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Palaeoenvironmental conditions of hardgrounds formation in the Late Turonian-Coniacian of Mangyshlak Mountains, Western Kazakhstan

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ABSTRACT:

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A carbon and oxygen isotope stratigraphic profile has been made, for the first time, through the Late Turonian-Coniacian sedimentary sections containing regionally widespread firm- and hardgrounds of Mangyshlak Mountains, western Kazakhstan. Generally, Turonian and Coniacian time has been considered as a transitional stage between two Oceanic Anoxic Events (OAE), because of the peculiar pattern of variation of the $\delta^{13}C$ and $\delta^{18}O$ values. Unfortunately, there is no such record in the sections we examined, thus the Mangyshlak Sea behaved uniquely compared to the majority of seas and oceans at that time. The process of hardground formation is polygenetic but involved stopping deposition of calcium carbonate and initiation of the hardground over the large area of the sea floor. Normal causes of cessation of calcium carbonate seem unlikely and the expected drastic changes of hydrochemistry of the bottom waters cannot be detected in any of the minerals within the hardground sediments. Also, changes in climate, if there were any, are very difficult to estimate. Moreover, winnowing of the carbonate sediment is also not detectable from the characteristics of the hardground surface. Because the sedimentary sequence containing that regional hardground formation is transgressive, the most plausible reason for cessation and deposition of calcium carbonate is acceleration of the transgression. This might release sufficient amounts of carbon dioxide and bicarbonate to slow precipitation and deposition of calcium carbonate. Also, the greater distance from the shore might have reduced the supply of nutrients which decelerated photosynthetic activity, which in turn decreased consumption of carbon dioxide, thus enhancing precipitation of calcium carbonate. Some additional winnowing of calcium carbonate sediments would have helped in subsequent development of the hardground. Finally, deceleration of the transgression renewed precipitation and deposition of calcium carbonate.

Key words: Palaeoenvironment, Hardground, Carbonate cementation, Late Turonian-Coniacian, Mangyshlak Mts.

INTRODUCTION

The purpose of this paper is to interpret, for the first time, the carbon and oxygen isotope stratigraphic profile through the Late Turonian-Coniacian sedimentary sequence of the Mangyshlak Kazakhstan. The sedimentary sequence contains regionally widespread firm- and hardgrounds. Interpretation of the $\delta^{13}C$ and $\delta^{18}O$ record across the Late Turonian-Coniacian sedimentary succession is compared with the well established geochemical model. Interpretation of the detailed pattern of the $\delta^{13}C$ and $\delta^{18}O$ values across the selected hardground is to identify the main causes of formation of such a hardground.

Hardgrounds are very characteristic structures related to early cementation of calcium carbonate sediments. Early cementation of calcium carbonate is quite widespread in recent marine sediments (see BRICKER 1971, BATHURST 1975, SCHNEIDERMANN & HARRIS 1985; for review), from the beach (TAYLOR & ILLING 1969, ALEXANDERSSON 1973), through offshore sediments (SHINN 1969, DRAVIS 1979) and reef buildups (GINSBURG & *al.* 1971, FRIEDMAN & *al.* 1974) to deep-water sediments (FISHER & GARRISON 1967). Specific products of early calcium carbonate cementation include lithified submarine sedimentary horizons creating a hard substrate for boring bivalves, sponges and other specific organisms and a variety of encrusting bryozoans, corals, brachiopods, bivalves, and polychaetes. These horizons are called hardgrounds (for definition see BROMLEY 1975). Specificity of hardgrounds is related not only to a problem of early cementation of calcium carbonate bottom sediments, but also to the problem of cessation of precipitation and/or deposition of calcium carbonate which allows colonisation of the substrate by boring and encrusting organisms. In comparison, it is easier to understand the process of cementation of calcium carbonate bottom sediments, where the environmental conditions led to supersaturation with respect to calcium carbonate, which in turn initiated spontaneous calcium carbonate precipitation within the sediment. The relevant circumstances may include flushing bottom waters rich in calcium carbonate through the sediment, or photosynthetic activity of microorganisms consuming carbon dioxide and leading to precipitation of calcium carbonate. In addition, dissolution of minute, unstable calcium carbonate particles would cause subsequent supersaturation with respect to calcium carbonate and re-precipitation of the carbonate. However, in the real world such precipitation on a seafloor is very variable not only in terms of the crystals' shape or arrangement, but also for their primary mineralogy (BATHURST 1980).

Thus, a rather complex environmental system controls spontaneous carbonate cementation. Moreover, for the formation of hardgrounds a crisis of precipitation and/or deposition of calcium carbonate is also required. For recent hardgrounds, hydrodynamic activity seems to be the major factor controlling cessation of calcium carbonate deposition, thus allowing cementation of the seafloor and its exposure to boring and encrusting colonizing fauna. For example, extreme storms within the Persian Gulf cause the onshore movement of a large mass of sediment, mainly shell debris. That sediment becomes winnowed gradually, meanwhile however, dissolution of calcium carbonate within the storm lag provides a lot of calcium carbonate to cement the sediment underneath. This all leads to formation of multiple hardgrounds (SHINN 1969). In the case of ancient hardgrounds, the problem of their origin is still controversial. For example, either decrease in the rate of subsidence leading to extreme shallowness (KAŹMIERCZAK & PSZCZÓŁKOWSKI 1968) or increase of water depth and/or climatic changes (PURSER 1969) have been invoked as the major processes responsible for the formation of hardgrounds. Some other factors have been mentioned as being crucial for the creation of hardgrounds, such as eustatic and/or tectonic movements and regressive-transgressive cyclicity (GRUSZCZYŃSKI 1986, FÜRSICH & *al.* 1992), and storms at times of climatic instability (MOLENAAR & ZIJLSTRA 1997). Quite recently, formation of some Early Kimmeridgian (Jurassic) hardgrounds have been suggested to have been initiated either by hydrodynamic activity or chemical undersaturation with respect to $CaCO_3$. The concept of stronger waves or currents sweeping out carbonate sediments and preventing the sea floor from continuous deposition, is applicable only to some local hardgrounds. Otherwise, chemical undersaturation with respect to $CaCO_3$ over large areas of the sea floor was associated with the existence of stratified seawater zones within the shallow water carbonate platform (GRUSZCZYŃSKI, COLEMAN, MACKENZIE, GOLDRING, ISAACS, in prep.). The question we have tried to answer is: What was the primary reason for cessation of deposition of calcium carbonate and what casused the Late Turonian-Coniacian regional hardground formation?

