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Isotopic Composition of Biogenic Carbonates and Holocene Paleogeographic Reconstructions of the Western Caspian Seashore

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The Caspian Sea is remarkable for multiple strong sea level fluctuations during its geological history. Alternating transgressions and regressions stimulated the formation of several different-aged marine terraces along the coast that reflect the geomorphological development of the sea. The New Caspian transgression, which began approximately 10 ka ago and reached the level of –20 to –22 m, was the latest large transgression [3].

Reconstruction of paleogeographic conditions is needed for adequate interpretation of the nature of Caspian Sea level fluctuations. We attempted to reconstruct one of the stages in the New Caspian transgression based on the study of stable oxygen and hydrogen isotopes, as well as some metals in shells of bivalve mollusks. The study of samples collected from growth layers of shells revealed seasonal dynamics of their isotopic and chemical compositions. We were also able to calculate seawater temperature and salinity for the studied period. No such studies were ever performed for the Caspian coast.

The samples for this study were obtained in 2002 in the Turali-7 camp area of Moscow State University located 5 km south of the town of Kaspiisk at the Dagestan coast of the Caspian Sea. Shells for the isotope studies were sampled from the exposure at the eastern bank of Lake Bol'shoe Turali (OT-21).

The upper 95-cm-thick section of the exposure is composed of sandy–pebbly sediments with molluscan shells. Its middle part is nonuniform and composed of the following units: reddish (locally brown) sand with small pebble and shells (interval 95–104 cm); reddish to light brown (locally rusty) sandy loam with scarce shells (104–110 cm); whitish fine-grained sand with thin (2–3 mm) light brown loamy interlayers (110–116 cm); and brown sandy loam with rusty spots and interlayers (116–120 cm). The lower part of the exposure (up to 175 cm) is composed of whitish fine-grained sand with rare molluscan shells.

The complete regressive–transgressive sedimentary succession is exposed at this site. The fine-grained sand in the lower part of the section was likely deposited in relatively calm marine settings during the low sea level stand. Overlying sandy loam represents a buried marsh soil that formed on dried territory. The occurrence of light brown interbeds in overlying fine-grained sand indicates intermittent development of H_2S-contaminated environments and, most likely, the onset of a sea level rise. Similar laminated sediments with ferruginous interbeds, which are typical of the present-day beach, formed in the rear part of the prograding coastal bar at the transgressive stage. The section above the level of 110 cm is composed of a transgressive sedimentary succession that includes lagoonal sediments, sands of the maritime part of the lagoon, and sediments of the coastal bar crowning the section.

Shells of the molluscan species *Didacna* cf. *trigonoides* were sampled from three beds of the studied sequence for isotopic studies. Shells are intact, which indicates in situ occurrence and makes them suitable for paleogeographic reconstructions. Modern representatives of this species live on sandy–muddy sediments at a depth above 30 m and salinity of 7–12‰ [2]. The fossil mollusk habitat was probably similar.

The age of shells was inferred from the ^{14}C content determined by the AMS method in the laboratory of Utrecht University (the Netherlands). The results obtained show that shells from marine sands of the terminal phase of regression (Sample DAG10A) are 2500 yr old. Shells from overlying lagoonal sediments are 2300 to 2400 yr old (Samples DAG9B and DAG11). It is likely that one of the New Caspian regression gave way to the next sea level rise 2500 yr ago [11].

