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Stable oxygen isotopes in modern ostracods from the Caspian Sea

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Abstract

This paper is the first one to investigate the stable oxygen isotope values of modern ostracods sampled across the whole area of the Caspian Sea. Six taxa were analyzed for $\delta^{18}\text{O}_{\text{ost}}$. The correlation between $\delta^{18}\text{O}_{\text{ost}}$ and some parameters of the aquatic environment, such as water temperature, salinity and $\delta^{18}\text{O}_{\text{water}}$, was examined, providing the basis for reliable paleoenvironmental reconstructions in the future using oxygen isotope data. The results of 105 $\delta^{18}\text{O}_{\text{ost}}$ measurements taken from 76 sites are consistent with the temporal and spatial indicators of the bottom water masses, as impacted by regional hydrography and physical processes. It has been proven that the $\delta^{18}\text{O}$ of Caspian ostracods is mainly determined by a species-specific isotopic offset with an average value of +1‰. The corresponding inference allows to successfully identify the properties of the water mass, where the carapace has been formed, and also enables to recognize the climatical signal in the $\delta^{18}\text{O}$ records. The vital offset for the mixed ostracod samples was found to be equivalent to the average species-specific isotopic offset calculated on the mean annual and winter temperatures of the Caspian Sea water; it equals to +1 (± 0.5) ‰. The regression analysis showed correlations to temperature and salinity parameters that may also facilitate the prediction of water-mass characteristics when being applied to core sediment records. The predicted temperatures correspond to actual measured temperatures at the site of collection, and the oxygen isotope composition of the studied species can be a reliable indicator of water temperatures corresponding to the period of shell calcification. However, in the context of the Caspian Sea environmental changes during the Quaternary period, such attempts of calculating paleotemperatures may lead to false results, since the paleotemperature equation and its variations are only applicable to a water body in its steady state.

Introduction

The Caspian Sea (CS) is the unique, world's largest endorheic inland basin in terms of area and volume. Connections between the CS and the World Ocean took place repeatedly during the Quaternary. Nowadays, it is a closed (lake-type) water basin. However, the CS is called a sea due to its brackish water environment, size, and geological history. Its regional setting has predetermined the peculiarities of its evolution in many aspects (Kvasov 1975; Rychagov 1997; Yanina 2012, 2014). The CS is divided into three sub-basins: north, central (or middle) and south, deepening southwards. The water depth increases from a few meters in the northern part up to 1,025 m in the south (Baidin and Kosarev 1986). It is a brackish water body; surface salinity increases from around 1 – 4‰ (per mille) in the north near the Volga delta to 13‰ in the southern part (Tuzhilkin and Kosarev 2005). The highest salinity (except for Kara-Bogaz-Gol Bay), up to 13.5‰, is determined along the eastern coast of the middle and southern parts of the sea. The salinity decreases in proximity to large river mouths. In deep waters vertical changes in the salinity are negligible. The CS water temperature values are heterogeneous: the water column down to the depth of 350 m is subject to seasonal fluctuations; the deeper water temperature varies from +3.80 °C to +5.35 °C, with an average value of +4.5 °C (Baidin and Kosarev 1986). The upper water column (100 m depth) is subject to the strongest seasonal changes: in summer, shallow waters warm up to +25 – +26 °C in both the northern and southern basins. In winter, the North CS is partially covered by ice. Wind-driven currents prevail in the CS. Along with winds, the main factors influencing the currents are: spatial heterogeneity of water density, shoreline shape and bottom topography, as well as river inflow (Lebedev et al. 2015). The general pattern of currents has a counterclockwise circulation form, which can be explained by the input of large amounts of river water into the North CS and strong evaporation over the southern water area. According to some researchers (Gorbarenko 1972; Ferronsky et al. 2014), average values of $\delta^{18}\text{O}$ for near-bottom waters (hereafter $\delta^{18}\text{O}_{\text{water}}$) of the Central and South Caspian are -1.7‰, -1.5‰.

Quaternary history of the CS is described by transgressive-regressive cycles of different amplitude and duration (Svitoch 1991; Rychagov 1997; Yanina 2012; Krijgsman et al. 2019). Its own regime of water level changes is characterized by significant centennial, interannual, and seasonal fluctuations. Stable isotope studies are enormously powerful and diverse tool that enable detailed understanding of lake paleogeography. Nevertheless, such works are rare for the Caspian region (Gorbarenko 1972; Nikolaev 1995; Ferronsky et al. 1999; Froehlich et al. 1999). This fact can probably be explained by the general difficulty of studying isolated water bodies in terms of stable isotope geochemistry (Lemeille et al. 1983; Talbot 1990), and by the complexity of the Caspian Sea's dynamics itself (Rychagov 1970; Svitoch 1991; Krijgsman et al. 2019; Badyukova 2021; Berdnikova et al. 2023; Makshaev and Tkach 2023). Here we examine stable oxygen isotope values on calcitic valves of ostracods (hereafter $\delta^{18}\text{O}_{\text{ost}}$) from the surface Caspian sediments for successful future application in the CS paleolimnology. For such study the importance of ostracods – small crustaceans with calcite shells known to be sensitive to environmental changes (von Grafenstein et al. 1999; Holmes and Chivas 2002; Holmes and DeDecker 2012) – grows exponentially since foraminifera along with other groups of microfauna widely used in the stable oxygen isotope studies (Erlenkeuser and von Grafenstein 1999) are rare or lacking in the Quaternary sediments of the CS.

Ostracods are extremely useful both for biostratigraphic and paleoenvironmental studies (Holmes and Chivas 2002). They use bicarbonate and carbonate ions from the surrounding water to build their shells rapidly – within a few hours (Turpen and Angell 1971) or a few days (Chivas et al. 1983; Roca and Wansard 1997). Therefore, $\delta^{18}\text{O}_{\text{ost}}$ provides a record of the water conditions

at the discrete time of calcification (Holmes and DeDeckker 2012) and reflects discrete environmental conditions (Turpen and Angell 1971).