Geological setting of the area

The area is represented by three sections (Shakh-Bogota, Shyrkala-Airakty and Koksyrtau-Aksyrtau) distributed within the Central Mangyshlak Anticlinorium (Text-fig. 1). The Mangyshlak Anticlinorium itself is dominated by Createaceous and post Cretaceous sediments. The detailed description of the sections and their faunal content (from the Late Albian to the Coniacian-Santonian boundary) was published by MARCINOWSKI & *al.* (1996).

Brief lithological descriptions of the sedimentary sequence

The sedimentary sequence comprising hardground formations begins in the Late Turonian (Text-figs 2-4). Interestingly, this sedimentary sequence is strikingly similar in all the three sections, thus the similarity extends over a distance of 100 km (Text-fig. 1). The lowermost sediments are phosphatic conglomerates within a mixed carbonate-siliciclastic coarse-grained matrix. These sediments form typical massive non-graded beds (KELLING & MULLIN 1975). They pass upwards gradually into fine-grained carbonates, the siliciclastic content decreasing upward. This unit is commonly bioturbated with some local omission surfaces of hardground and firmground characteristics (KAŹMIERCZAK & PSZCZÓŁKOWSKI 1968, BROMLEY 1975, BROMLEY & GALE, 1982). The top of the unit is coincidentally the hardground surface excavated by numerous burrows and borings (Text-figs. 2- 4). The hardground surface is overlain by very fine-grained carbonates, densely bioturbated just above the hardground surface with some local firmgrounds and hardgrounds, particularly in the bottom part of this unit. In one case (Aksyrtau- Koksyrtau section) the very fine-grained limestone unit is also topped by the hardground surface (Text-fig. 4).

Material and methods

All the hand specimens were taken by two of the authors (RM and IW), during the Mangyshlak Expedition in summer 1999. Some additional samples were collected in 1992 during their first study in the Mangyshlak Mountains (MARCINOWSKI & *al.* 1996). General sedimentological features were observed on polished rock slabs using a standard binocular microscope. Petrological studies were made on thin sections under plane- and cross-polarized light. Homogeneous samples of non-skeletal and skeletal carbonates were selected for isotopic and elemental analyses at the Postgraduate Research Institute for Sedimentology, University of Reading. Sequential isotopic and elemental analyses of the same calcium carbonate sample were performed using the method of COLEMAN & *al.* (1989). Carbon dioxide for isotopic analysis, prepared from the sample by its dissolution in orthophosphoric acid, was analysed on a VG SIRA Mass Spectrometer. The residual sample solution after isotopic analysis was analysed for chemical composition using a 8060 Phillips ICP instrument.

RESULTS AND DISCUSSION

Because the sedimentary succession containing the hardgrounds encompass quite an extent of time, at least the Late Turonian and Early Coniacian, and in one case the Late Turonian and the whole Coniacian (Aksyrtau - Koksyrtau), we would like to discuss the isotope results for the whole of that stratigraphic range and then concentrate on the formation of hardgrounds.

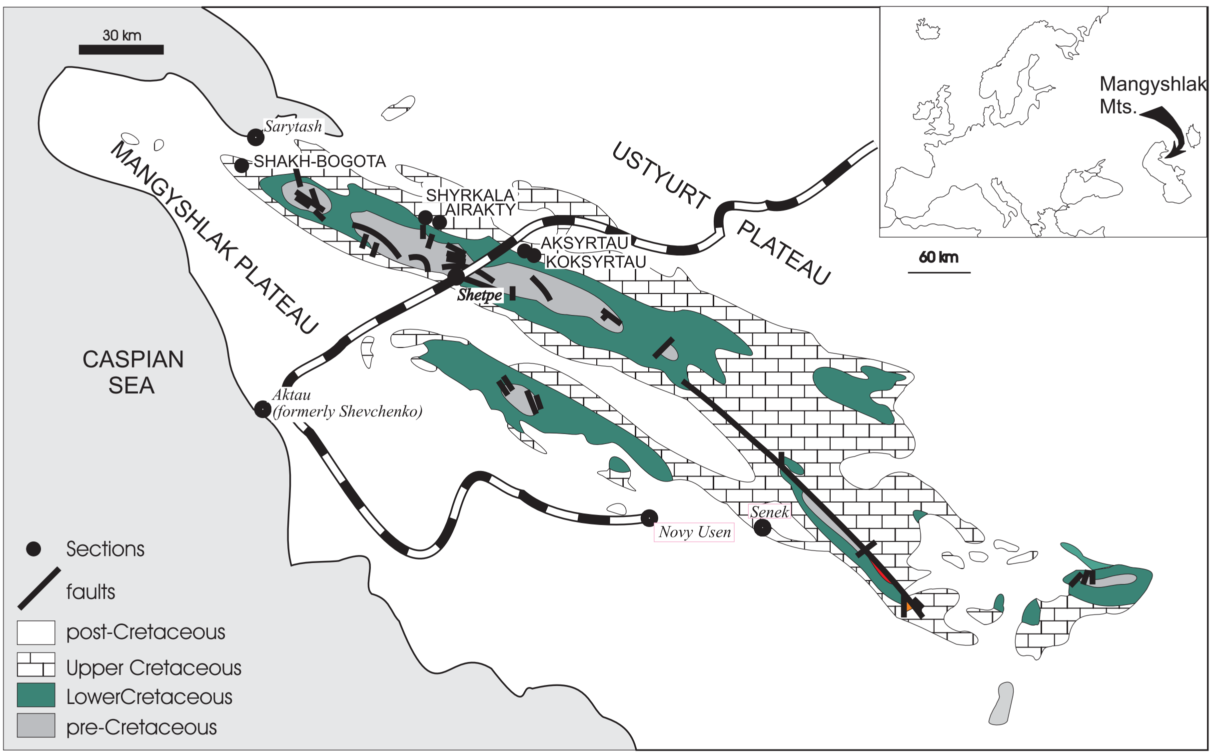


Fig. 1. Geological sketch-map of the Mangyshlak area showing the location of the investigated sections

General pattern of the $\delta^{13}C$ and $\delta^{18}O$ values for the Late Turonian and Coniacian

