rich, with numerous belemnite rostra and pectenid shells. Locally preserved in sections in the Belbek river valley: Maloe Sadovoe, Tankovoe, Fig. 1). Thickness is 0–5 m
			XXIII	Aleurolites, limestones, sandstones, usually glauconite-rich. Thickness is 20–30 m
			XXII	Marl, yellow–gray, with sparse silification. Thickness is 25–50 m
	Lower	Belemnella sumensis	XXI	Marl, gray, with sparse silification. Thickness is 25–50 m
		Belemnella lanceolata	XX	Marl, gray, sometimes clayey, low-silty. Thickness is 50 m

In addition, the equations for aragonite, calcite, Mg calcite, and dolomite were established. It is also necessary to take variations in isotope composition after the burial of carbonate as a result of dissolution and redeposition into account.

Thus, it should be noted that the $\delta^{18}O$ values in $CaCO_3$-unsubstituted skeletons are determined not only by the seawater temperature, but also the isotope composition of the water, the mineral composition of shells, and, probably, metabolic effects. In total, 13 whole-rock samples of biogenic carbonate (marl and limestone) and carbonate (clay marl, sandy marl, sandy limestone) rocks (4 from section 1 and 9 from section 2) were studied (except for a sample from section 1).

The Characteristics of Maastrichtian Deposits of the Crimean Mountains

Maastrichtian deposits, which extend as a narrow zone along the second range of the Crimean Mountains, unconformably rest on upper Campanian deposits with signs of a short stratigraphic hiatus and are overlain by an unconformity that varies in amplitude by Paleocene (Danian) limestones and calcareous sandstones (Alekseev, 1989).

In southwestern Crimea the lower Maastrichtian deposits compose two zones: a lower Belemnella lanceolata zone (sub-units XX-1 and XX-2 of unit XX) and upper Belemnella sumensis Zone (sub-unit XX-3 of unit XX and unit XXI). Upper Maastrichtian deposits are characterized by a Neobelemnitella kazimiroviensis zone (table). The thickness of predominantly carbonate (with a small fraction of terrigenous material) Maastrichtian deposits in southwestern Crimea varies from 0 to 150 m (Alekseev, 1989).

Based on foraminiferal assemblages, the zones of Brotzenella complanata (sub-units of XX-1, XX-2, and the lower part of sub-unit XX-3 of unit XX), Gavelinella midwayensis (the upper part of sub-unit XX-3 of unit XX and the lower part of unit XXI), and Brotzenella praeacuta (the upper part of unit XXI) were distinguished in Lower Maastrichtian deposits of the Besh-Kosh plateau section (Alekseev and Kopaevich, 1997). In Upper Maastrictian deposits of Mt. Besh-Kosh zones of Brotzenella praeacuta (the base to the upper part of unit XXII) and Hanzawaia ekblomi (the upper part of unit XXII, unit XXIII) were distinguished. The most complete Maastrichtian succession among those considered in this work is located on the Besh-Kosh plateau. The thickness of lower Maastrichtian deposits (units XX–XXI) is consistent and is usually 75–80 m (Alekseev, 1989).

The Besh-Kosh section (Figs. 1 and 2) has a thickness of Lower Maastrichtian deposits of 94 m (Alekseev and Kopaevich, 1997).

Unit XX (66 m, plateau Besh-Kosh). Marl and limestone, dark gray to pale gray, sometimes clayey at the base, low silty. The lower Maastrichtian age of this unit is confirmed by the occurrence of ammonites: *Hoploscaphites constrictus*, *Hauericeras sulcatum*, and *Diplomoceras cylindroceum*, as well as, rare belemnites: *V. lanceolata* and *V. sumensis occidentalis*.

The unit contains a rich assemblage of pelecypods: *Chlamys*, *Entolium*, *Nucula*, *Lopha*, *Pycnodonte*, *Acutostrea*, and *Pholadomya* (Alekseev, 1989). Unit XX is subdivided into three sub-units (Alekseev and Kopaevich, 1997):

Sub-unit XX-1. Pale gray spotted marl. The content of insoluble residue increases from bottom (7%) to top (14–20%) of the section. The unit is poorly exposed. Rhythmicity is not visible. The thickness in the Besh-Kosh section is 20 m.

Sub-unit XX-2. Pale gray and yellowish sandy marly limestones. The content of insoluble residue is 10–28%. The thickness in the Besh-Kosh section is 23 m.

Sub-unit XX-3. Gray sandy marl with pyrite nodules. Thickness of 23 m. The content of insoluble residue is 17–22% (Alekseev and Kopaevich, 1997).

The middle and upper sub-units of unit XX contain trace fossils *Thallassinoides*.

Unit XXI is exposed in a rocky ledge. Marl, dark gray to pale gray, weakly silty, with pyrite nodules, thickness of 25–30 m. The thickness of the unit in the

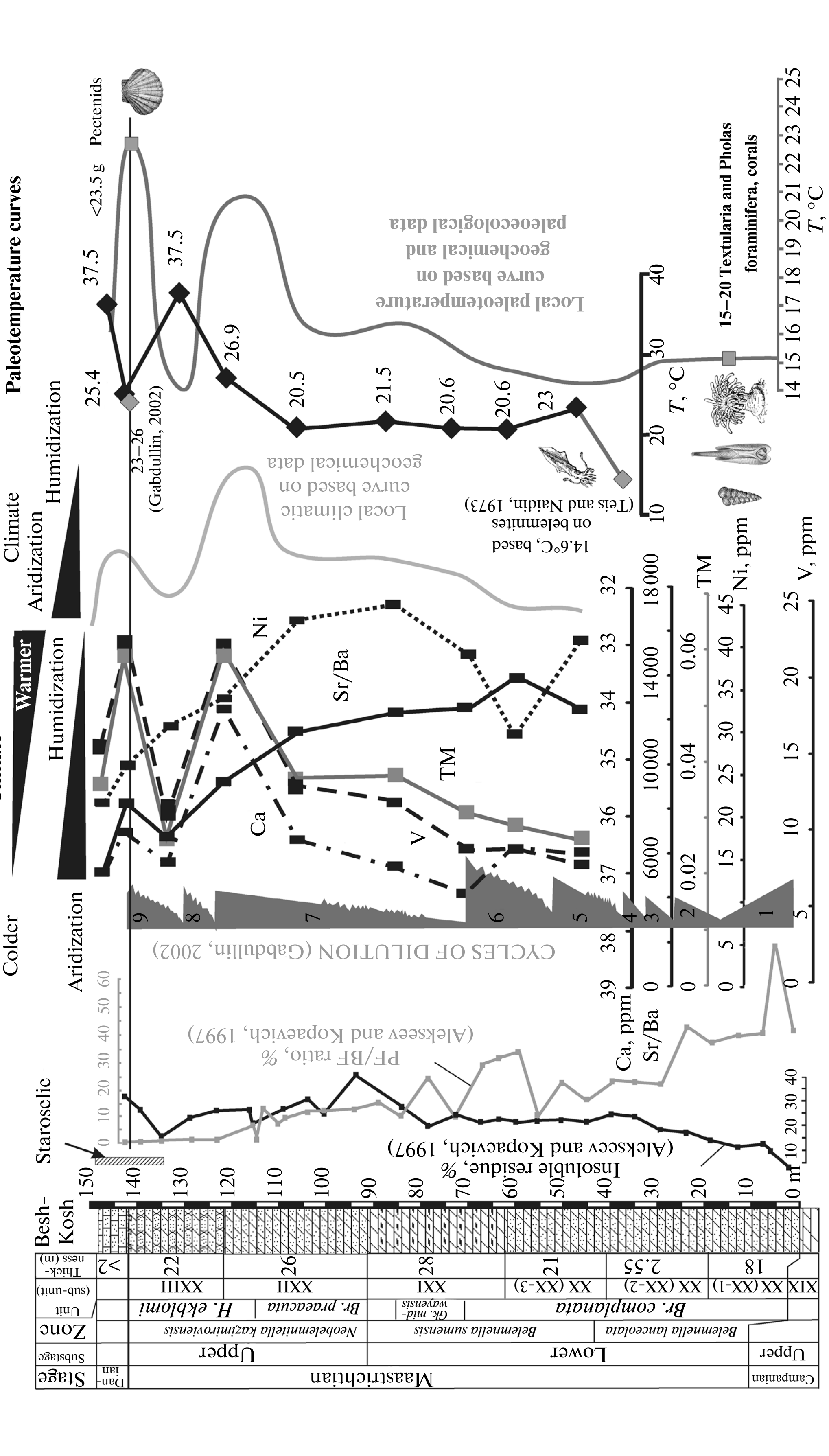

Fig. 2. The lithological, paleontological, and geochemical characteristics of the section of the Besh-Kosh plateau in connection with climatic variations. See the symbols in Fig. 1.

section on the plateau Besh-Kosh is 28 m (Alekseev and Kopaevich, 1997). The unit contains trace fossils *Thallassinoides*.

Units XX and XXI contain a rich assembalage of gastropods (*Haustator* sp., *Athleta* sp., etc.), hexacorals (*Parasmilia biseriata*, etc.) and octocorals, brachiopods, crustaceans, and sponges. There are findings of hexacorals fish scales and fish bones. Fossil echinoids *Echinocorys* sp., starfishs, and sea lilies are rare (Alekseev, 1989).

Upper Maastrichtian deposits, represented by units XXII–XXIII, were studied in the Mt. Besh-Kosh section and beyound the training facility of MSU in the environs of the villages of Maloe Sadovoe and Tankovoe (units XXII-XXIV) in the Belbek river valley (Gabdullin, 2002, 2008). They are conformably overlain by lower Maastrichtian deposits. Thickness is 40–80 m (Alekseev, 1989).

The Besh-Kosh section (Fig. 2): the thickness of upper Maastrichtian deposits is estimated to be 48 m (Alekseev and Kopaevich, 1997).