The greater part of the modern CS ostracod fauna is endemic mostly due to geographical isolation (especially during the most extreme) and unique brackish-water habitat. (Agalarova 1961; Gofman 1964, 1966; Mandelstam et al. 1962; Boomer 2005; Chekhovskaya et al. 2018; Berdnikova et al. 2023). At the same time the Caspian ostracod fauna shows some elements in common with the Black Sea as a result of connection between the basins and invasion through the Manych Strait during the CS highstands (Rögl 1999; Popov et al. 2006). The detailed data on the distribution and ecology of the modern ostracod species in the surface sediments of the CS were presented earlier (Gofman 1964, 1966; Boomer 2005). However, the retention of open nomenclature for many of the taxa in this work should be noted (Schornikov 2011). Here, we use the term ‘valve’ to denote one of the two components that are joined together to form the bivalved carapace; and the term ‘shell’ – more generally to mean either a valve or carapace after Holmes and DeDeckker (2012).

Wider application of the stable oxygen isotope analysis into paleoenvironmental studies of the Caspian region could undoubtedly contribute to the establishment a relationship between the oxygen isotope records of the CS, its transgressive-regressive cycles and climatic changes in the Northern Hemisphere during the Quaternary. Though, its successful application based on ostracods requires an initial investigation of the multiple factors governing $\delta^{18}\text{O}_{\text{ost}}$ (and associated $\delta^{18}\text{O}_{\text{water}}$) values. Suchlike works (Didie and Bauch 2002; Gemery et al. 2021) inspire to expand the corresponding research and involve other regions of the world in it. Therefore, the overarching goal of this study is to examine the general principles being applied to isotopic reconstructions, to evaluate the feasibility of using ostracod shells as stable oxygen isotope proxy of temperature or water mass properties in the CS.

The Caspian Sea has a global importance as it produces a large proportion of the world oil and gas and its coastal infrastructures are heavily dependent on sea-level changes. The population in the Caspian catchment basin is estimated at around 80 million and is growing. The Caspian basin is the economical, industry, and socio-ecological-cultural-political space. Its lake systems and biota have experienced profound changes throughout its geological history. Yet a variety of human impacts has accelerated changes affecting its environment. To protect the unique basin, we need to learn its long and dynamic history starting by studying modern patterns.

Materials and methods

The research is based on the study of the paleontological collection of E.A. Gofman. It is currently being stored at the Paleogeography Laboratory of Recent and Pleistocene Sediments, (Faculty of Geography, Lomonosov Moscow State University, Moscow, Russia). The key publication – and primary data source – (Gofman 1964) provides information on species descriptions and habitat conditions, however, the author has not completed that work. Up to date, there are no existing analogues to Gofman’s collection, containing ostracod shells from the bottom sediments spanning across the entire CS area. Here we study 76 of its most representative sampling sites (Fig. 1).