We have observed different patterns of the $\delta^{13}C$ and $\delta^{18}O$ values for the Late Turonian and Coniacian for certain sections. At Shakh-Bogota, the $\delta^{13}C$ values rise gradually from +0.5‰ for the phosphatic conglomerate to more than +2‰ for the rest of the Late Turonian (Text-fig. 2). In the Coniacian, the $\delta^{13}C$ values oscillate around a value of +2.5‰. $\delta^{18}O$ values for the bulk rock samples show a very stable course, apart from the value of –4‰ for the phosphatic conglomerate, oscillating around –2.5‰ in the Late Turonian. In the Coniacian, the $\delta^{18}O$ values continue the same trend with only minor perturbations (Text-fig. 2). $\delta^{13}C$ values for the bivalve (inoceramid) shells are very stable in the Late Turonian: between +2 and +2.5‰. This value is more positive in the earlier Late Turonian than the values for the bulk rock samples, whereas close to the general trend of the values for the bulk rock samples in the later Late Turonian. Similarly, the $\delta^{18}O$ value for the bivalve (inoceramid) shells is more positive, +1‰, than those values for the bulk rock samples in the earlier Late Turonian, and almost identical to those values for the bulk rock samples in the later Late Turonian (Text-fig. 2). There is also no visible perturbation of isotope values at the hardground.

At the Shyrkala-Airakty section, the $\delta^{13}C$ values show a rather stable trend, oscillating above +1.5‰ for the Late Turonian. At the Late Turonian-Coniacian transition, within the hardground formation, the $\delta^{13}C$ values are more variable. In the Coniacian, the $\delta^{13}C$ values rise to 2‰ and stabilize at that level (Text-fig. 3). Otherwise, the $\delta^{18}O$ values are more variable decreasing initially and then increasing substantially in the latest Turonian. At the Turonian-Coniacian transition, the $\delta^{18}O$ values show a gradual decrease. Then, in the Coniacian, the $\delta^{18}O$ values rise gradually to –2‰ and stabilize at that level.

At the Aksyrtau-Koksyrtau section, the $\delta^{13}C$ values show the same tendency as those values at the Shakh-Bogota section, rising gradually from +0.5‰ to +1.5‰ at the end of Late Turonian, with some perturbations at the Turonian-Coniacian transition, where the hardground occurs, and then continue rising up to +2.5‰ and stabilise at that level during the Coniacian. At the Coniacian-Santonian transition, where another hard-

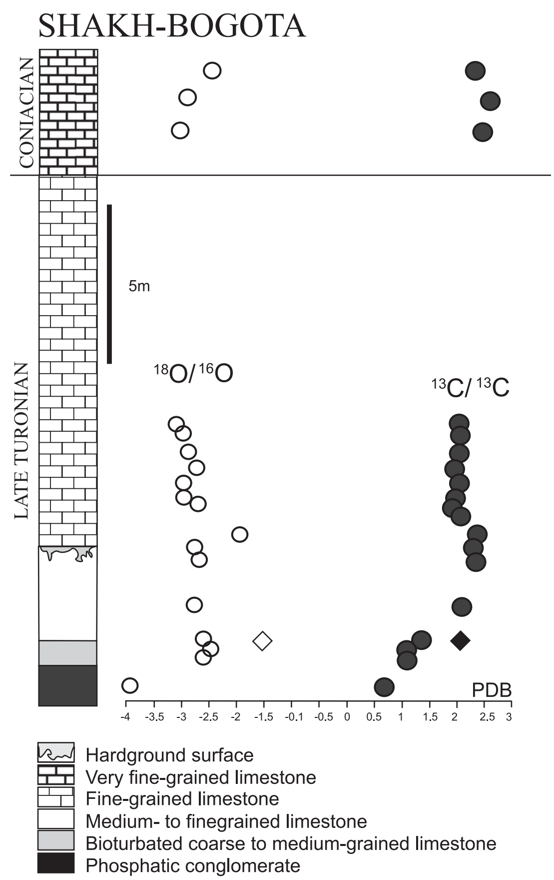


Fig. 2. General pattern of $\delta^{13}C$ and $\delta^{18}O$ values for the Late Turonian and Coniacian at the Shakh-Bogota section. Solid and open circles are the bulk rock samples whereas rhombs denote bivalve (inoceramid) shell samples

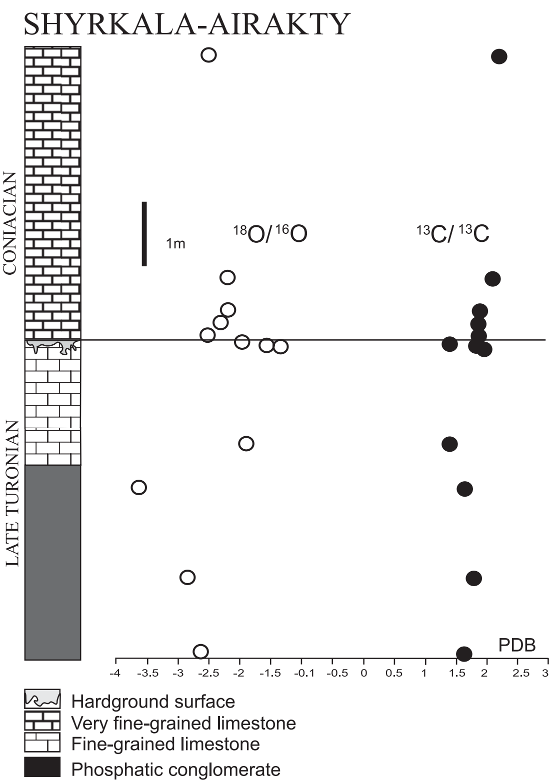


Fig. 3. General pattern of $\delta^{13}C$ and $\delta^{18}O$ values for the Late Turonian and Coniacian at the Shyrkala Airakty section