Unit XXII. Gray to yellow–gray sandy marls with fragments of sponges and silicified trace fossils (*Thallassinoides*). There are several distinct layers of dense marl in the weathering profile.

The content of terrigenous admixture reaches 32–38%. The thickness of the unit is 25–50 m (Alekseev, 1989); in the Mt. Besh-Kosh section it is 26 m (Alekseev and Kopaevich, 1997).

Unit XXIII. Limestone, yellowish-gray, sandy, glauconite-rich, with frequent layer surfaces of the "hard bottom" type, lenses with oysters (*Exogyra*, *Gryphaeostrea*, *Pycnodonte*, *Lopha*, etc.) and pectenids (*Chlamys*, *Entolium*, *Camptonectes*). There are pelecypods of genus *Pholadomya*. The unit contains belemnite rostra *Neobelemnella kazimiroviensis* and ammonite cores *Pachydiscus* ex. gr. *neubergicus*, which confirms its Late Maastrichtian age. The deposits of unit XXIII contain a rich assemblage of macrofossils. A section of the unit is crowned by greenish-gray glauconite carbonate (up to 65% carbonate) sandstones (Alekseev, 1989). The thickness of the unit is 20–30 m, in the section on the Besh-Kosh plateau it is 22 m (Alekseev and Kopaevich, 1997). There are trace fossils Thallassinoides.

Unit XXIV. Marl, yellowish to purple, silty, glauconitic, with numerous belemnite rostra of *Neobelemnella kazimiroviensis* and large pectenid shells *Entolium* sp.

The thickness of the unit is 0–5 m (Alekseev, 1989), in the section on the Besh-Kosh plateau this unit was not identified (Alekseev and Kopaevich, 1997).

Sections in the Environs of the Villages of Maloe Sadovoe and Tankovoe

(Fig. 1) are located to the north of these villages in the Belbek river valley (Bakhchisaray area of south-western Crimea) and described in the geological literature (Naidin and Benyamovsky, 2000; Gabdullin, 2002, 2008).

Unit XXIV. Marl and calcareous marl, yellowish-greenish-gray, silty, glauconitic, with numerous belemnite rostra *Neobelemnella kazimiroviensis*. Identification of the Maastrichtian-Danian boundary in the terminal part of the upper Maastrichtian of this unit is problematic due to the presence of two hiatal surfaces. Both upper and lower hardground surfaces contain belemnite rostra. The distance between the erosional surfaces in the section is 2.3–2.4 m. The thickness of the section is 3.5–5.9 m.

The geochemical features of the Maastrichtian succession in the Crimean Mountains allowed us to calculate the concentrations (ppm) of 29 elements and compounds, as well as six ratios (modules), which are necessary to clarify the sedimentation conditions and genesis of rhythmicity (Figs. 2–11). This technique has been widely discussed (Sklyarov, 2001; *Klimat*..., 2004; Engalychev and Panova, 2011). Sometimes some of the parameters are contradictory in terms of their paleogeographic interpretation, which requires further consideration.

Below, we briefly and selectively discuss the variations in the concentrations of elements, their compounds and ratios.

In order to analyze variations in paleotemperatures (Figs. 2, 6, 9, 11), following concentrations of elements and their ratios have been used: V, Ca, Ni, Ca/Sr, the titanium module (TM), Mn, and Si/Al. Variations in paleotemperature can also be evaluated with the following ratios: Ca/Mg, Sr/Ba, Zn/Nb, and (Ce, Nd, La, and Ba)/Yb (Y and Zr).

An increase in Ca, Sr, and Mg concentrations may indicate arid climatic conditions; an increase in Sc, Ni, Zn, Y, W, U, C, V, and rare earth elements (REEs) may mean humid sedimentation conditions.

Titanium module (TM) is the TiO_2 vs Al_2O_3 ratio, which depends both on the dynamic facies sedimentation and teh titanium module of the provenance area. Accordingly, if we regard the facies factor as a constant, the TM is a good indicator of basic or acid rocks in a provenance area. The difference between TM values indicates variations in climatic conditions. Humid climate sandy-silt deposits are characterized by higher TM values than those of arid climate deposits. The same tendency is noted for clayey rocks. It is possible to use this module to reconstruct climatic sedimentation conditions only if a permanent provenance area is established. In some cases, dynamic sorting of terrigenous material and the composition of the provenance area affect the TM value much more than the climatic index. In summary, the TM value tends to increase with the arid-humid zone; within the humid zone, TM increases following from abyssal to coastal marine and continental zones (Engalychev and Panova, 2011).

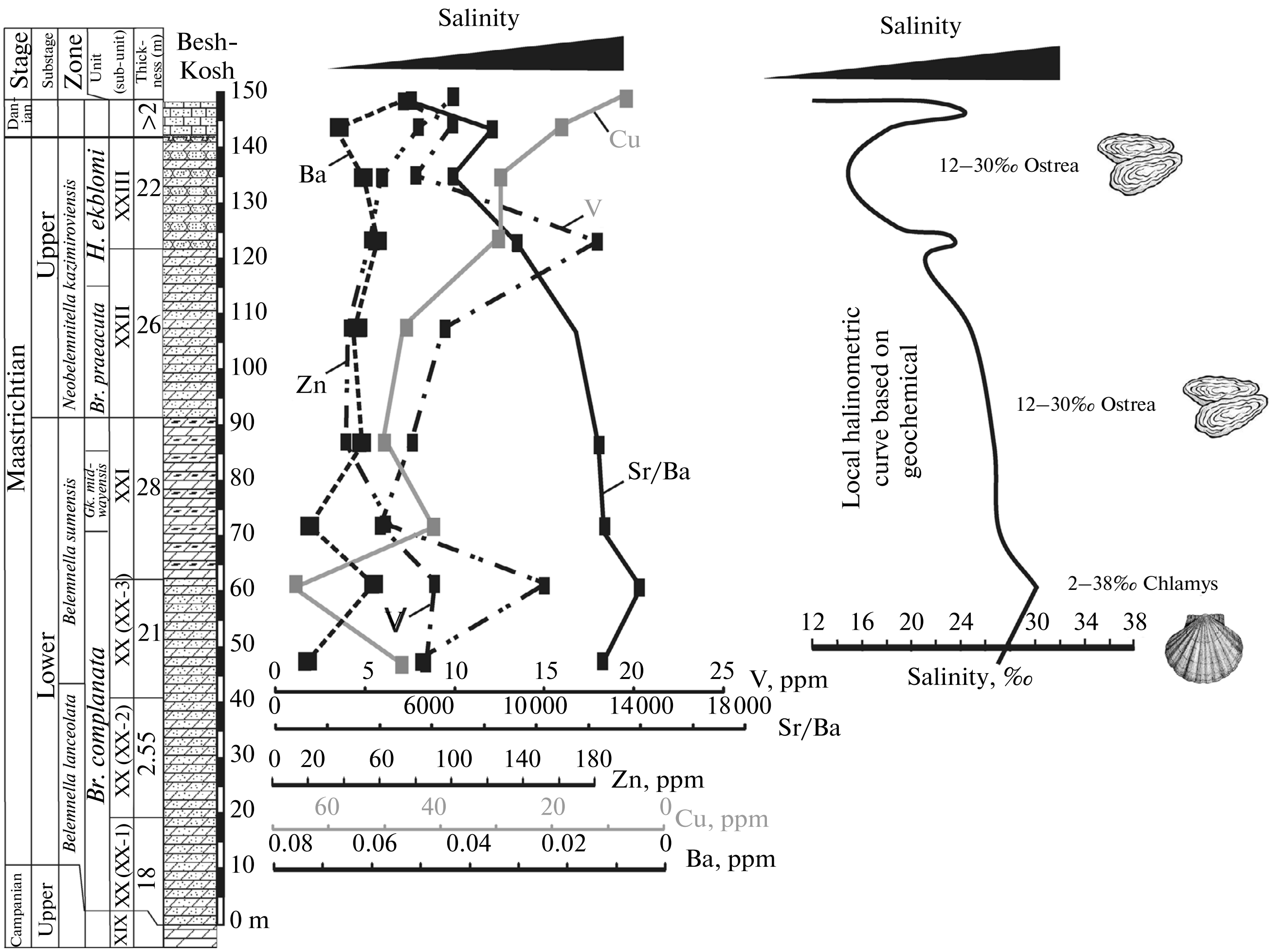

Fig. 3. The lithological, paleontological, and geochemical characteristics of the section of the Besh-Kosh plateau in connection with variations in salinity. See the symbols in Fig. 3.

The Fe/Mn and Ti/Mn ratios, titanium module (TM), sodium module (SM), and potassium module (PM), as well as variations in the contents of Zn, Pb, Al, Mn, Cu, Sr, and Ba, constraining the shift in facies boundaries, characterize the depth variations in a sedimentary basin (Figs. 4, 7, 10).

The Fe/Mn ratio. The decrease in the Fe/Mn ratio is related to an increase in depth, as well as shelf to pelagic facies transition. This trend is due to the absorption of manganese by the sediments from marine water, which is increasing in deep-water conditions. According to the Fe/Mn ratio, sedimentary rocks can be subdivided into deep (<40), shallow (~80) and shallow-water coastal with predominantly terrigenous provenance areas (>160).

The Fe/Mn ratio can also be applied to classifying clayey or clay-containing deposits, and, to a lesser extent, to carbonate deposits (Sklyarov, 2001).

The Potassium module (PM = K_2O/Al_2O_3) is determined by the intensity of chemical weathering processes in an erosion area. Potassium, which is a constituent of feldspars, accumulates during their decomposition in continental sediments under arid climatic conditions. Under humid climatic conditions of sedimentation, potassium is transferred in the form of solutions, suspensions, and concentrates in marine and lacustrine sediments. Aluminum is associated with the clayey constituent of rocks; its contents in sediments increases towards the open sea. Low PM values are typical for continental sediments, while in the littoral and pelagic sediments its value increases (Engalychev and Panova, 2011).