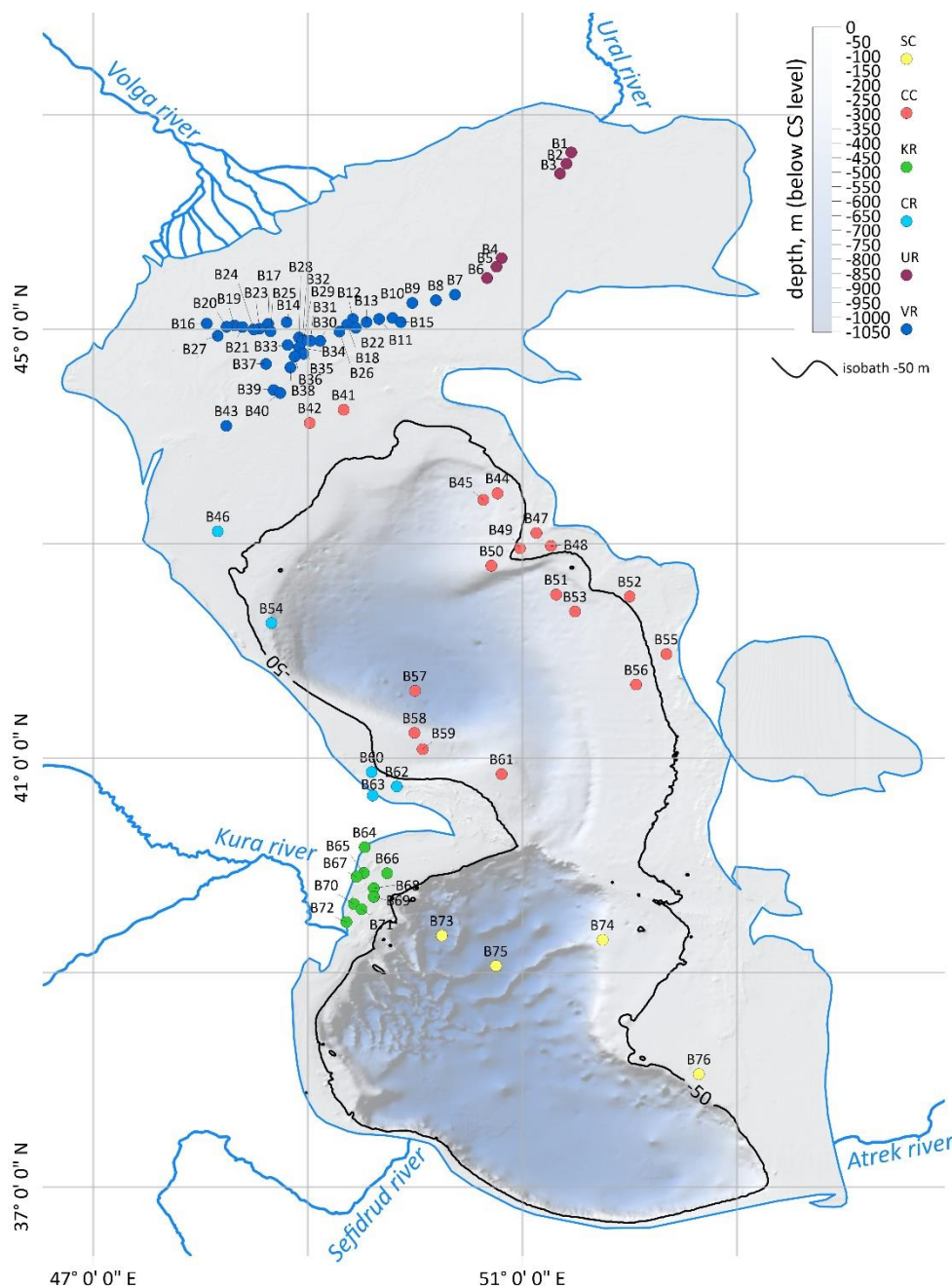


Fig. 1. Location of sediment and bottom water sampling sites ($n = 76$) in the Caspian Sea. The names are abbreviated: the first letter “B” refers to “bottom”. Site numbers increase from north to south. The color shows affiliation with a particular water mass. Abbreviations: VR = Volga River; UR = Ural River; CR = Caucasus Rivers; KR = Kura River; CC = Central Caspian; SC = South Caspian. Isobath -50 m corresponds to the boundary of the shallow-water zone.

Ostracods from surface sediment samples ($\sim 0 - 5$ cm) were collected during the summer seasons of 1961-1963 using a bottom sampler. Each dry sediment sample weight was 100 g. These samples were washed with tap water through a $63 \mu\text{m}$ sieve, the remaining $>63 \mu\text{m}$ -size fraction was air-dried. Using a binocular microscope, ostracod shells were hand-picked from the dried sediment using a fine-tipped brush and transferred to a slide (Krantz-Cells or microcells). Bottom water temperature and salinity were measured at the same sampling sites, where ostracod sediment samples were taken (Gofman 1964, 1966). As relevant $\delta^{18}\text{O}_{\text{water}}$ we used the earliest data on the CS water isotopic composition being available (Gorbarenko 1972), which provide a fairly detailed picture of its distribution along the CS during the summer period (Suppl. A). We assume that

$\delta^{18}\text{O}_{\text{water}}$ has not changed over the time period of about 10 years that separates the sediment and water sampling.

The CS waters represent a mixture of water masses primarily differentiated by their salinity, temperature and depth. Thus, all samples were subdivided into several groups according to water masses prevailing at the sampling site (Fig. 1) since the water mass properties influence the $\delta^{18}\text{O}_{\text{ost}}$ values. In total six types of water masses (designated based on properties listed in Suppl. A.) were derived: VR (Volga River) – corresponds to the water mass in the North Caspian influenced by Volga waters; UR (Ural River) – by Ural waters, respectively; CR (Caucasus Rivers) – by the river waters from the Caucasus within the territory of Russia; KR (Kura River) – the water mass in the mouth zone of the Kura River; CC (Central Caspian) and SC (South Caspian) – the deep-water masses of the Middle and South Caspian, respectively. We presume $\delta^{18}\text{O}_{\text{ost}}$ values reflect both the $\delta^{18}\text{O}_{\text{water}}$ values and water mass properties of the sampling period (summer season, Suppl. A) when the majority of ostracods reach maturity and adult specimens selected for this study's analysis calcified their shells. While data on bottom water temperature and salinity are available for the entire CS (Suppl. A), $\delta^{18}\text{O}_{\text{water}}$ values are only published for the Middle and South Caspian basins (Gorbarenko 1972), meaning that for the North Caspian (VR and UR water masses), we can only present $\delta^{18}\text{O}_{\text{ost}}$ measurement results (Suppl. B).

Six common ostracod species were chosen for stable oxygen isotope analysis: shallow-water *Euxinocythere virgata* and *Tyrrhenocythere amnicola donetziensis*; deeper-water *Candona shweieri*, *Paracyprideis* sp., *Bacunella dorsoarcuata* and *Camptocypria* sp. The biogeography and ecology of these taxa were examined earlier (Gofman 1964, 1966; Chekhovskaya et al. 2018; Berdnikova et al. 2023). When selecting ostracod shells for stable oxygen analysis, we followed the criteria established by Holmes and Chivas (2002): only adult-stage valves and carapaces with well-preserved morphology were used for measurements. Juvenile species were excluded from this study since conflicting data have been reported about the consistency of $\delta^{18}\text{O}_{\text{ost}}$ values of juvenile and adult specimens (Xia et al. 1997a, 1997b; Didie and Bauch 2002; Keatings et al. 2002; Gemery et al. 2021). Three to six shells from the same species in the same sample were used depending on the valves weight.

Prior to stable isotope measurements, all samples must be cleaned, as valves and carapaces can be contaminated by adhering sediments or soft tissues. As was noted before (Caporaletti 2011), there is no commonly-accepted cleaning standard for ostracods and the effects of chemical pre-treatment are not completely investigated, although some authors have tried to establish a conventional procedure. In order to determine the optimal pre-treatment technique reasonable for the CS ostracods, five most-applicable ones (Xia et al. 1997a, 1997b; von Grafenstein et al. 1999; Keatings et al. 2002; Berdnikova and Javadova 2022) have been considered. The results show that chemical pre-treatment procedures have no significant effects on the $\delta^{18}\text{O}_{\text{ost}}$ – small and non-systematic offsets were reported (Berdnikova and Javadova 2022), which complies with other observations (Xia et al. 1997a; Li et al. 2007). Here we use a fine brush and distilled water to pick up the shells and remove any adhering sediment. The valves or carapaces selected for the stable isotope analysis were as clean and transparent as possible. If necessary, carapaces were opened to get two single valves, and soft parts from within the shell were removed with a fine brush or a dissecting needle.