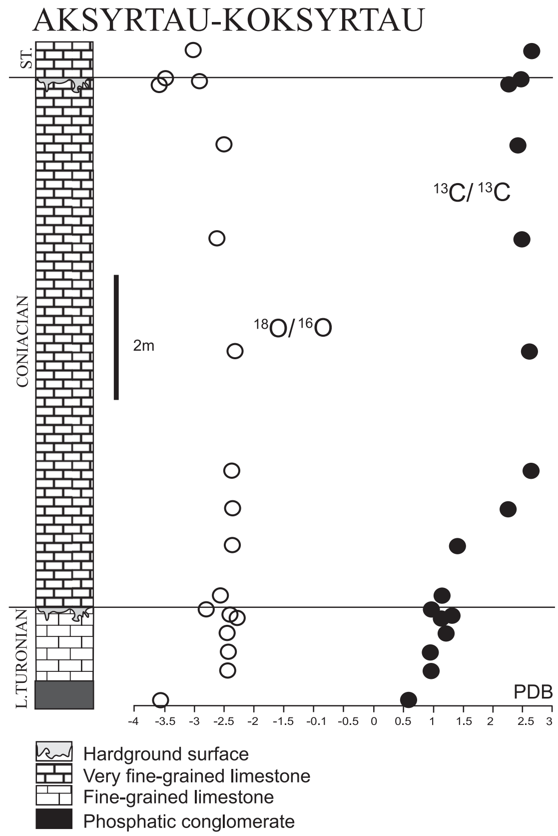


Fig. 4. General pattern of $\delta^{13}C$ and $\delta^{18}O$ values for the Late Turonian and Coniacian at the Aksyrtau. Koksyrtau section

ground occurs, the $\delta^{13}C$ values show a slightly decreasing oscillation, and then rise to +2.5‰ again, in the Early Santonian (Text-fig. 4). $\delta^{18}O$ values stabilise earlier at –2.5‰ after a rise of 1‰ from the more negative values characteristic of the phosphatic conglomerate. Then, these values decrease slightly at the very Late Turonian-Coniacian boundary, the lower hardground sequence, and then stabilise at the level of –2‰ throughout the Coniacian. Exactly at the Coniacian/Santonian boundary, the upper hardground sequence, the $\delta^{18}O$ values decrease again, and then rise to –2.5‰ in the Early Santonian.

Discussion of the results

In general, the overall results plotted in the diagram of $\delta^{13}C$ values against $\delta^{18}O$ values (Text-fig. 5) suggest little diagenetic alteration (BRAND & VEIZER 1981, see also MARSHALL 1992). There are a few results, apart from those which clearly are primary, for which diagenesis seems to affect either both isotope values or only the oxygen value (MARSHALL 1992). The lowest values of both $\delta^{13}C$ and $\delta^{18}O$ are characteristic of the phosphatic conglomerate which is not surprising. This phosphatic conglomerate is built up of coarse-grained components suggesting rapid deposition of a primary, rather porous bed. The secondary calcium carbonate cement is an effect of supersaturated pore waters, presumably at the time of early burial. These waters represent a carbonate system which is usually enriched in light carbon and oxygen isotopes (HUDSON 1977). In terms of the primary environment, the whole pattern of both the $\delta^{13}C$ and $\delta^{18}O$ values for all the three sections might describe transgression and development of a vast shallow water marine basin. Also, there is a very narrow range of oscillations of the $\delta^{13}C$ and $\delta^{18}O$ values to give a stabilised trend of those values for the latest Turonian and Coniacian. This suggests, that the shallow-water sea was characterised by an established equilibrium between the different fluxes of carbon. These fluxes are opposite in sense to each other, either attempting to change the carbonate system to isotopically lighter values, because of runoff and respiration, or heavier, more positive values through photosynthesis and C_{org} burial. Marine calcium carbonate sediments from the Mangyshlak sedimentary basin display a range of the $\delta^{13}C$ values, between +2 and +4‰, the same as for theoretically precipitated $CaCO_3$ under conditions of isotopic equilibrium (ARTHUR 1983).

$\delta^{18}O$ values, showing such a narrow range, might only reflect changes in temperature and/or salinity. However, palaeosalinity estimations for such a developing subtropical basin could only be speculative. Estimated palaeotemperatures from $\delta^{18}O$ values for the bivalve inoceramid shell fragments give 19° to 23°C for the Late

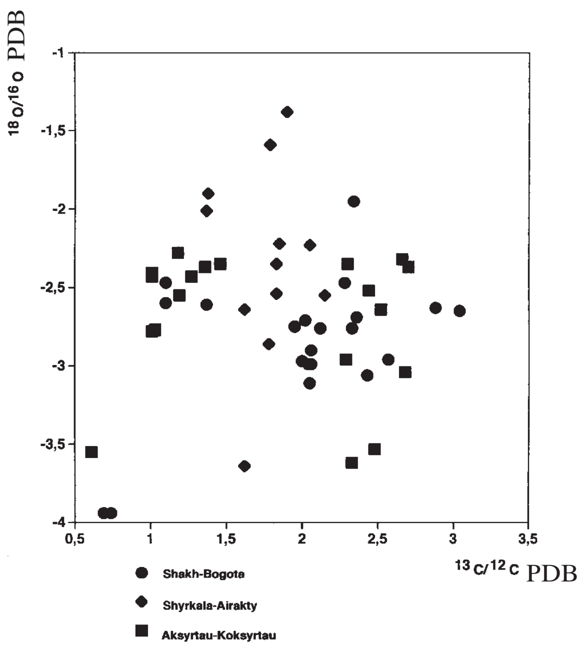


Fig. 5. The isotope results for the each bulk rock samples of the Late Cretaceous sections plotted as the $\delta^{13}C$ against the $\delta^{18}O$ values

Turonian. Including all the $\delta^{18}O$ results for the latest Turonian and Coniacian, the range of estimated temperatures is even narrower, from 22 to 24°C, assuming a water isotopic composition for the Cretaceous oceans without polar ice caps (HUDSON & ANDERSON 1989).

This very general and brief reconstruction is quite different from the global models for the Mid and Late Cretaceous. The Late Turonian to Late Coniacian is regarded as a transition separating Oceanic Anoxic Event 2 (OAE 2) and Oceanic Anoxic Event 3 (OAE 3) (SCHLANGER & JENKYNS 1976). This is manifested by a general continuous decrease of $\delta^{13}C$ values from +4 to +1‰ (ARTHUR & *al.* 1985), which is confirmed by the detailed isotope-geochemistry studies of the Mid Cretaceous sedimentary sequences (e.g. JARVIS & *al.* 2001). In the case of the Late Turonian / Coniacian Mangyshlak Sea, it is the other way round. The same discrepancy exists in palaeotemperature determinations, although all the temperatures for the Mangyshlak Sea are close to the range of temperatures, i.e. 21-24°C, for the Turonian of approximately 40° N latitude. However, the general trend for the Turonian is for a temperature decrease, whereas for the Mangyshlak Sea it is the other way round.