The sodium module (SM = Na_2O/Al_2O_3). Sodium is usually transferred in the form of solutions and suspensions; the maximum Na concentration is characteristic of continental sediments under arid climatic conditions, as well as of marine and lacustrine sediments under humid climatic conditions. Coastal-marine sediments are characterized by the lowest contents of sodium (Engalychev and Panova, 2011).

Sr and Ba contents. The increase in the Sr content indicates the distance of terrigenous material from a provenance area; in contrast, an increase in the Ba

Paleobathymetric curves

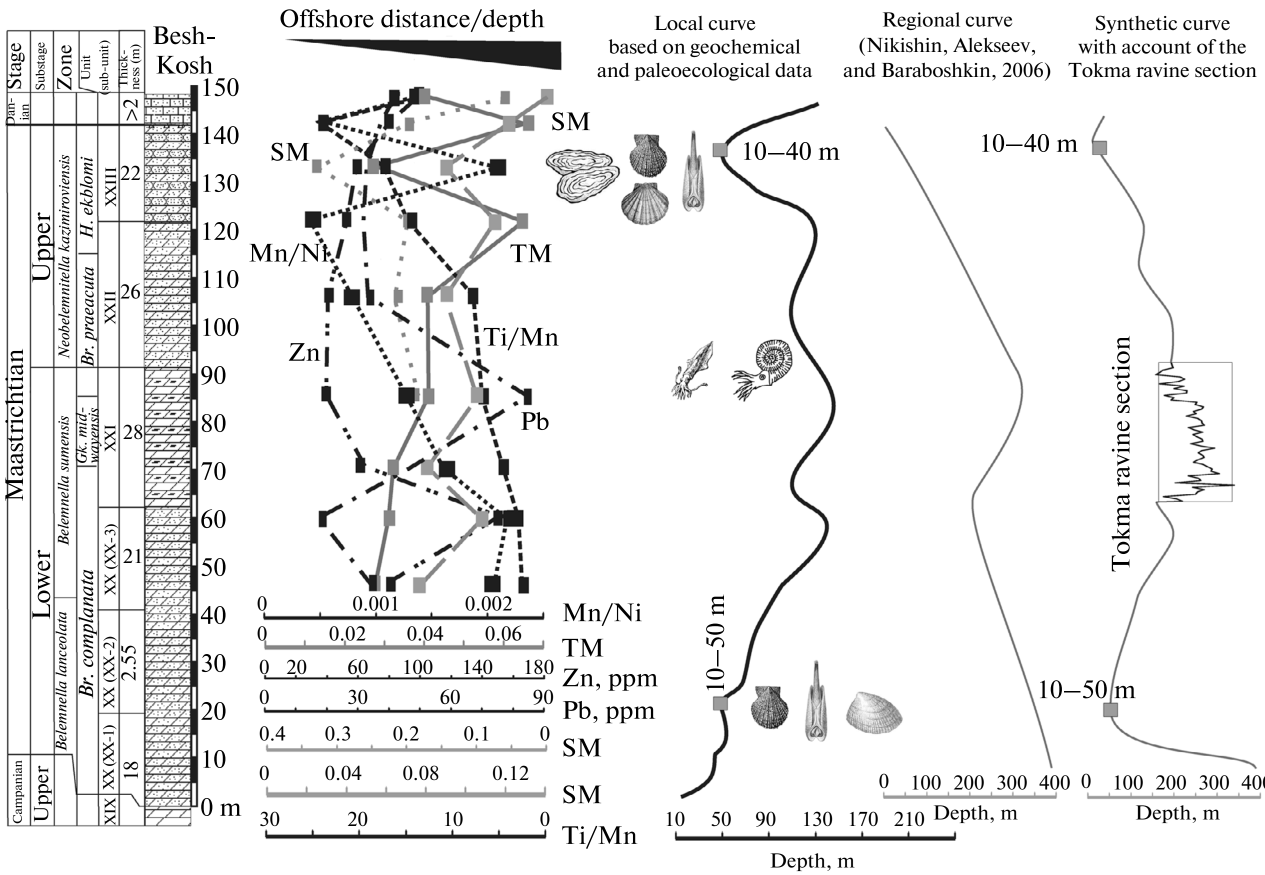

Fig. 4. The lithological, paleontological, and geochemical characteristics of the section of the Besh-Kosh plateau in connection with variations in a depth. See the symbols in Fig. 1.

content indicates the closeness of a provenance area. With increasing depth of the sedimentation basin, Ba goes increasingly into solution. At a depth of 4–5 km, however, its concentration can reach the maximum value, as it reacts with the environment and precipitates.

Pb and Zn contents. The increase in Pb and Zn contents is caused by the proximity to a provenance area and/or the increase in salinity of the sedimentation basin.

In order to analyze variations in salinity (Figs. 3, 8, 10), we considered the Sr/Ba and Ca/Sr ratios. In the case of the violation of the physical and chemical equilibrium of a saline solution, because of its burial some minerals in the system dissolve (for example, calcite), while others precipitate (dolomite). As a result, an essential transformation of brine composition with selective concentration of chemical elements, including Ca, Sr, and Ba, takes place.

The same tendency is evident for over-saline solutions, where Ca concentration decreases to almost zero with increasing salinity, as it is replaced by Mg contained in sediments. Consequently, an increase in Sr/Ba and Ca/Sr ratios indicates the higher salinity of solution. The concentrations of B, Ba, S, Cr, Cu, Ga, Ni, and Y in marine sediments are higher than those in freshwater sediments.

Zn and Cu are also indicators of the salinity of solution; the mobility of these elements depends on the salinity.

The Cu content in river waters is almost always constant. Due to this, when river and sea waters are mixed, the precipitation rate of Cu in sediments decreases with increasing salinity of the resulting solution. The Zn mobility also decreases with increasing the salinity.

Discussion of Geochemical Data

The data we obtained allowed us to reconstruct the sedimentation conditions in the Maastrichtian in the Crimean Mountains.

Climate. In general, analysis of the geochemical data in the Mt. Besh-Kosh section (Fig. 2) shows a

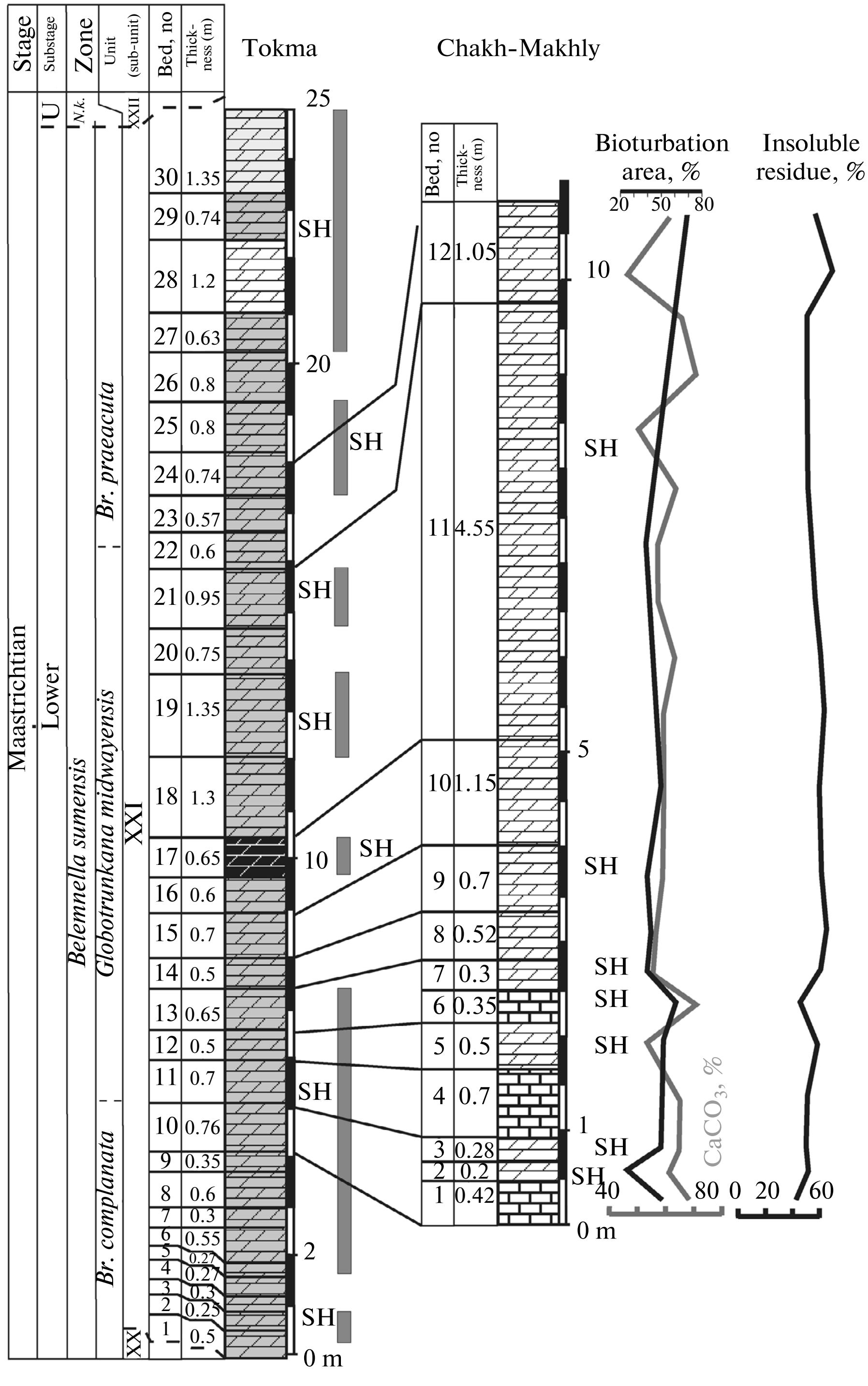

Fig. 5. The correlation scheme and lithology of Lower Maastrichtian sections (unit XXI) in the Bodrak stream valley (the Tokma and Chakh-Makhly ravines). See the symbols in Fig. 1

tendency towards climate warming and humidization (except for unit XXIII). Cyclical climatic variations are correlated with the elemental rhythmicity in Maastrichtian deposits, which includes nine cycles of dilution, that is, an increased offshore drift of the terrigenous material (Gabdullin, 2002). In the section (from bottom to top) this is confirmed by the sanding of carbonate rocks (marl) and an increase in the concentration of insoluble residue from 5% for the Early Maastrichtian to 35–40% in the Late Maastrichtian (Alekseev and Kopaevich, 1997).