The measurements of $\delta^{18}\text{O}$ are carried out at the Far East Geological Institute FEB RAS, (Vladivostok, Russia) with a standard deviation of $\pm 0.05\text{‰}$ using a Finnigan MAT 252 isotope ratio mass spectrometer (ThermoFinnigan). ThermoFinnigan Isotope Data acquisition software (ISODAT) is used to control the CF-IRMS system (Velivetskaya et al. 2009). Oxygen isotope values are reported in parts per thousand, or per mil (‰) deviations of the $^{18}\text{O}/^{16}\text{O}$ isotope ratios relative to the VPDB (Vienna Pee Dee Belemnite) scale using laboratory standard Coral-1 ($\delta^{13}\text{C}_{\text{VPDB}} = -0.28\text{‰}$, $\delta^{18}\text{O}_{\text{VPDB}} = -3.69\text{‰}$) (Velivetskaya et al. 2009) obtained from an aragonite of the modern coral *Porites lutea* (New Caledonia), calibrated against NBS-18 ($\delta^{13}\text{C}_{\text{VPDB}} = -5.01\text{‰}$,

$\delta^{18}\text{O}_{\text{VPDB}} = -23.0\text{‰}$), NBS-19 ($\delta^{13}\text{C}_{\text{VPDB}} = +1.95\text{‰}$, $\delta^{18}\text{O}_{\text{VPDB}} = -2.2\text{‰}$) (Coplen et al. 2006) (National Bureau of Standards). To check measurement precision, reproducibility and the variability of shell $\delta^{18}\text{O}$ values within the same sample, all runs were carried out at least twice (Suppl. B) as was previously recommended by Holmes and Chivas (2002) and Gemery et al. (2021). To convert $\delta^{18}\text{O}_{\text{water}}$ on the Vienna Standard Mean Ocean Water (VSMOW) scale into $\delta^{18}\text{O}_{\text{water}}$ on the VPDB scale, we followed Hut (1987). The expected equilibrium calcite values ($\delta^{18}\text{O}_{\text{expected}}$) were estimated using O'Neil et al. (1969) equation. The difference between measured $\delta^{18}\text{O}_{\text{ost}}$ and the corresponding $\delta^{18}\text{O}_{\text{expected}}$ values ($\delta^{18}\text{O}_{\text{ost}} - \delta^{18}\text{O}_{\text{expected}}$) represents a species-specific vital effect fractionation (usually referred to as “vital offsets” or “vital effects”). Its average values were determined for each adult species from all measured values for that species.

Results

We performed a total of 105 measurements at 76 sampling locations in the CS (Fig. 1, Suppl. B) to assess the $\delta^{18}\text{O}_{\text{ost}}$ applicability of six Caspian ostracod species.

An average $\delta^{18}\text{O}_{\text{ost}}$ value (\pm standard deviation) was generated for each species: -1.42‰ (± 0.75) for *E. virgata*; -1.37‰ (± 1.42) for *T. amnicola donetziensis*; 1.65‰ (± 1.01) for *C. shweieri*; 1.29‰ (± 0.44) for *Paracyprideis* sp.; 2.25‰ (± 0.66) for *B. dorsoarcuata* and 2.83‰ (± 0.66) for *Camptocypria* sp.

Obtained results confirmed that the Caspian ostracods do not secrete their carapace in equilibrium with ambient water. Rather, studied species showed a positive vital offset – the observed species-specific effect averaged about 1‰ . This is consistent with other researchers' data that ranged from $+1.5\text{‰}$ to $+0.5\text{‰}$ (Xia et al. 1997a, b; von Grafenstein et al. 1999; Didie and Bauch 2002; Gemery et al. 2021).

Discussion

Water mass characteristics and $\delta^{18}\text{O}_{\text{water}}$ relationships

The temperature (T) variability (as well as oxygen content, for example) mainly depends on the severity of the winter season, since the influx of oxygen from the atmosphere and its solubility in the water are significantly increased during severe winters. In addition, the aeration of deep waters is higher due to intense convection. On the other hand, salinity values (S) are mainly controlled by external factors (e.g., the volume of river input), which are weakly correlated with each other.

In general, the $\delta^{18}\text{O}_{\text{water}}$ value is continuously changing due to evaporation and condensation processes. Simple regression analysis (Fig. 2) showed a close relationship between $\delta^{18}\text{O}_{\text{water}}$, T and S, which is particularly remarkable for the central zones of the South Caspian basin.