The oxygen and hydrogen isotopic compositions were determined in the Mass Spectrometry Laboratory of Vrije University, Amsterdam. Using the special

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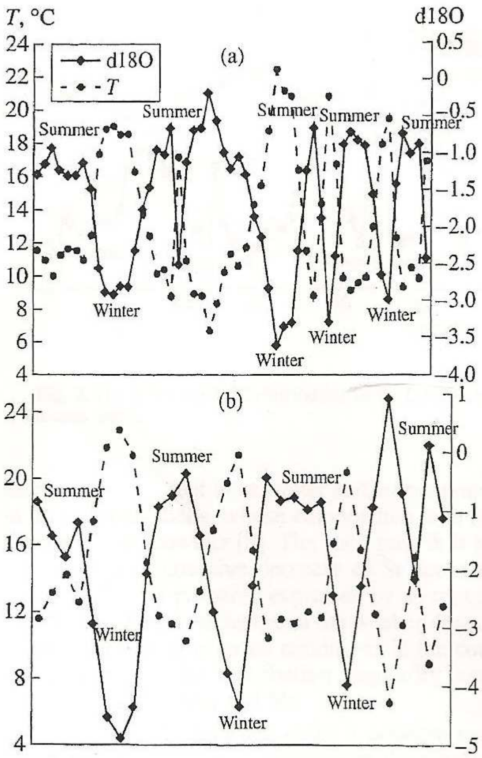

Fig. 1. The $\delta^{18}O$ values (d18O) and calculated water temperatures for (a) DAG9B and (b) DAG10A molluscan shells. In all figures, the shell growth is from the left to right.

superfine drill "Merchantek Micromill," 70–100 samples were taken for this purpose from each molluscan shell. The $\delta^{18}O$ and $\delta^{13}C$ values in biogenic carbonates were determined in odd samples using a Finnigan MAT 252 mass spectrometer. The Sr, Ba, Fe, and Mg contents were determined using the ICP-AES method.

The $\delta^{18}O$ values in studied samples are highly differentiated with several fluctuation cycles (Fig. 1), suggesting seasonal variability of the molluscan habitat (in particular, the water temperature).

Bivalve mollusks accumulate calcium carbonate during isotopic equilibrium with water [7]. The isotope fractionation coefficient in the $CaCO_3$–water system depends on the temperature. Therefore, the oxygen isotopic composition in $CaCO_3$ equilibrated with water is also governed by the temperature [4]. This dependence for aragonite material of bivalve shells is described by the formula $T°C = 20.6 - 4.34\ (\delta^{18}O_{carb} - \delta^{18}O_{water})$ [9].

The $\delta^{18}O$ value of water significantly depends on salinity, which is particularly important for the Caspian Sea water, whose salinity varies from 0 to 13‰. The dependence of the $\delta^{18}O$ value in the Caspian water on salinity was shown in [1]. For example, the $\delta^{18}O$ value for water with salinity of 12‰ is 3.3‰. Using this dependence and knowing the salinity of seawater, one can determine its temperature during the growth of a molluscan shell. The seawater salinity during accumulation of sediments under consideration was likely close to the present-day one [13].

Calculations show that the minimal and maximal temperatures for Sample DAG9B at a seawater salinity of 12‰ were 6 and 21°C, respectively (Fig. 1a). The data obtained also imply decelerated growth of the shell in the course of the mollusk aging (the observed peaks become narrower). This indicates that the mollusk lived in a shallow lagoon where the temperature experienced relatively strong variations at normal seawater salinity.

Similar results were also obtained for other shells of *Didacna* cf. *trigonoides*. In all cases, paleotemperatures range from 4 to 25°C.At the same time, dwelling conditions in the open sea were likely more favorable for mollusks than in the lagoon. The higher growth rate of DAG10A is supported by wide peaks in the $\delta^{18}O$ plot (Fig. 1b). Also noteworthy is the tendency for seawater temperature rise in the course of the mollusk growth.

The $\delta^{13}C$ distribution in DAG9B is less contrasting as compared to that of $\delta^{18}O$ (Fig. 2). Analysis of curves shows that the early stage of the mollusk growth was characterized by an inverse dependence between $\delta^{18}O$ and $\delta^{13}C$, while the adult stage shows a synchronous change of these parameters. As was noted, the high ^{13}C content in shells indicates an intense photosynthesis and abundance of C_{org} in seawater. Therefore, high $\delta^{13}C$ values should be observed during summer, when seawater is characterized by low $\delta^{18}O$ values [9]. Precisely such a relationship between stable carbon and oxygen isotopes is typical of the earliest stage of the studied shell.