This cyclicity is also correlated with cyclical variations in relationship between planktonic and benthic foraminifera (Alekseev and Kopaevich, 1997), which

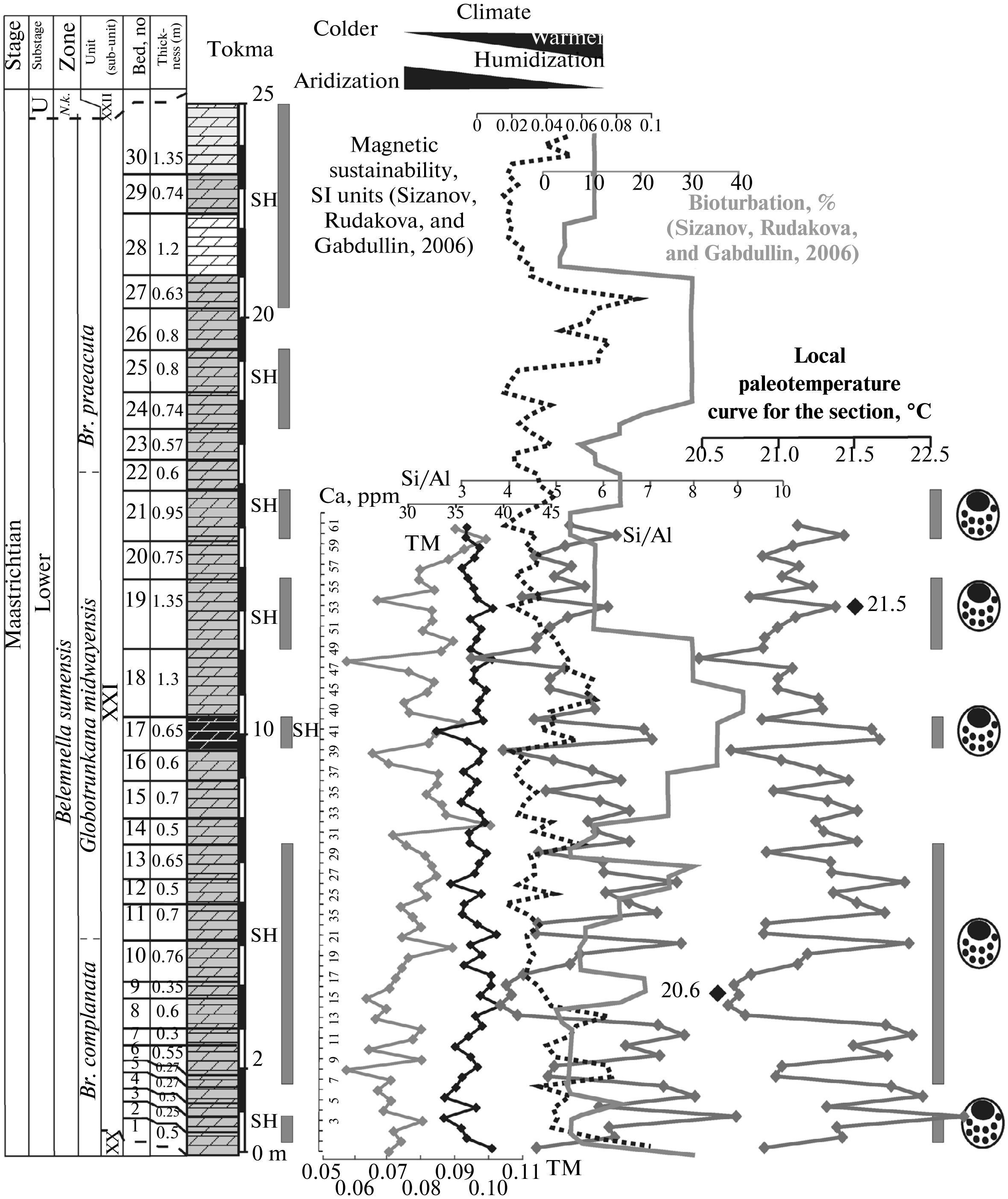

Fig. 6. The lithological, paleontological, petromagnetic, and geochemical characteristics of the Lower Maastrichtian section (unit XXI) in the Tokma ravine in connection with climatic variations. See the symbols in Fig. 1.

indicates variations in the paleodepth. There are two trends in distribution of geochemical parameters along the section. The concentration curves for V, Ca and TM are similar and show an increase in temperature and climate humidization; the distribution curves of the Sr/Ba ratio and Ni concentration, in contrast, show an inverse dependence, viz., successive cooling and climate aridization. The occurrence of thermophilic corals and Bulimina foraminifera, which is common for temperate waters, allows us to suggest the presence of warm or warm-temperate waters in the Belemnella sumensis zone.

According to the isotope data, this period was characterized by an increase in the seawater temperature

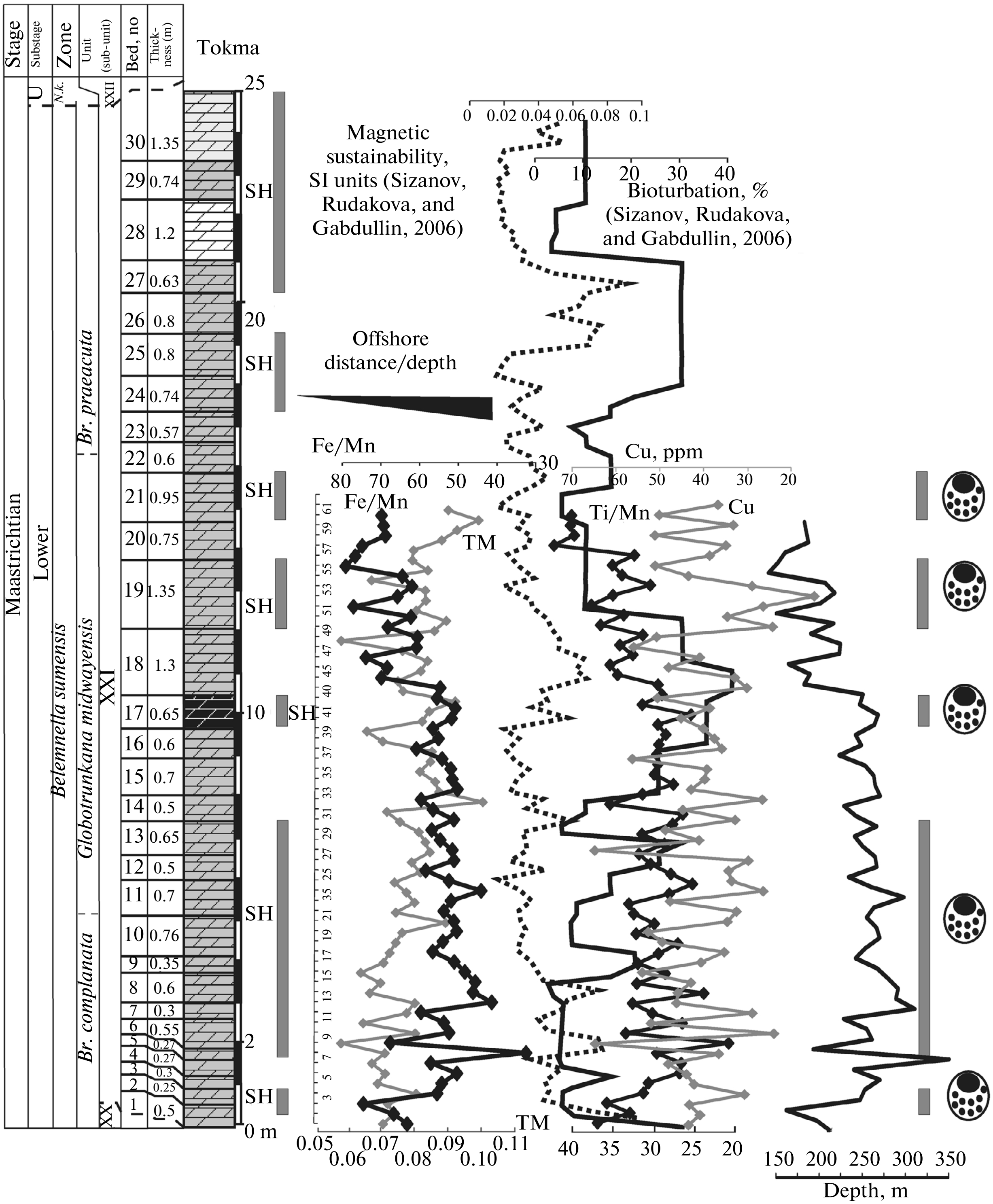

Fig. 7. The lithological, paleontological, petromagnetic, and geochemical characteristics of the Lower Maastrichtian section (unit XXI) in the Tokma ravine in connection with variations in a depth. See the symbols in Fig. 1.

from 14.6°C (Teiss and Naidin, 1973) at the top of unit XX (zone Br. Complanata) to 37.5°C (our data) in unit XXIII (zone N. ekblomi). The minimum paleotemperatures (20.6°C) were obtained for the boundary between units XX and XXI, as well as the middle part of unit XXII (20.5°C). The relatively low temperatures at the beginning of Early Maastrichtian were also paleontologically confirmed by the occurrence of corals,