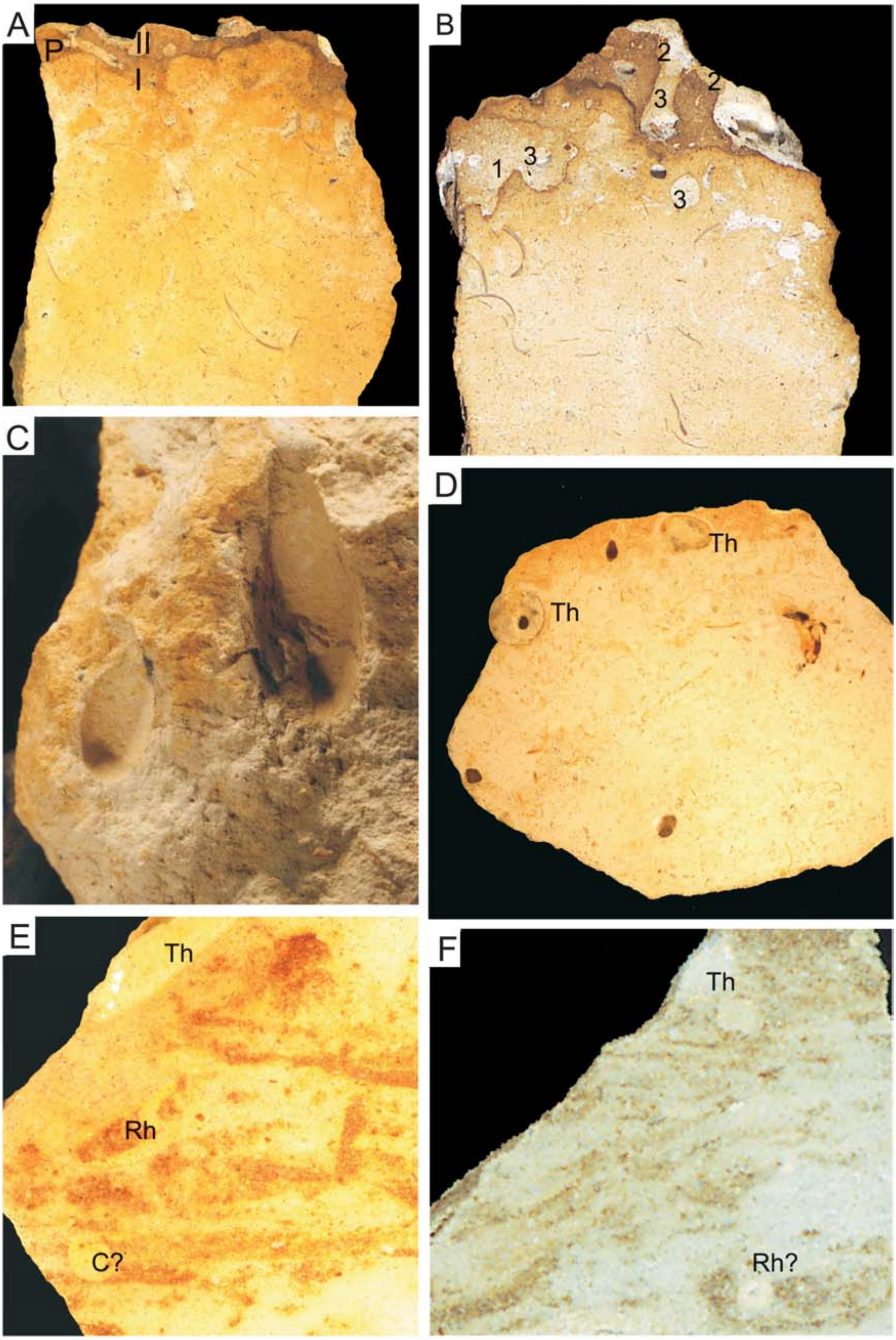
Detailed carbon and oxygen isotope survey for the Late Turonian hardground

Prior to interpretation of the detailed examination of carbon and oxygen isotopes across the Late Turonian hardground we would like to underline some specific features of these hardgrounds. Unlike the Chalk hardgrounds characterised by large and numerous excavations of burrowing animals which became cavities and crevices (BROMLEY 1967), and phosphatic and iron/manganese crusts (see BATHURST 1975 for review), the Mangyshlak Late Turonian hardground is not so spectacular.

One can see densely excavated the Shakh-Bogota hardground surface by burrows presumably of the *Thalassinoides* type (MARCINOWSKI & *al*. 1996, Pl. 2, fig. 4) creating hummocky surface (see BROMLEY 1975). The preomission suite *sensu* BROMLEY (1975) cannot be detected for the hand specimens of the hardground sequence are anot available. One can only see openings of bivalve borings (*Lithophaga*?), polychaetes (*Trypanites*?), and scarce and unclear openings of sponge (*Entobia*? – BROMLEY 1970) marking the omission suite *sensu* BROMLEY (1975) on the close-up view of the hardground surface (MARCINOWSKI & *al*. 1996, Pl. 2, fig. 5). The postomission suite *sensu* BROMLEY (1975) is represented by fine-grained limestone including quite amount of bioturbations.