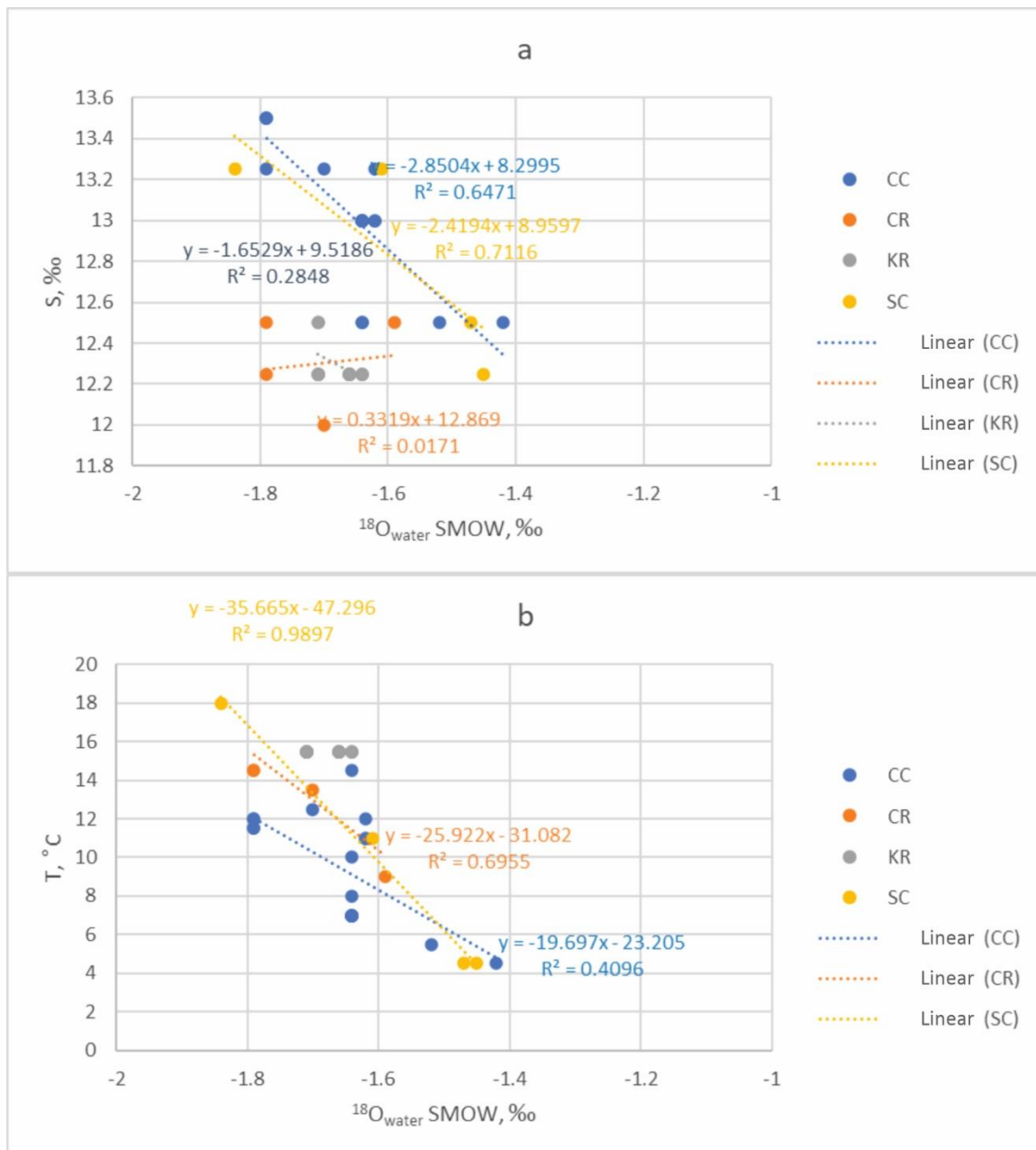


Fig. 2. The relationship among $\delta^{18}O_{\text{water}}$ and water mass characteristics (a – mean annual bottom water salinity (S); b – mean annual bottom water temperature (T) listed in Suppl. A) Simple regression analysis was conducted on samples sorted by water mass: CR – Caucasus Rivers, KR – Kura River, CC – Central Caspian and SC – South Caspian.

All water masses can be characterized by a certain pattern (Fig. 2): $\delta^{18}O_{\text{water}}$ increases with decreasing temperature, which, in turn, decreases with the depth – the coefficient of determination shows a significant relationship ($R^2 = -0.76$).

In the CS, the river inflow makes a great contribution to the salinity distribution – powerful surface water currents with a low $\delta^{18}O$ values flow into the sea with a relatively high $\delta^{18}O$ values. This mostly applies to the northern part of the CS, but in other areas of the basin located in the proximity to the river mouths a mixing of isotopically lighter and heavier waters is also present. It is particularly obvious in the shallow waters near the western shore of the South Caspian (to the north of the Kura River mouth), where S decreases to 12‰ in the area of maximum concentration of sampling sites (Fig. 1). Despite the fact that processes resulting in changes of $\delta^{18}O_{\text{water}}$ values (e.g., evaporation or precipitation, ice melt, river input, to name a few) also result in changes of

the water salinity (Epstein et al. 1951; LeGrande and Schmidt, 2006), the expected linear relationship between S and $\delta^{18}\text{O}_{\text{water}}$ has not been proved (Fig. 2). While on a global basis, for every one unit decrease in salinity, a corresponding 0.6‰ decrease in $\delta^{18}\text{O}_{\text{water}}$ value is expected (Craig and Gordon 1965), the obtained results show that for every one unit decrease in salinity, a corresponding 0.4‰ increase in $\delta^{18}\text{O}_{\text{water}}$ can be expected for CS areas not affected by the desalination effects of inflowing rivers. In other words, $\delta^{18}\text{O}_{\text{water}}$ values are higher in waters with lower salinity. Such pattern in this study can simply be caused by an increase in sampling depth within the same type of water mass. It is mostly noticeable in CC and SC, where the depth difference is maximum and reaches several hundred meters, while the linear relationship between salinity and $\delta^{18}\text{O}_{\text{water}}$ for CR meets expectations.

The $\delta^{18}\text{O}_{\text{ost}}$ values generally reflect water properties (mainly temperature) for the summer period, when organisms reach their maturity and productivity peaks (Horne 1983; Gemery et al. 2021). On the contrary, our results (Suppl. B) show close relationship between $\delta^{18}\text{O}_{\text{ost}}$ and winter temperatures: the average difference ($\delta^{18}\text{O}_{\text{ost}} - \delta^{18}\text{O}_{\text{expected}}$) is the smallest when $\delta^{18}\text{O}_{\text{expected}}$ is calculated using average winter water temperatures (+0.98‰). For summer water temperatures the average difference was +3.16‰. The average vital effect calculated using mean annual CS water temperatures equals to +0.99‰.

The investigated relationship between $\delta^{18}\text{O}_{\text{water}}$, T and S clearly shows the determinative influence of the water depth at the sampling site. The proximity of rivers and seasonal variations in the water masses characteristics contribute to it as well. Without acknowledging of this much more complicated relationships and factors that ultimately determine the stable oxygen isotope results obtained in the laboratory, irrelevant conclusions can be made.

Species-specific vital effect fractionations

Several strong species-specific vital effects were observed in our results (Fig. 3). The mechanisms to explain vital offsets in ostracod shells are poorly understood (Gemery et al. 2021). It has been suggested (Kim and O'Neil 1997) such effects are related to the isotopic fractionation resulting from some biological process (Decrouy 2012). According to Xia et al. (1997a), physiological factors like metabolic rate, environmental stress, light penetration or food quantity contribute to this fractionation process. Decrouy and Vennemann (2013) studied freshwater and brackish ostracods and suggested that vital effects within one taxon may be related to water chemistry. The role of water alkalinity and the state of calcite saturation has also been noted by Decrouy (2012) and Devriendt et al. (2017). These observations persuade that a set of factors must be studied to fully explain the species-specific vital offsets measured.