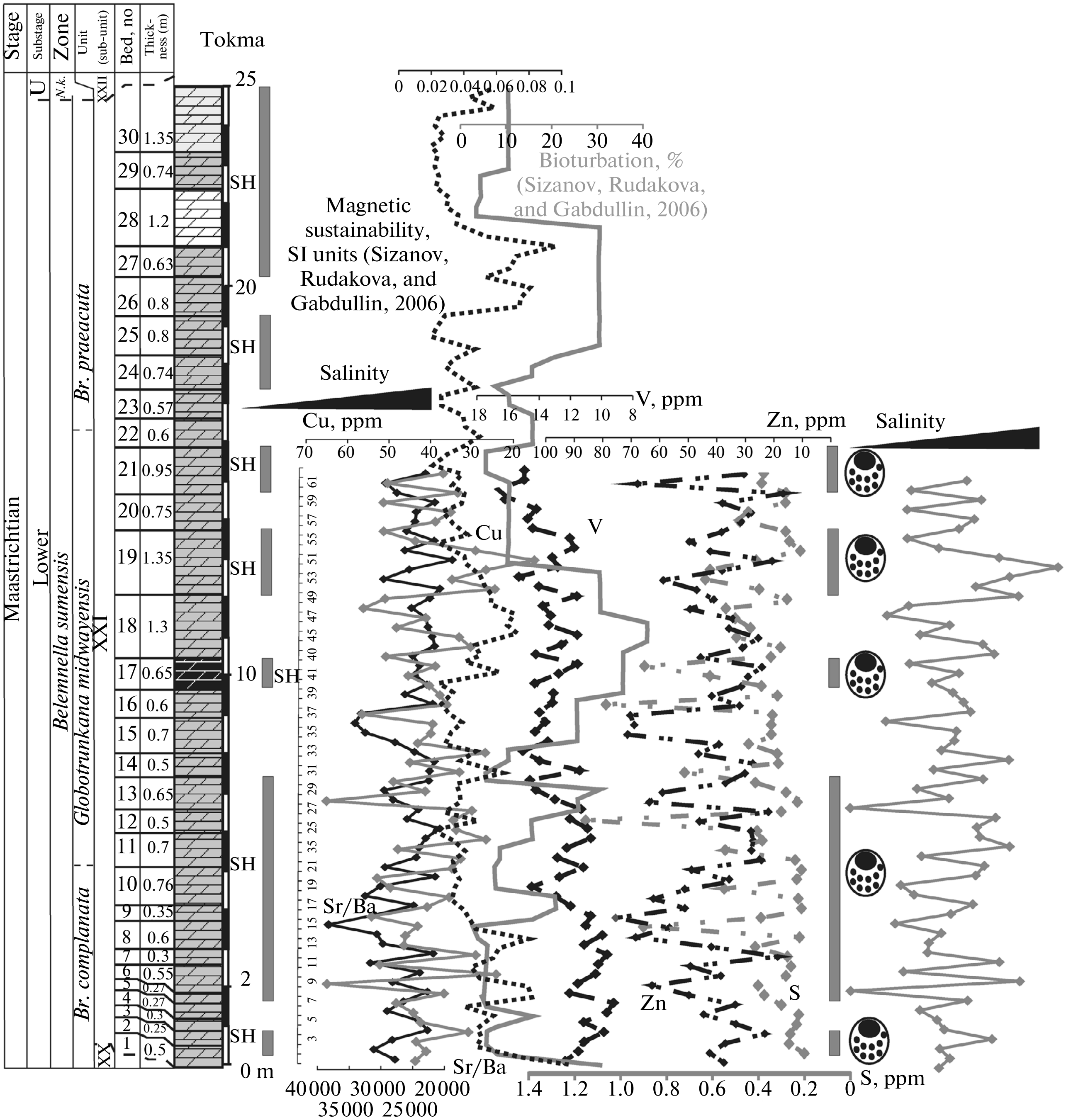

Fig. 8. The lithological, paleontological, petromagnetic, and geochemical characteristics of the Lower Maastrichtian section (unit XXI) in the Tokma ravine in connection with variations in salinity. See the symbols in Fig. 1.

Pholas and *Textularia* foraminifera, which indicate the temperature range from 15 to 20°C. The occurrence of vegetal spores in Hanzawaia ekblomi Zone (the top of Belemnitella kazimiroviensis Zone) enables the reconstruction of the coastal vegetation. The flora was represented by mangroves, which are typical of a warm tropical climate (Alekseev, 1989).

The uppermost Maastrichtian deposits (units XXIII, XXIV) are characterized by the occurence of pectenid banks, which generally inhabit waters that do not exceed 23.5°C. The temperature range of 23–26°C was determined for unit XXIV (section Maloe Sadovoe, Crimea). The relatively small dataset for this section only makes it possible to talk about fundamental variations in temperature (warming), in comparison, for example, with the detailed characterized section in the Tokma ravine. This is the reason that we chose the geochemical model of warming and humidization that

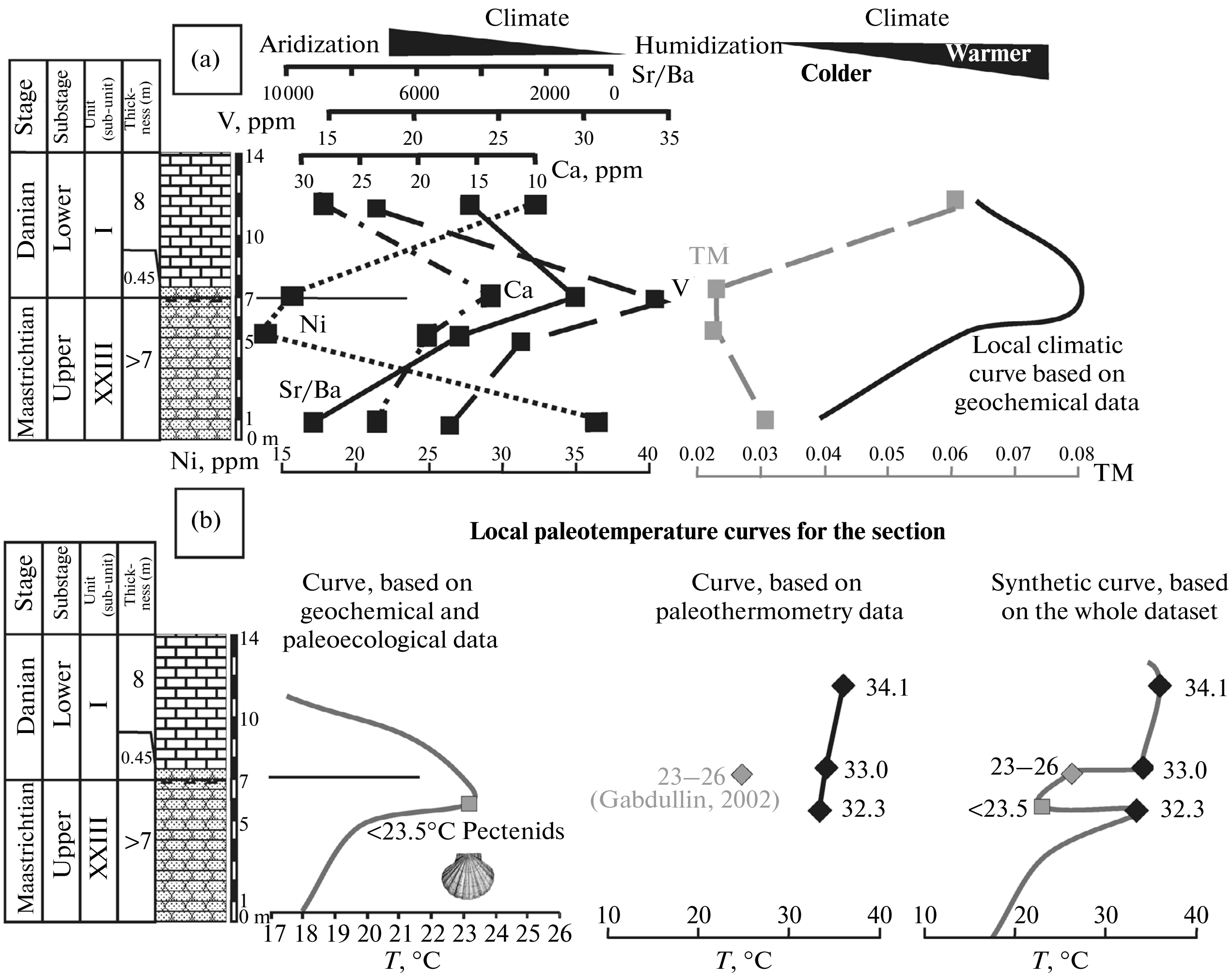

Fig. 9. The lithological, paleontological, and geochemical characteristics of the Cretaceous-Paleogene boundary section in Staroselie in connection with climatic variations. See the symbols in Fig. 1.

was confirmed by the paleotemperature data. The uppermost Maastrichtian (the deposition time of unit XXIV) is characterized by a range of sea-water temperatures from 23 to 26°C (Gabdullin, 2002).

Salinity. Analysis of the distribution curves of Zn and Ba concentrations (Fig. 3) shows a weak, almost background variation in salinity. The V and Cu concentrations increase up the section. The Sr/Ba ratio decreases to the top of the Maastrichtian deposits. In unit XX, euryhaline bivalves of genus *Chlamys* that exist in a wide salinity range of 2–38% were found (Gabdullin, 2002). The obtained Foraminifera-based cyclic variations in salinity in the rhythmic section of Belemnella lanceolata Zone indicate fluctuations in salinity (Gabdullin, 2002). Interlayers with *Cibicides* and *Bolivina* foraminifera (normal salinity, favorable conditions) alternate with those that are enriched by *Textularia* foraminifers (unfavorable conditions). Units XXI and XXIII contain euryhaline oysters of the genus *Ostrea* that lived in water with a relatively smaller range of water salinity, 12–30% (Gabdullin, 2002). Having compared paleontological and geochemical data, we constructed a local halinometric synthetic curve that shows that the ocean water salinity gradually decreased with certain episodes of salinization at the boundary between units XX and XXI, at the top of unit XXII, and at the boundary between units XXIII and XXIV.