Substitution of the isotope relationship for the inverse type in the adult stage of the molluscan shell can result from environmental changes, such as development of the anoxic (H_2S-contaminated) setting in bottom waters and sediments. Processes of sulfate reduction are most intense in summer. They are accompanied by a decrease in intensity of photosynthesis and corresponding reduction of $\delta^{13}C$ values. In winter, when sulfate reduction is weaker and mixing of seawater is stronger, the oxygen content in water increases and photosynthesis is more intense. This results in higher ^{13}C contents in biogenic carbonates. The lower growth rate of the shell at later stages of mollusk development is manifested by narrower $\delta^{18}O$ peaks in Fig. 1b. This can also be explained by deteriorated habitat conditions.

The Sr distribution in molluscan shells is another indicator of changes in dwelling environments [6, 10, 12]. Early stages of the development of mollusks were characterized by intense accumulation of Sr, mainly during winter seasons (Fig. 3). In summer, the Sr content in water is lower because of its intense consumption by rapidly developing organisms. The burial of plant remains during cold seasons is responsible for an

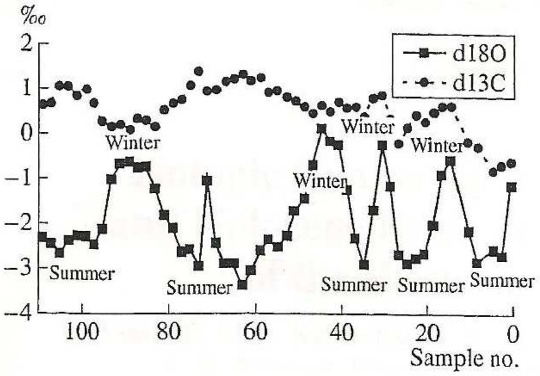

Fig. 2. The $\delta^{18}O$ and $\delta^{13}C$ distribution in the DAG9B molluscan shells.

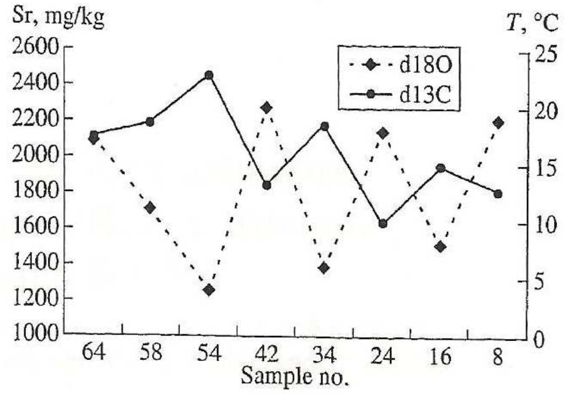

Fig. 3. The Sr distribution in the DAG9B molluscan shell and calculated temperatures based on the $\delta^{18}O$ values.

increased Sr content in seawater and, correspondingly, in invertebrate shells, whose composition is in equilibrium with the seawater [8]. The shell growth is accompanied by a progressive decrease of Sr accumulation intensity. This is probably explained by an ontogenetic effect [5], which is reflected in the weaker dependence of an organism on external conditions in the course of its growth. Similar distribution regularity was also noted for Ba, Fe, Mg, and Mn.

Thus, the data obtained make it possible to reconstruct paleogeographic conditions in the Caspian Sea based on isotopic and chemical compositions of biogenic carbonates. The changes of $\delta^{18}O$ values in molluscan shells with their growth provide information on the temperature and salinity of the paleobasin. The $\delta^{13}C$ values indicate the intensity of organic matter accumulation in the basin. Cyclic changes in Sr and Ba contents in molluscan shells can serve as indicators of paleobasin conditions.

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