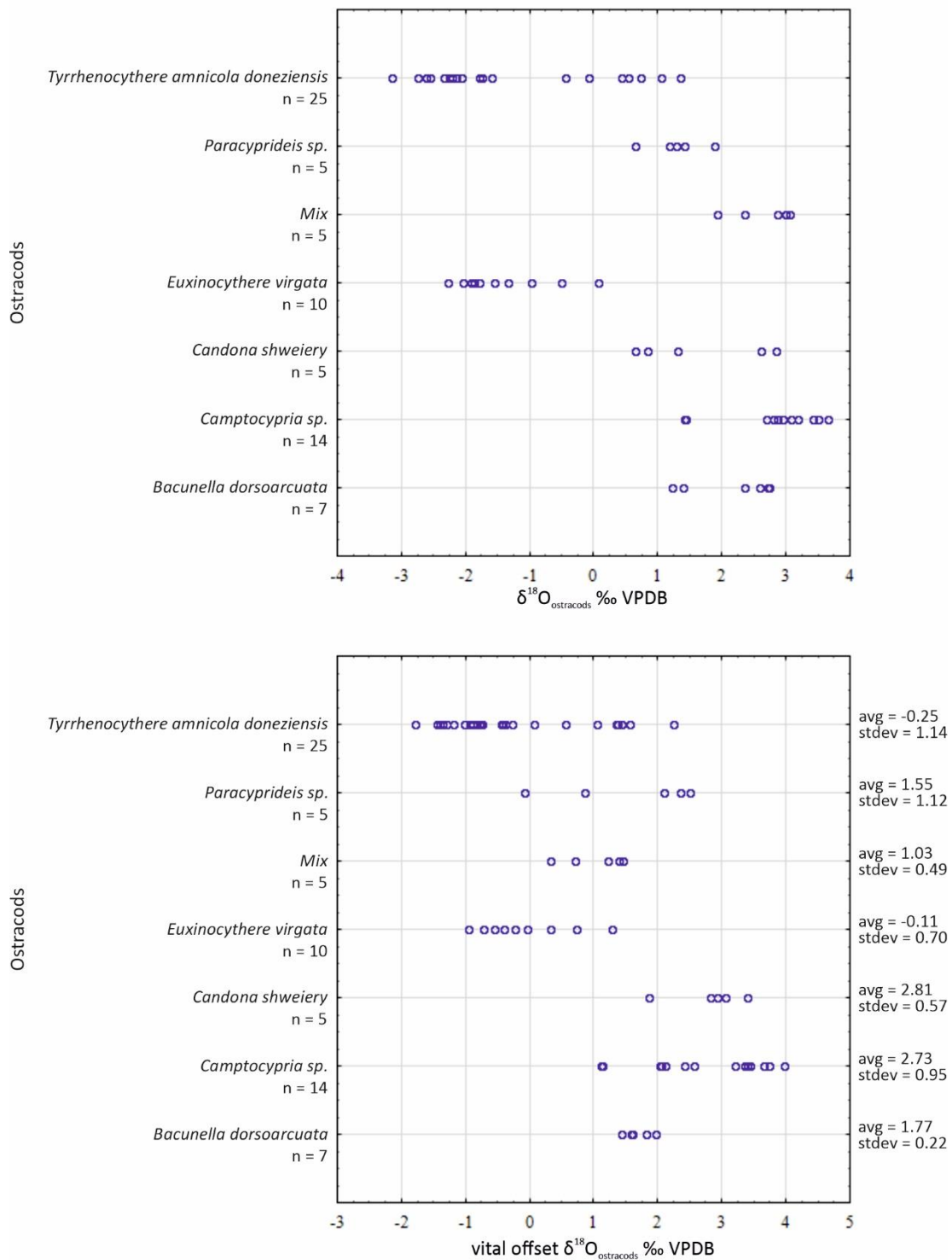


Fig. 3. Results $\delta^{18}\text{O}_{\text{ost}}$ for each species from each sample and calculated species-specific vital offsets for each respective species.

For *B. dorsoarcuata* with offset averaged at +1.77‰, the standard deviation was only 0.22. The strongest vital offset was recorded for *C. shweieri* (+2.81‰), although the standard deviation for the species was only 0.57‰. This result is consistently demonstrated by the majority of studied ostracods of this species, and thus, in the context of paleoreconstructions, the species is well-suited for measurements and study along with *B. dorsoarcuata*. A strong isotopic offset (2.73‰) was recorded for *Camptocypria sp.* and the standard deviation was also higher (0.95‰). Same pattern is obtained for *Paracyprideis sp.*; despite a relatively average offset (+1.55‰), the range of values

is large (standard deviation reaches 1.12‰ – it is higher only for *T. amnicola donetziensis* (1.14‰)). For the mixed ostracod samples (consist of different species) reported offset showed to be equivalent to the average offset calculated for mean annual and winter Caspian water temperatures, it equals +1‰ (± 0.5). If compared, this value is -2.25‰ for *Cardium edule* and *Didacna trigonoides* Caspian mollusks, and -3.27‰ in Caspian carbonate muds (Ferronsky et al. 1999).

For shallow-water species *E. virgata* and *T. amnicola donetziensis*, the species-specific fractionation leads to a decreasing of $\delta^{18}\text{O}$ values. The offset is negative (-0.11‰ for *E. virgata* and -0.25‰ for *T. amnicola donetziensis*, respectively). The highest standard deviation was also recorded for *T. amnicola donetziensis* (1.14‰), and it is quite high for *E. virgata* (0.7‰). This pattern can be easily explained by the sampling location. Many of the studied samples were collected near the Kura River delta – the source of isotopically lighter waters, while the remaining samples not. Moreover, the water depth at these sampling sites did not exceed 33 m. Meanwhile, the benthic and deep-water ostracods generally have positive (isotopically heavier) offsets (Xia et al. 1997a; von Grafenstein et al. 1999), and $\delta^{18}\text{O}_{\text{ost}}$ values in shallow waters are subject to greater variations due to high hydrologic variability. For example, bottom salinity deviations (as well as temperature) of the deep-sea site are much smoother if compared to the shallow water ones. The same holds for wider deviations of calcite $\delta^{18}\text{O}_{\text{ost}}$ values from equilibrium observed for shallow water sites. The vital effect is constant (about 1‰) for deep waters sampling sites, where temperature amplitudes are not significant. But it could be +4.5‰ at shallow depth where water temperature reaches 20-25 °C in summer and drops to 4 °C in winter. These observations are consistent with other researches (Erlenkeuser and von Grafenstein 1999) stating that higher hydrologic variability at shallow depths causes $\delta^{18}\text{O}_{\text{ost}}$ values to deviate much more from the equilibrium value.