The Shyrkala/Airakty hardground reveals preomission suite, although trace fossils are hard to see after they have been cemented. At least we could identify some *Planolites* burrows (see BROMLEY 1990) among many unidentified bioturbation remains. Intensity of bioturbation can be detected by amount of phosphatic angular bits scattered randomly in the micrite matrix of the hardground body. The omission suite is marked by *Thalassinoides*? burrows, and by borings of bivalve *Lithophaga*? and *Trypanites*, and sponge *Entobia*? (Text-fig. 6 A, B). The latter are, however, very unclear borings of sponge (personal inf. of BROMLEY). Within the burrows we found also bits of phosphatic granules. Taphonomical analysis suggests three episodes of hardground colonisation. The first episode is marked by relic borings, hard to see for they have been cemented by micrite. Then, a period of dissolution-reprecipitation of calcium carbonate and phosphatisation occurred. At that time burrows were modified to form cavities and crevices, and a dark brown phosphatised subsurface layer was created (Text-fig. 6A, B). After this, new colonisers arose, rejuvenating the old burrows and forming new boring crypts (Fig. 6A, B). This second episode of colonisation was terminated by formation of phosphatic varnish coating all the burrows and borings (Text-fig. 6A, B). The following sedimentary sequence started with a fine-grained carbonate filling cemented by micrite within the burrows. This filling as well as hardground surface were excavated by the last generation of *Lithophaga*?, *Trypanites*, and unclear *Entobia*? (Text-fig. 6B). Such a cemented filling was partly eroded and re-deposited within the burrows and borings, which were finally filled with the white fine-grained carbonate, typical of the Coniacian sediment (Text-fig. 6B). Unfortunately, one cannot tell bioerosion was important during the omission. It might be, however, it is difficult to draw suggestion from a few pieces of the hardground body. The fine-grained carbonate, marking postomission suite is slightly bioturbated judging from the distribution of skeletal and phosphatic particles.

Fig. 6. Photos of the rock slabs showing details of the Late Turonian-Coniacian hardground. A,B, are the polished slabs of the hardground in the vicinity of Shyrkala-Airakty showing the following details: (1) the first generation of boring bivalves; (2) the second generation of borings; (3) the third generation of borings; (I) the first generation of fine-grained sediment filling the burrows and cemented inside them; (II) the second generation of fine-grained sediment filling the burrows and borings; (P) phosphatised layer; C is a slab of the hardground in the vicinity of Aksyrtau-Koksyrtau showing numerous *Lithophaga* borings; D is a polished slab of the hardground in the vicinity of Aksyrtau-Koksyrtau showing *Thalassinoides* (Th) burrows filled with the fine-grained carbonate sediment with admixture of phosphatic granules; E-F are polished slabs of the firm-ground overlying the hardground in the vicinity of Aksyrtau-Koksyrtau showing dense bioturbation including plaussible *Cylindrichnus* (C?), *Rhizocorallium* (Rh) and *Thalassinoides* (Th)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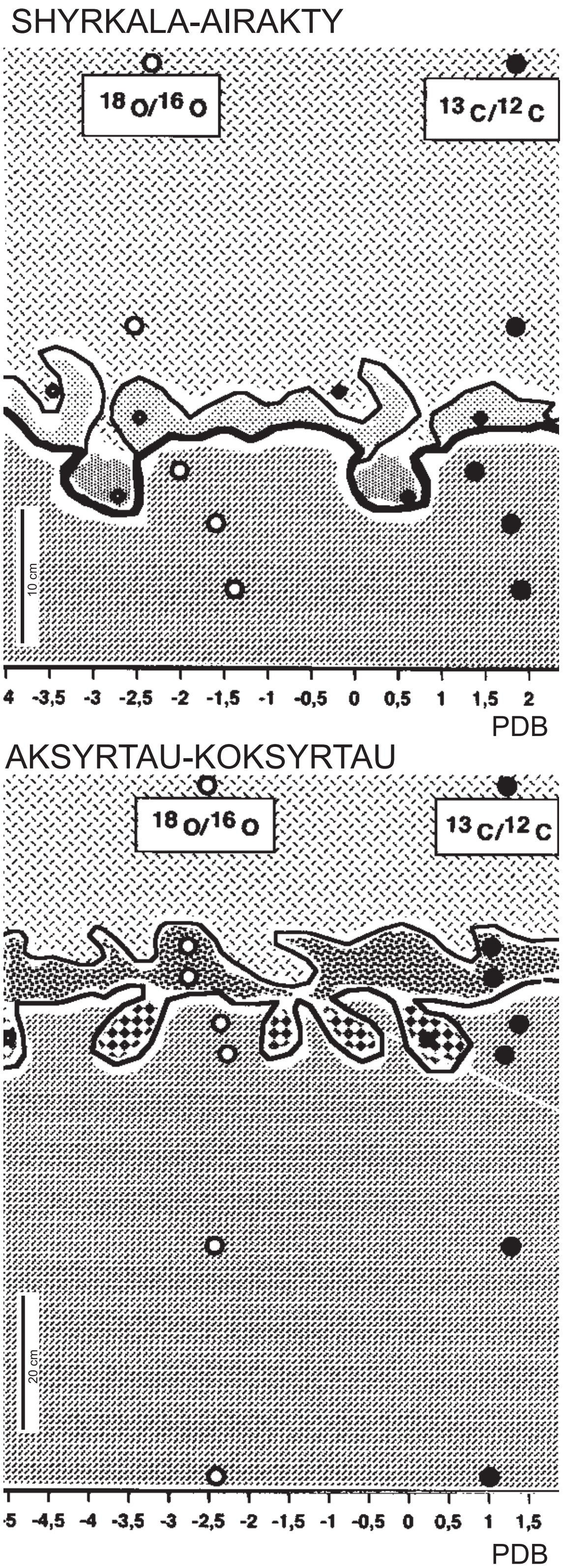

Fig. 7. The isotope results in a form of the $\delta^{13}C$ and $\delta^{18}O$ values for the Late Turonian-Coniacian regional hardground in the vicinity of Shyrkala-Airakty and Koksyrtau-Aksyrtau

The Aksyrtau-Koksyrtau hardground is of a composite nature. It starts with the hardground for which the preomission suite is marked by rather intense bioturbation of unidentified burrows underlined by aureoles or concentrations of phosphatic grains (Text-fig. 6D). The omission suite includes *Thalassinoides* burrows and numerous *Lithophaga* (personal inf. of BROMLEY) borings (Text-fig. 6C). There are at least two generations of borings, both *Lithophaga* and *Trypanites* hardly visible, for they were filled and cemented by micrite. *Thalassinoides* burrows are partly filled with the fine-grained carbonate with admixture of phosphatic granules, cemented by micrite (Text-fig. 6D). This hardground passes upwards into a firmground. Thus, the postomission for the hardground marked by numerous, unidentified burrows (Text-fig. 6E, F), is the preomission for the firmground. Apart from the unidentified burrows, ther is a cross section of the burrow, of *Cylindrichnus* type (GOLDRING 1996, 1999), filled with a fine-grained carbonate(Text-fig. 6E). However, it could be also a cross section of *Rhizocorallium* which together with *Thalassinoides* (Text-fig. 6E, F) mark the omission suite for the firmground. The postomission for the hardground is represented by sedimentation of fine-grained limestone slightly disturbed by bioturbation.