Depth. The distribution curves of geochemical parameters (Fig. 4) are difficult to interpret. It is evident that there were variations in these parameters. Combination of these curves enables us to construct a local paleobathimetric curve with fixed paleodepth ranges that were established based on molluscs-indicators in units XX, XXI, and XXIII. Unlike units XX and XXIII, in which there are complexes of bivalves *Pecten* and *Pholadomya*, as well as *Chlamys* (unit XXIII) and *Nucula* (pack XXI), that coexisted together in a depth range of ≤40–50 m, unit XXI contains nektonic molluscs, viz. ammonites and belemnites, indicating a relatively great paleodepth. Deposits of Belemnella lanceolata Zone are characterized by

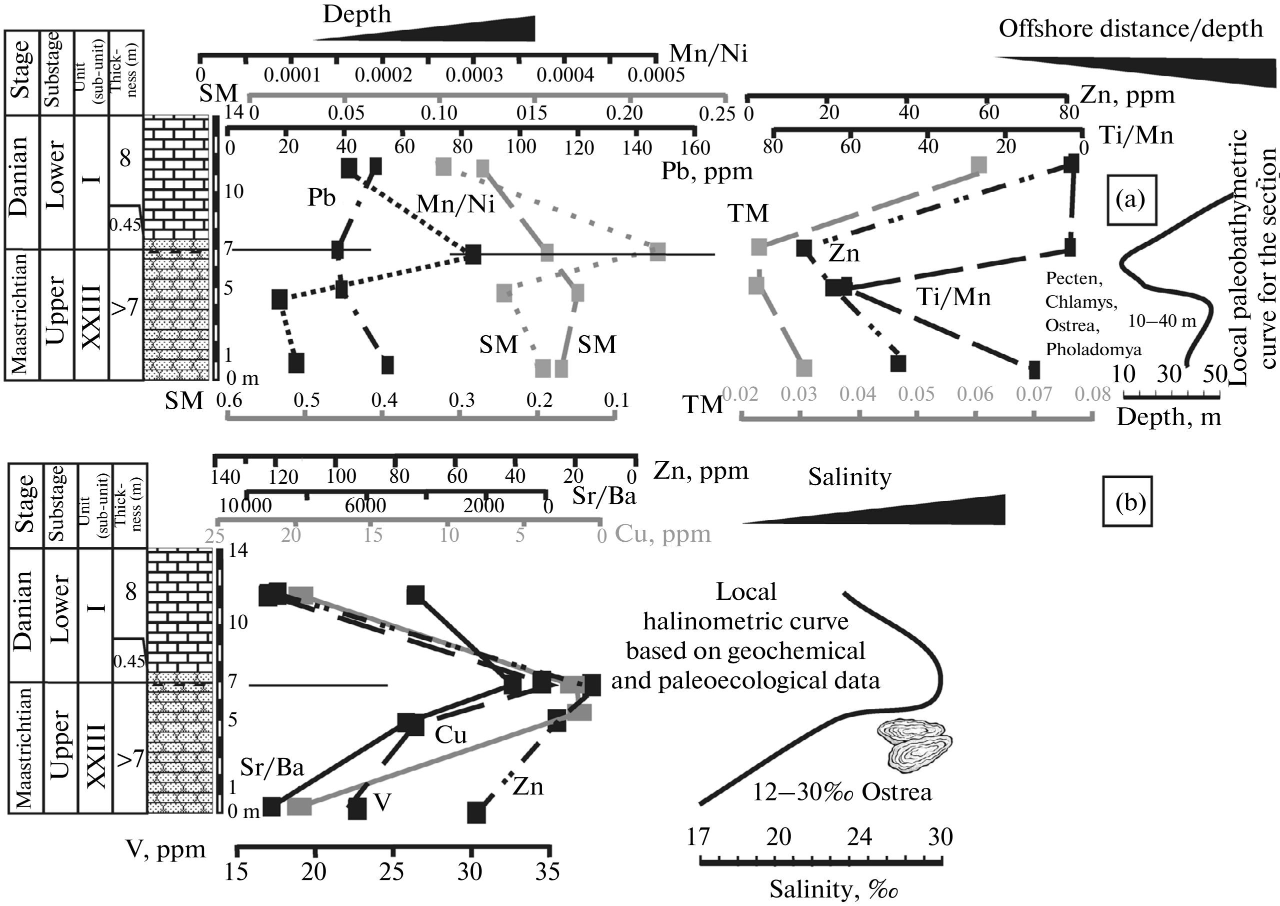

Fig. 10. Lithological, paleontological, and geochemical characteristics of the Cretaceous-Paleogene boundary section in Staroselie in connection with variations in depth (a) and salinity (b). See the symbols in Fig. 1.

the *Cibicides–Bolivina* foraminiferal assemblage, regularly distributed in the rhythms. Layers with *Cibicides* and *Bolivina* foraminifera (relatively less deep) alternate with *Bolivina* foraminifera layers (relatively deep). The composition of the paleocenosis includes plankton with carbonate skeletons. The benthic macrofossils predominate (more than 30 genera, 42 species) over nekton macrofossils (3 genera and 3 species). A significant proportion of pelecypods (Alekseev, 1989) in the biocenosis (15 genera, 24 species) are evidence of a relatively shallow basin (Gabdullin, 2002). The Brotzenella complanata Zone (the base of Belemnitella kazimiroviensis Zone) contain deep-water *Cibicides–Bolivina* foraminiferal assemblage. There were variations in a basin depth that follows from a cyclic distribution of foraminifera in the rhythmic section. Interlayers with *Cibicides* foraminifera (relatively shallow) alternate with interlayers *Bulimina–Bolivina* foraminiferal assemblage (relatively deep) and subordinate *Cibicides*. Pelecypods are absent; there are rare ammonites and belemnites.

The structure of the paleocenosis in sediments of the Hanzawaia ekblomi Zone (the top part of Belemnitella kazimiroviensis Zone) includes plankton with carbonate skeletons; benthic macrofossils predominate (20 genera, 29 species) over the nekton ones (2 genus, 2 species). In addition, the composition of paleocenosis includes the following macrofauna: pelecypods, brachiopods, crustaceans, belemnites, and ammonites (Alekseev, 1989), which is evidence of the relative shallowness of the basin. These deposits include a large number of pelecypods, which are usually regarded as depth indicators: *Pecten*, 10–50 m, *Chlamys*, 2–50 m, *Ostrea*, 40–100 m, and *Pholadomya*, 1–10 m. The estimated depth of the basin was 10–40 m, which confirms the variations in the paleodepth of the sedimentation basin.

Based on geochemical and paleontological data we have constructed the local paleobathymetric curve, which is well correlated with a most part of the regional paleobathymetric curve. The regional paleobathymetric curve (Nikishin et al., 2006) shows a decrease in eustatic ocean level during the Maastrichtian with a short transgressive phase during the formation of unit XXI (Gk. midwayensis Zone). Taking the summarized dataset into account the synthetic paleobathymetric curve was constructed. A fragment of this curve can be constructed in more detail using the

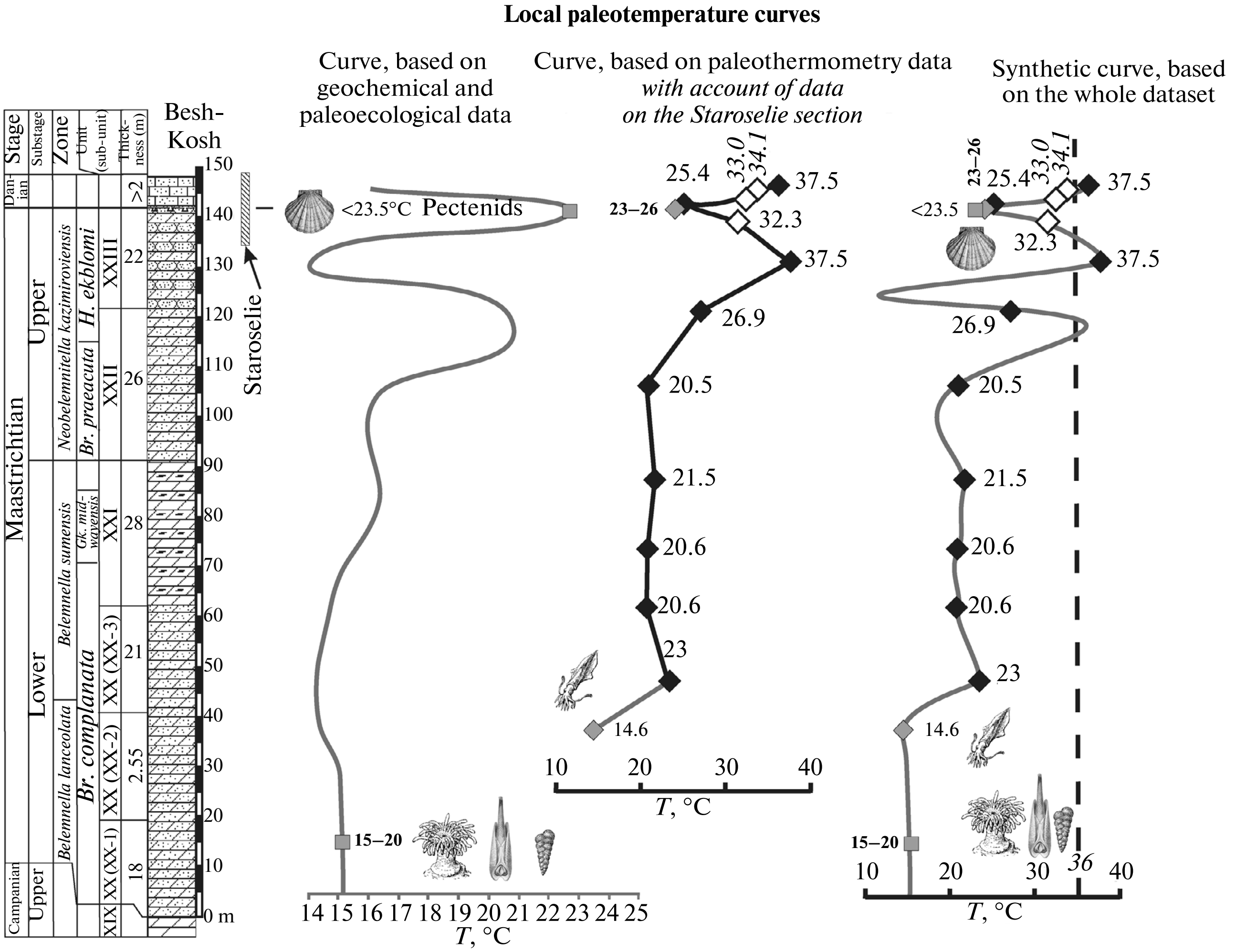

Fig. 11. Paleotemperature characteristics of the Besh-Kosh plateau section. See symbols in Fig. 1. The isotherm corresponding to the highest temperature of 36°C in modern seawater and oceanic basins is shown by dashed line.

detailed studied section of unit XXI in the Tokma ravine. The paleodepth in the Maastrichtian throughout the Crimea varied from 10 to 400 m.