To eliminate (or at least reduce) the isotopic signal of such hydrologic variability and to better estimate species-specific vital effects, some researchers (Simstich et al. 2004; Gemery et al. 2021) use only sites from >40-50 m water depth.

Following a similar strategy, samples from ≤ 50 m water depth were excluded (Fig. 1). However, for *B. dorsoarcuata* the vital offset remained the same – all samples were taken at depths of about 150 m since the species does not live in shallow waters. A similar pattern is observed for *Paracyprideis* sp. and the mixed ostracod samples. For *C. shweieri*, the offset showed to be slightly higher (+2.94‰), but the standard deviation for the species was only 0.16‰ – significantly lower than the average value. For *Camptocypria* sp., the reported isotopic effect decreased to +2.45‰, while the range of values remained approximately the same. Meanwhile, *E. virgata* and *T. amnicola donetziensis* do not inhabit waters deeper than 50 m.

Relationship of species $\delta^{18}\text{O}_{\text{ost}}$ to temperature, salinity and $\delta^{18}\text{O}_{\text{water}}$

Not all variations in $\delta^{18}\text{O}_{\text{ost}}$ values can be accounted for by species-specific vital offsets. The resulting analysis shows that samples separate out geographically and by water mass (Fig. 4).



Fig. 4. The relationship of $\delta^{18}\text{O}_{\text{ost}}$ to T (a), S (b), $\delta^{18}\text{O}_{\text{water}}$ (c), and depth (d) of the Caspian Sea corrected for the isotopic shift. Grouping of the studied ostracods was carried out on the basis of their species affiliation (reflected by an icon type) and taking into account their belonging to a particular type of water masses (shown by an icon color).

The greatest range of $\delta^{18}\text{O}_{\text{ost}}$ values corresponds to the group of ostracods in VR water mass. Figure 4 illustrates weakening of the Volga River desalination impact as the sampling sites moving away from its delta. The greater evaporation process (during the summer and autumn seasons in the modern CS) is accompanied by an increase in the volume of higher salinity waters, although bottom water salinity variations in the deep-sea areas remain the same throughout the year. This explains the dense concentration of sampling sites in the Middle and South Caspian in one section of the graph (Fig. 4). The Western Caspian area, unlike the Eastern one, is subject to desalination by river waters to the greater extent (this, in particular, explains introduction of a CR water mass type). The same applies to the deviations of the $\delta^{18}\text{O}_{\text{ost}}$ rates – the Kura delta with the lowest salinity and oxygen isotope values is obviously distinguished, while the eastern province is characterized by higher salinity and heavier $\delta^{18}\text{O}_{\text{ost}}$ values.

Variability of the $\delta^{18}\text{O}_{\text{ost}}$ values in shallow waters (Fig. 4) can be explained by the high-amplitude temperature variations for different seasons, while in deep-waters homothermic conditions are observed and such contrasts are alleviated. The $\delta^{18}\text{O}_{\text{ost}}$ values increase along with the depth growth is consistent with previously published data (Xia et al. 1997a; von Grafenstein et al. 1999). One can conclude that the $\delta^{18}\text{O}$ values of deep-sea ostracods are isotopically heavier.

The studies of Simstich et al. (2004) and Gemery et al. (2021) showed that due to oceanic or marine circulation, the selected types of water masses depended mainly on cold and warm currents, rather than on the depth stratification of water masses, as in the CS. Thus, the samples collected at the same depth showed differences in $\delta^{18}\text{O}_{\text{ost}}$ values, thereby reflecting differences in the aquatic environment parameters (temperature in particular). It is crucial to clarify that in the CS the higher $\delta^{18}\text{O}_{\text{ost}}$ values corresponding to the temperature decrease is actually related to an increase in water depth since water temperature drops with depth. In the modern CS the same temperature conditions are maintained at the same depths, so it is not possible to compare $\delta^{18}\text{O}$ results for shells formed at the same depths but under different temperature conditions. Only such a study could reveal the true temperature signal. In other words, the depth factor in modern samples concealed a climatic (temperature) signal.

The pattern of increasing $\delta^{18}\text{O}_{\text{water}}$ value with a temperature decrease has already been discussed above. Meanwhile, the $\delta^{18}\text{O}_{\text{ost}}$ values should largely depend on $\delta^{18}\text{O}_{\text{water}}$ (Fig. 4). While the $\delta^{18}\text{O}_{\text{water}}$ varies from site to site within just 0.4‰, the range of bottom water temperature and salinity variations at the sampling sites is much greater, thus the influence of $\delta^{18}\text{O}_{\text{water}}$ is less evident.

The observed patterns lead to the conclusion that $\delta^{18}\text{O}_{\text{ost}}$ values of studied species can be reliable proxies of changes in temperature, salinity and isotopic composition of seawater and, in turn, can help in identification of the water mass properties.

Validation of the oxygen isotopic composition as a water temperature indicator

The studies of isotopic equilibrium in the calcium-carbonate shell systems are based on Urey (1947), where water temperature and the isotopic composition of water were established to be the primary factors controlling the fractionation of oxygen isotopes in biogenic carbonates (CaCO_3). We tested our $\delta^{18}\text{O}$ data (corrected for vital offset) using the paleotemperature equation by Epstein et al., (1951, 1953) later modified by Craig (1965), which was calibrated for biogenic carbonates in a temperature range of 7 to 29 °C for common ostracod species (*C. shweieri*, *B. dorsoarcuata*, *Camptocypria* sp. and *Paracyprideis* sp.) and the mixed ostracod samples collected from >50 m water depth:

$$T = 16.9 - 4.2 * (\delta^{18}\text{O}_{\text{ost}} - \delta^{18}\text{O}_{\text{water}}) + (\delta^{18}\text{O}_{\text{ost}} - \delta^{18}\text{O}_{\text{water}})^2 \quad (1)$$

As the equation was standardized using PDB-derived CO_2 , conversion of $\delta^{18}\text{O}_{\text{water}}$ VSMOW to VPDB was required.