According to the boring bivalves domination among omission fauna, one can postulated the water depth less than 50 m, and if sponge borings are absent it might suggest even the intertidal environment (personal inf. of BROMLEY).

Results of the detailed isotope survey across those hardground sites are shown in the Text-fig. 7.

In the case of Shyrkala-Airakty hardground, both the $\delta^{13}C$ and $\delta^{18}O$ values display a clear pattern. These values decrease gradually from depth towards the point just beneath the hardground surface. Then, the $\delta^{13}C$ values increase within the subsurface phosphatised layer and overlying fine/grained Coniacian limestone, and stabilise at the level of those values at a depth below the hardground surface. On the other hand, the $\delta^{18}O$ values decrease continuously, including the subsurface phosphatised layer, and stabilised at that level within the overlaying Coniacian limestone. For the fine-grained and cemented fillings of burrows and borings, the first generation of filling, both the $\delta^{13}C$ and $\delta^{18}O$ values are depleted by 1.5‰ compared to those values beneath the hardground surface. The second generation of filling is characterised by the most depleted $\delta^{13}C$ and $\delta^{18}O$ values, being less than 0‰ as for carbon and –3,5‰ for oxygen.

The pattern of the $\delta^{13}C$ and $\delta^{18}O$ values in the case of Aksyrtau-Koksyrtau hardground is not so clear. $\delta^{13}C$ values increase beneath the lower hardground surface, then decrease slightly beneath the upper firm-ground surface, and stabilise finally in the overlying Coniacian limestone.

$\delta^{18}O$ values decrease slightly below the lower hardground surface and continue decreasing within the upper firmground, and then increase in the overlying Coniacian limestone. As in the case of Shyrkala-Airakty, both the $\delta^{13}C$ and $\delta^{18}O$ values drop, being just above 0‰ for carbon and less than -5‰ for oxygen.

The process of hardground cementation

We start with the question of how the sea floor subsurface sediment might have been cemented. As always we have at least two alternative answers to such a question. Thus we produced a table of processes and factors which might be involved in the process of cementation:

Factor	Processes related to cementation	Sedimentary record
Hydrodynamic + *Chemical*	Flushing of calcium carbonate rich waters through the surface sediments Deposition of sedimentary lag full of detritus and skeletal debris And Dissolution of small-size calcium carbonate particles making carbonate rich pore-waters within subsurface sediments	Undetectable Bioturbated layer with a firm -ground on the top? Undetectable
Hydrologic + *Chemical*	Influx of rain and/or fresh runoff waters because of intertidal environment And Dissolution of small-size calcium carbonate particles, and then, after reaching saturation state, re-precipitation of calcium carbonate	Domination of bivalve borings and possible absence of sponge boringsv Both the $\delta^{13}C$ and $\delta^{18}O$ values depleted in subsurface sediment
Biochemical + *Chemical*	Degradation of organic matter in aerobic and anaerobic environment And Dissolution of small-size calcium carbonate particles, and then, after reaching saturation state, re-precipitation of calcium carbonate in the oxic (OX) and sulphate reduction (SR) zones and Precipitation of calcium carbonate from pore -waters within nitrogen reduction (NR), iron reduction (FeR), and manganese reduction (MnR) zones	Both the $\delta^{13}C$ and $\delta^{18}O$ values depleted in subsurface sediment Both the $\delta^{13}C$ and $\delta^{18}O$ values depleted in subsurface sediment

Looking at the table, a scenario for hardground development involving influx of rain and/or fresh runoff waters seems to be rather implausible. Of course, fresh runoff waters may dissolve calcium carbonate sediments on a sea floor and then, after reaching saturation state, calcium carbonate may precipitate, however not at the same place where it has been dissolved (PEGLER & KEMPE 1988). It makes such a calcium carbonate sediment or cement almost undedectable. The most complicated point is a change from submarine to fresh water or mixing conditions in a relatively short time, for the hardground was colonised by marine organisms three times. This implies not only a substantial change of climate to being very humid, but also cyclical deluges. However, from the palaeogeographical maps of DERCOURT & *al.* (1991), at that time the Mangyshlak Sea was situated within the subtropical region of a huge continental plate. On the other hand, in subtropical regions, runoff to the shallow water marine basins might increase oxygen isotope values as in the recent case of runoff from Everglades to Florida Bay.

Thus, a scenario for hardground development involving hydrodynamic and biochemical factors seems to the only reasonable alternative.

Scenario of hardground formation

This scenario assumes the hardground development and moderation under totally submarine conditions. The only additional assumption is that during carbonate sedimentation enough organic matter was deposited as well.

1. After cessation of carbonate sedimentation, which might have been intermittent in some places (Koksyrtau-Aksyrtau), the substrate began to be colonised by burrowing animals. Irrigation of the sediment by bioturbation pumping sea-water through the sediment (e.g. ALLER 1980) and oxygen diffusion through surface sediment pore/waters led to degradation of organic matter. Oxidation of C_{org} caused increase of bicarbonate ions according to the reaction:

$CH_2O + O_2 = CO_2 + H_2O = HCO_3^- + H^+$.

This must have caused dissolution of calcium carbonate:

$CaCO_3 + HCO_3^- + H^+ = Ca^{2+} + 2HCO_3^-$

in order to buffer pH (BEN-YAKOV, 1973). In due course this had to supersaturate pore waters with respect to $CaCO_3$ and to re-precipitate calcite with depleted $\delta^{13}C$ values (IRWIN & *al.* 1977, IRWIN 1980, COLEMAN 1985). Below the Ox zone (COLEMAN 1985), sub-oxic (FROELICH & *al.* 1979) or post-oxic (Berner 1981) conditions might be created. In the sub-oxic=post-oxic zone, where nitrate, iron and manganese act as the oxidants. In our case, the probable low reaction rate of iron (COLEMAN 1985) and small quantities of manganese, made nitrate reduction the only effective process. However, carbonate cement precipitated by nitrate reduction should incorporate light carbonate, thus in this case the effect of precipitation might be seen only just beneath the hardground surface. There is also no evidence of the SR zone (COLEMAN 1985) within the hardground. SR conditions initially cause rapid dissolution of calcium carbonate because of a lowering of pH, however supersaturation with respect to $CaCO_3$ is rapidly re-established (BOUDREAU & CANFIELD 1993). But precipitated calcite cement is enriched in the light isotope of carbon (COLEMAN 1985). Hence, colonisation of burrowing infauna coincided with cementation of calcium carbonate sediment, and then the hard substrate was invaded by boring bivalves.