Sections in the Tokma and Chakh-Makhly Ravines. The sections of deposits of unit XXI were studied in the Tokma ravine (Sizanov, Rudakova, Gabdullin, 2006) and Chakh-Makhly ravine (Gabdullin et al., 2007), which are located on the opposite banks of the Bodrak river in the environs of the village of Skalistoe. The location scheme of these sections is shown in Fig. 1 and the correlation scheme is given in Fig. 5. The unit is presented by rhythmically interbedded marls, some of which contain a large number of sponges (so-called sponge horizons (SH). Sponge horizons may vary from a few decimeters to several meters in thickness. The correlation scheme shows that the thicknesses of the layers (or groups) are almost always similar in these two sections. In section of the Tokma ravine gray marl with single layers of black (layer 17), pale gray (layer 30), and white (layer number 28) marls occurs. In the section of the Chakh-Makhly ravine one can distinguish limestone layers (1, 4, and 6) in the thick marl unit XXI. The content of insoluble residue, as calculated from thin sections, the $CaCO_3$ concentration, determined by the chemical method, as well as bioturbation area in deposits of the Chakh-Makhly ravine section vary insignificantly.

An analysis of the complex of physical, chemical, paleontological, and petrographic data together with macroscopic observations allowed us to establish that there are no fundamental differences between the sponge and sponge-free horizons in the Chakh-Makhly ravine. Such rhythmicity is explained by a periodic additional supply of allochtonous sponges from the shallower parts of the basin against the background of eustatic variations in sea level and/or reorientation of the bottom currents (Gabdullin et al., 2007).

Based also on similarities of the sponge and sponge-free layers in the Tokma ravine section, Sizanov et al. (2006) proposed a new method for identifying reservoir cyclites, which correspond to transgressive and regressive events and phases of climate warming and cooling. Owing to this method, transgressive (layers 1, 3–7, 8–12, 14–16, 17–20, etc.) and regressive (layers 2, 13, 21–25, etc.) stages, as well as the stages of relative warming (layers 2–3, 8–12, 15–16, 17–20, 21, etc.) and cooling (layers 1, 3–7, 12–14, etc.) were established (Sizanov et al., 2006).

Sponge horizons are related to the beginning of the warming and climate humidization (Fig. 6). The correlation of the SH with an increase in the admixture of terrigenous material and volume of bioturbated deposits is ambiguous. Climatic variations are geochemically confirmed by variations in the Si/Al ratio, as well as the TM and Ca concentration.

The Si/Al ratio distribution curve is regarded as a key curve for estimating the climatic variations. Having compared the sampling sites for which there are paleotemperature data, in the section of unit XXI on Mt. Besh-Kosh and in the Tokma ravine section, we were able to determine the range of seawater paleotemperature variations (from 20.5 to 22°C). As a rule, the beginning (base) of the sponge horizon corresponds to the warming; its end (top) corresponds to the cooling.

Variations in the Paleodepth (Fig. 7) were confirmed by the character of the distribution of Cu concentration, as well as the TM, Fe/Mn and Ti/Mn ratio values. The Fe/Mn ratio distribution curve is the most representative. In order to construct a local paleobathymetric curve, we used depth values from the regional curve (Nikishin et al., 2006) and the previously published data.

The beginning (base) of the SH usually coincides with the relative submergence of the basin and/or the possible weakening of drift of terrigenous material; the termination (top) coincides with the relative shallowing and/or possible intensification of drift. Variations in the paleodepth are also confirmed by the shape of the magnetic-susceptibility distribution curve in the section (Fig. 7).

The decrease in the magnetic susceptibility is related to the transgression stage and the offshore distance (a source of ferromagnetic minerals) and the increase is related to the regression stage and the proximity of a provenance area. The good correlation between the magnetic susceptibility and Fe/Mn ratio curves should be emphasized.

Variations in Salinity are correlated with variations in Zn, V, Cu, as well as the Sr/Ba ratio (Fig. 8). The distribution curve of the Cu concentration is regarded as the most representative curve for estimating the variations in salinity. The beginning of the formation of the SH is correlated with an increase in salinity; the end of the formation is correlated with a decrease in salinity. As a result, the sponge horizon is related to a single climatic cycle (cooling–warming), a single eustatic cycle (transgression–regression), and single cycle of variations in salinity (salinity–desalination).

The Staroselie section is a low-thickness section of terminal Maastrichtian and basal Danian deposits (Fig. 9), which was investigated in the area of the former village of Staroselie, the northeastern outskirts of Bakhchisaray (Fig. 1, section 1).

Climatic and temperature variations are confirmed by rhythmic variations in Ca, V, and Ni concentrations, as well as Sr/Ba and TM values. Only the Ni concentration and TM values are off of the general trend of the distribution of the other parameters listed above. Having summarized the distribution of Ca and V and the Sr/Ba ratio, we constructed a local paleoclimatic curve based on geochemical data (Fig. 9a). We then correlated the results we obtained with data on the distribution of fossils, indicators of environmental conditions (pectenids, for example) and paleotemperature data (32.3–34.1°C) and constructed a synthesized local paleotemperature curve (Fig. 9b), taking the literature data into account (Gabdullin, 2002). As follows from the analysis of this curve, the Cretaceous–Paleogene boundary deposits in the Staroselie section is related to the stage of cooling to 23°C.

Variations in the basin paleodepth in this section at the end of Maastrichtian are constrained by variations in the Pb and Zn concentrations, as well as the values of the Mn/Ni and Ti/Mn ratios and the TM, PM, and SM modules. However, the distribution of the KM module and the Mn/Ni ratio are characterized by a trend that is opposite to that of the above-listed parameters. Taking the identified bivalves into account, indicators of environmental conditions (*Pecten*, *Chlamys*, *Ostrea*, *Pholadomya*), that coexist in a depth range of 10–40 m, as well as the regional paleobathymetric curve (Nikishin et al., 2006), we constructed a local paleobathymetric curve for the Staroselie shallow-seawater section. Salinity in this marginal part of the Tethys Ocean increased in the late Maastrichtian (Fig. 10b), but it did not exceed 30 ppm (the critical value for oysters of the genus *Ostrea*). This tendency was established based on variations in the distribution of V, Cu, and Zn, as well as the Sr/Ba ratio. Thus, the dataset we obtained by studying four sections in the Bakhchisaray area and taking data on the Sevastopol area into account allows us to clarify the paleotemperature estimates that are given in Fig. 11.

The calculated paleotemperature values for the terminal Maastrichtian deposits in the Staroselie and Besh-Kosh sections are well correlated with each other.

CONCLUSIONS

Based on a comprehensive study of Maastrichtian deposits in four sections (Staroselie, Besh-Kosh, Chakh-Makhly, and Tokma) in the Bakhchisaray area and two sections in the Sevastopol area (Maloe Sadovoe and Tankovoe) the sedimentation conditions on the southern margin of the Tethys Ocean were