2. This precipitation of calcium carbonate might have been accompanied by phosphatisation (Shyrkala-Airakty) with depleted $\delta^{18}O$ values. The episode of phosphatisation, might have interrupted further colonisation, and had its source in the sea-water, because its $\delta^{13}C$ value is similar to those for the carbonate matrix.

Some hydrodynamic activity led to episodic sedimentation with burrowing animals community inhabiting the substrate in the vicinity of Aksyrtau-Koksyrtau and faunal colonisation of the hard substrate in the vicinity of Shyrkala-Airakty. This activity caused episodes of sedimentation, cementation of the sediment that filled burrows and erosion. The cemented substrate was excavated by boring bivalves and *Trypanites*. Both the first and the second generation of the sediment fills of the burrows and borings are depleted in ^{13}C because of the presence of an appreciable amount of organic matter.

4. Depletion of the light oxygen and carbon isotopes at the beginning of renewed sedimentation might be produced by the same cause, implying oxidation of organic matter trapped in quite a small amount of initial sediment. However, that the same effect might have been achieved by the burial water penetrating the sediments, as in the case of the sediment filled bored crypts in the vicinity of Aksyrtau-Koksyrtau, which display $\delta^{18}O$ values of less than –5‰.

The origin of the hardground

The primary factor or factors controlling carbonate precipitation leading to a crisis of that precipitation might be deduced from the facts we have collected so far. The most widely accepted factor that is a significant control on the genesis of widespread regional hardgrounds is eustatic sea level change, locally altered by tectonics (GRUSZCZYŃSKI 1986, PRATT 1990, FÜRSICH & *al*. 1992). We can be confident that hardground formation and development cannot be attributed to a major change in sea water chemistry. This means we can consider two alternative ways of stopping the calcium carbonate sedimentation with reference to either regressive or transgressive sequences. The first is, the minimum amount of water over a seafloor causing either all the carbonate sediment to be swept away at even the lowest hydrodynamic activity, or enrichment of runoff in carbon dioxide and bicarbonate because of increased erosion of soils. The second way, the rapid deepening of seawater led either to increased hydrodynamic activity replacing areas of sediment erosion and deposition, in shallow waters, or to increase of carbon dioxide and bicarbonate within the bottom carbonate system because of cooling, in deeper waters. The Late Turonian/Coniacian hardground of the Mangyshlak Sea developed within the transgressive sequence, similarly to other Cretaceous hardgrounds described from France (JARVIS & GALE 1984) and Britain (JARVIS & WOODROOF 1984). However, in our case there are neither signs of very strong hydrodynamic activity, as in the Recent example of the Persian Gulf (SHINN 1969), nor dramatic change of the sedimentary regime below and above the hardground which might be interpreted as sudden deepening (PURSER 1969).

Thus, another explanation must be sought. When we look at the general carbon isotope record we have to assume a stable balance between the fluxes of runoff, photosynthesis, and respiration over a long time. However, episodic perturbations within the carbonate system may be easily achieved when a transgressive sea approached wide, flat land areas. On the one hand, accelerating transgression caused an increasing distance from the shore and limited the supply of nutrients. On the other hand, much more soil was reworked and a lot of bicarbonate and carbon dioxide was released to the sea. In terms of calcium carbonate precipitation, this easily might have led to undersaturation with respect to $CaCO_3$, and stopped its precipitation over vast areas of the sea floor. Some hydrodynamic activity might winnow a loose sediment and deposit it elsewhere. By slowing the transgression it would have been easy to restore the conditions that had existed before the hardground was formed.

The possibility that change of the climate to a more humid regime could be associated with the hardground formation is very difficult to discuss.

CONCLUSIONS

Interpretation of carbon and oxygen isotope stratigraphic profiles through a sedimentary section of the Late Turonian-Coniacian of the Mangyshlak Mountains resulted in the following conclusions (both general and specific):

There are no differences in palaeoenvironmental conditions across the transgressive Mangyshlak sea basin. In general, the observed pattern of the both $\delta^{13}C$ and $\delta^{18}O$ values does not accord with the established models. The postulated transitional period between adjacent Late Cretaceous Oceanic Anoxic Events (OAE) is manifested by the decrease of $\delta^{13}C$ values interpreted as a decrease in C_{org} burial. In the case of the Mangyshlak Sea it is the other way round. Also, a speculative palaeotemperature trend in the Late Cretaceous is opposite to the established mode. This might suggest the Aristotelian rule "The Part is opposite to the Whole", thus the secular trend of the $\delta^{13}C$ and $\delta^{18}O$ values is a result of net balance of many specific seas, rather than a temporal trend of average values for the global ocean. Alternatively, the Late Cretaceous Mangyshlak Sea was an exception among other contemporaneous seas and oceans.

The crisis of calcium carbonate sedimentation was marked by the development of the hardground, which can be observed over a distance of 100 km. There were no large-scale hydrochemistry changes either in the bottom waters or in the pore waters during initiation and development of the hardground. Also, evidence for changes in climate at the time of the passage to more humid conditions which would be a plausible reason for that crisis are very difficult to assess. The most plausible explanation is a fast palaeogeographic change. Such a crisis of calcium carbonate precipitation over a substantial portion of that late Cretaceous basin was not connected with the transgression on large and flat land areas. Consequently, acceleration of transgression increased the distance from the shore and limited the supply of nutrients, which in turn limited primary producers and utilisation of carbon dioxide. This also caused introduction of more carbon dioxide and bicarbonate, from reworked soils to the sea floor, within the carbonate system. All this led to undersaturation with respect to $CaCO_3$, and stopped its precipitation and/or deposition over vast areas of the sea floor.

Finally, such a scenario for hardground formation and development, involving factors such as changes in palaeogeography and climatic or a hydrodynamic regime which controlled the crisis of calcium carbonate deposition, seems to be typical for the late Mesozoic and Cenozoic.

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