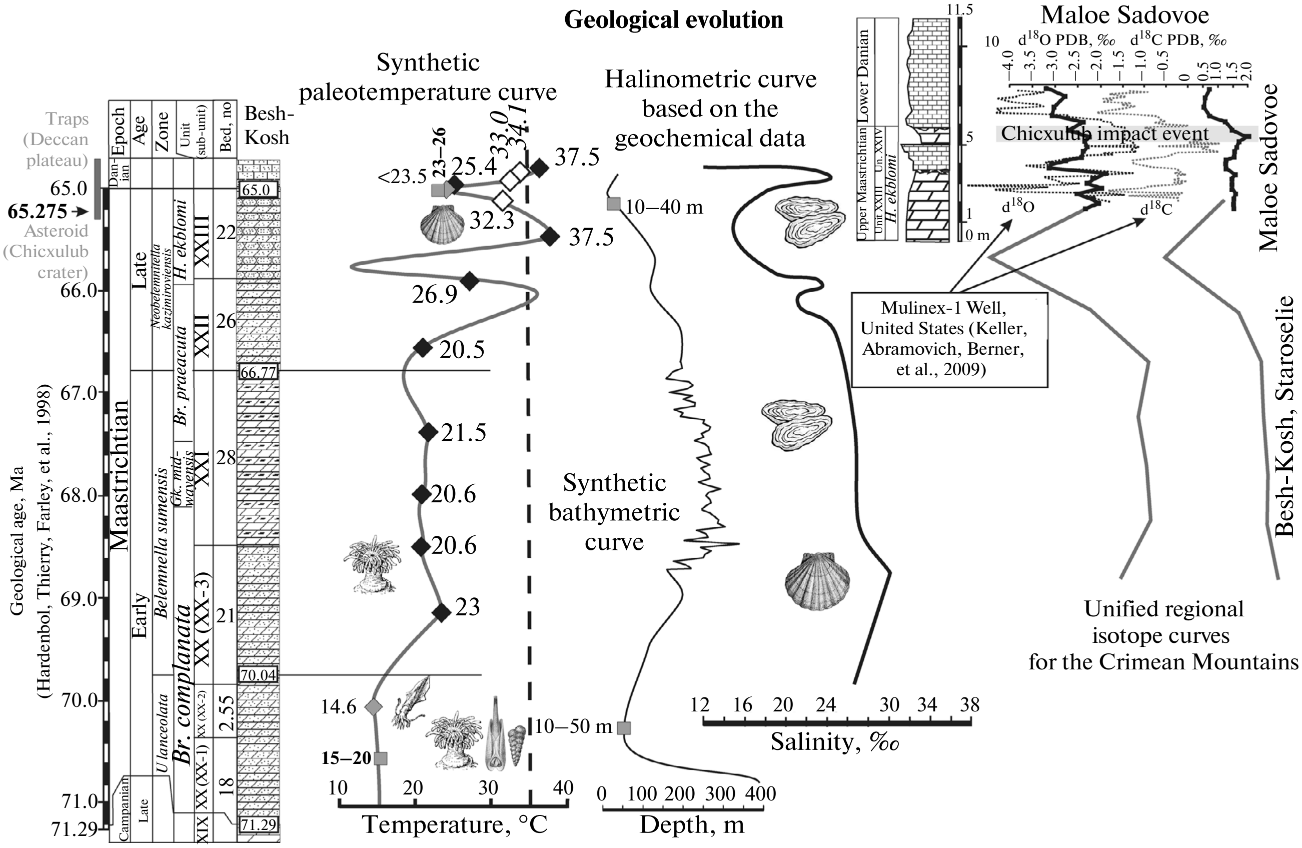

Fig. 12. The geological history of the Bakhchisaray area in the Maastrichtian. See symbols in Fig. 1.

specified (Fig. 12). For this purpose, we used the geochronological scale from (Hardenbol et al., 1998).

We propose models of the variations of temperature, salinity, and depth in the waters of the marginal part of the Tethys Ocean in the Maastrichtian.

In general, the temperature of the oceanic water from the Early to Late Maastrichtian increased from 14.6°C to 37.5°C, respectively. The warming of the climate took place against the background of a short-term regressive stage in the Early Maastrichtian, followed by successive transgression, which lasted until the Middle Maastrichtian. In the second half of the Maastrichtian Stage transgression was followed by regression with a short transgressive pulse at the end.

The variation in the depth range was different by an order of magnitude, approximately from 40 to 400 m. Transgression was accompanied by an increase in the salinity of oceanic waters (to 30 ppm); regression was accompanied by a decrease in the salinity (to about 12–24 ppm).

The strong paleotemperature variations and high T values at the end of the Maastrichtian could be connected with global planetary events: the fall of an asteroid with a diameter of about 11 km into the Atlantic Ocean (Chicxulub crater) and the outpouring of the Deccan trap basalts in India (Fig. 12).

In addition, the $\delta^{18}O$ variations can be connected with variations in the composition of accumulated carbonates and water salinity that eventually resulted in an increase in the temperature.

A detailed study of the nature of the rhythmicity in the deposits of unit XXI, which contains sponge and sponge-free interlayers, showed that, as a rule, the beginning (base) of the sponge horizons is related to the relative warming, submergence, and/or a possible weakening of the drift of terrigenous material and an increase in the salinity of the Tethys ocean waters; the end (top) is related to the cooling, relative shallowing and/or a possible intensification of the drift of terrigenous material and a decrease in the salinity of the waters of the Tethys Ocean.

Based on the data that are available on the sections of Staroselie, Besh-Kosh, and Maloe Sadovoe, consolidated regional curves of $\delta^{18}O$ and $\delta^{13}C$ variations were constructed for Maastrichtian deposits in the Crimean Mountains (Fig. 12).

Owing to correlation of these curves with curves of $\delta^{18}O$ and $\delta^{13}C$ variations in the Moulinex-1 section (Texas, United States (Keller et al., 2009), we obtained a good correlation with the hemostratigraphic scheme. The results we obtained allow us to determine the stratigraphic position of an impact event at the end of the Maastrichtian Stage in the sections of the Crimean Mountains, as well as to compile a hemostratigraphic correlation scheme of sections of the Crimean Mountains and other regions.

ACKNOWLEDGMENTS

This work was supported by Ministry of Education and Science (Strategic development program of Gagarin Saratov STU for 2012–2016, projects nos. SSTU-141 and SSTU-146, the theme 2.1.6. The development of educational-research laboratory of Engineering Geoecology) and Russian Foundation for Basic Research (projects nos.14-05-31171, 14-05-31538 mol_a). We performed stable isotope analyses of light elements using the Thermo Scientific Delta V Advantage mass spectrometer that was provided under the Development Program of Moscow State University.

REFERENCES

Alekseev, A.S., The Upper Cretaceous, in *Geologicheskoe stroenie Kachinskogo podnyatiya Gornogo Kryma. Stratigrafiya mezozoya* (Geological Structure of the Kacha Uplift of the Crimean Mountains. Mesozoic Stratigraphy), Mazarovich, O.A. and Mileev, V.S, Eds., Moscow: Izd. Moscow State Univ., 1989, pp 123–135.

Alekseev, A.S. and Kopaevich, L.F., Foraminiferal biostratigraphy of the uppermost Campanian–Maastrichtian in SW Crimea (Bakhchisaray and Chakhmakhly sections), *Bull. Inst. Roy. des sciences naturelles de Belgique. Sci. de la Terre*, 1997, vol. 67, pp. 103–118.

Engalychev, S.Yu. and Panova, E.G., Geochemistry and genesis of sandstones of eastern part of Main Devonian field in the northwestern part of the Russian Plate, *Litosfera*, 2011, no. 5, pp. 16–29.

Faure, G., *Principles of Isotope Geology*, New Your: John Wiley, 1986.

Gabdullin, R.R., *Ritmichnost' verkhnemelovykh otlozhenii Russkoi plity, Severo-Zapadnogo Kavkaza i Yugo-Zapadnogo Kryma* (Rhythms of Upper Cretaceous Deposits in the Russian Plate, Northwestern Caucasus and Southwestern Crimea (Structure, Classification, Models of Formation), Moscow: Izd. Moscow State Univ., 2002.

Gabdullin, R.R., Pervushov, E.M., and Tolstova, N.V., Structure and genesis of cyclic sequence with alternating horizons enriched in and barren of fossil sponges, the lower Maastrichtian of Bakhchisarai area in the southwestern Crimea, *Moscow. Univ. Geol. Bull.*, 2007, vol. 62, no. 1, pp. 10–14.

Gabdullin, R.R., Structure and accumulation conditions of Upper Maastrichtian sediments at the Tankovoe (Tank) settlement (Southwest Crimea), *Moscow Univ. Geol. Bull.*, 2008, vol. 63, no. 4, pp. 214–226.

Hardenbol, J., Thierry, J., Farley, M.B., et al., Mesozoic and Cenozoic sequence chronostratigraphic framework of European basins, in *Mesozoic and Cenozoic Sequence Stratigraphy of European Basins. SEPM Spec. Publ.*, 1998, vol. 60, no. 1, 1998.

Kaplin, P.A. and Yanina, T.A., *Metody paleogeograficheskikh rekonstruktsii: Metod. posobie* (Methods of the Palaeogeographical Reconstruction. A Toolkit), Moscow, 2010.

Keller, G., Abramovich, S., Berner, Z., and Adatte, T., Biotic effects of the Chicxulub impact, K–T catastrophe and sea level change in Texas, *Palaeogeogr., Palaeoclimat., Palaeoecol.*, 2009, vol. 271, pp. 52–68.

Hoefs, J., *Stable Isotope Geochemistry, 2nd ed.*, Springer, 1980.

Klimat v epokhi krupnykh biosfernykh perestroek (Climate in Epochs of Major Biospheric Reorganizations), Semikhatov M.A. and Chumakov, N.M., Eds., Moscow: Nauka, 2004.

Naidin, D.P. and Ben'yamovskii, V.N., Stage subdivision of the Paleocene, *Stratigr. Geol. Correl.*, 2000, vol. 8, no. 4, pp. 378–395.

Nikishin, A.M., Alekseev, A.S., Baraboshkin, E.Yu., et al., *Geologicheskaya istoriya Bakhchisaraiskogo raiona Kryma: Ucheb. posobie po Krymskoi praktike* (Geological History of the Bakhchisaray Area of the Crimea: A Guide to Crimean Practice), Moscow: Izd. Moscow State Univ., 2006.

Sizanov, B.I., Rudakova, A.V., and Gabdullin, R.R., New techniques of rhythm recognition and genesis interpretation by the example of lower Maastrichtian deposits in the Tokma ravine (Southwestern Crimea, Ukraine), *Moscow. Geol. Univ. Bull.*, vol. 61, no. 3, pp. 30–40.

Sklyarov, E.V., *Interpretatsiya geokhimicheskikh dannykh* (Interpretation of Geochemical Data), Moscow: Internet-Inzh., 2001.

Teis, R.V. and Naidin, D.P., *Paleotermometriya i izotopnyi sostav kisloroda organogennykh karbonatov* (Paleothermometry and Isotopic Composition of Oxygen in Organic Carbonates), Moscow: Nauka, 1973.

Verzilin, N.N., *Metody paleogeograficheskikh issledovanii* (Methods of Paleogeographic Studies), Leningrad: Nedra, 1979.

Vinogradov, V.I., Isotope factors of geochemical changes in sedimentary rocks, *Priroda*, 2011, no. 11, pp. 22–28.