We calculated the predicted temperatures (T_c) using $\delta^{18}\text{O}_{\text{ost}}$ and $\delta^{18}\text{O}_{\text{water}}$ data (Table 1) and compared to the measured temperatures (T_m) at sampling sites (Suppl. A). After the calculated vital offset was subtracted from the $\delta^{18}\text{O}_{\text{ost}}$ measurements, the $\delta^{18}\text{O}_{\text{ost}}$ values were close to expected equilibrium calcite values after accounting for expected temperature effects. The calculated temperatures exceeded the measured ones by only 0.45 °C. The strongest difference ($T_c - T_m$) is noted for the mixed ostracod samples (-1.72 °C). Nevertheless, even this result is equivalent to the average data obtained in Gemery et al. (2021). The difference for *B. dorsoarcuata* was -0.51 °C, while the other species showed values that are much closer to the actual ones – for example, for *Camptocypria* sp. the difference is -0.25 °C, for *C. shweieri* – it is 0.24 °C, and for *Paracyprideis* sp. – it is only -0.20 °C. Thus, the oxygen isotope composition of the studied species can be used as a reliable indicator of water temperatures for the time of calcification.

Table 1 Comparative table of predicted and measured water temperature at bottom sampling sites (>50 m depth)

Sampling site	Ostracods – Water masses	$\delta^{18}\text{O}_{\text{ost}}$ ‰ VPDB ± 0.05	$\delta^{18}\text{O}_{\text{w}}$ ‰ VPDB	Vital offset (average for species)	Depth of water, m	T_{m} °C	T_{summer} °C	T_{winter} °C	T_{c} °C	Difference between T_{m} and T_{c} °C	Average difference for species
B51	Bacunella dorsoarcuata - CC	2.74	-1.91	1.77	148	7.00	8.0	6.0	6.82	0.18	-0.51
B51	Bacunella dorsoarcuata - CC	2.36	-1.91	1.77	148	7.00	8.0	6.0	8.18	-1.18	
B45	Bacunella dorsoarcuata - CC	2.73	-1.91	1.77	150	7.00	10.0	4.0	6.85	0.15	
B50	Bacunella dorsoarcuata - CC	2.73	-1.91	1.77	150	7.00	8.0	6.0	6.87	0.13	
B50	Bacunella dorsoarcuata - CC	2.59	-1.91	1.77	150	7.00	8.0	6.0	7.37	-0.37	
B74	Bacunella dorsoarcuata - SC	1.40	-1.88	1.77	150	11.00	11.0	11.0	11.89	-0.89	
B74	Bacunella dorsoarcuata - SC	1.23	-1.88	1.77	150	11.00	11.0	11.0	12.56	-1.56	
B48	Camptocypria sp. - CC	3.52	-1.89	2.73	70	12.00	19.0	5.0	7.55	4.45	-0.25
B44	Camptocypria sp. - CC	3.07	-1.91	2.73	100	8.00	23.0	4.0	9.08	-1.08	
B53	Camptocypria sp. - CC	2.81	-1.91	2.73	119	7.00	8.0	6.0	10.04	-3.04	
B58	Camptocypria sp. - CC	3.42	-1.91	2.73	127	10.00	14.0	6.0	7.82	2.18	
B58	Camptocypria sp. - CC	3.67	-1.91	2.73	127	10.00	14.0	6.0	6.94	3.06	
B45	Camptocypria sp. - CC	2.88	-1.91	2.73	150	7.00	10.0	4.0	9.80	-2.80	
B45	Camptocypria sp. - CC	2.80	-1.91	2.73	150	7.00	10.0	4.0	10.09	-3.09	
B50	Camptocypria sp. - CC	3.18	-1.91	2.73	150	7.00	8.0	6.0	8.68	-1.68	
B56	Candona shweieri - CC	2.61	-1.89	2.81	75	11.00	16.0	6.0	11.20	-0.20	0.24
B56	Candona shweieri - CC	2.84	-1.89	2.81	75	11.00	16.0	6.0	10.32	0.68	
B57	Ostracoda mix - CC	2.35	-1.69	1.03	780	4.50	4.5	4.5	6.37	-1.87	-1.72
B57	Ostracoda mix - CC	2.87	-1.69	1.03	780	4.50	4.5	4.5	4.59	-0.09	
B75	Ostracoda mix - SC	1.92	-1.74	1.03	750	4.50	4.5	4.5	7.70	-3.20	
B56	Paracyprideis sp. - CC	0.66	-1.89	1.55	75	11.00	16.0	6.0	13.92	-2.92	-0.20
B56	Paracyprideis sp. - CC	1.88	-1.89	1.55	75	11.00	16.0	6.0	9.20	1.80	

B61	Paracyprideis sp. - CC	1.43	-1.91	1.55	100	14.50	21.0	8.0	10.82	3.68
B61	Paracyprideis sp. - CC	1.29	-1.91	1.55	100	14.50	21.0	8.0	11.34	3.16
B59	Paracyprideis sp. - CC	1.19	-1.79	1.55	300	5.50	6.0	5.0	12.22	-6.72

Regarding the cases, for which predicted temperatures were lower than measured values, it is likely that ostracods formed shells in lower temperature conditions (before the sampling season). At the same time, proximity to the coast may also have had the opposite effect due to a possible rapid temperature rise in summer, and this may have spread to deeper areas.

It is crucial to point out that the paleotemperature equation and its variations are applicable to a steady-state water basin only. The vital effect studied for modern ostracods samples along with measured temperatures at the sampling sites allow us to estimate the relationship between $\delta^{18}\text{O}_{\text{ost}}$ and $\delta^{18}\text{O}_{\text{water}}$ values, but it will be relevant only until the change of external factors. The uncertainty in the isotopic composition of previous-time water masses is a major problem in isotopic paleothermometry studies.

In other words, the isotopic composition of water masses does not remain constant over the time. This effect is even more noticeable in closed lake-type water basins, such as the CS, primarily due to the influence of meteoric waters and river inflows. For example, during the Quaternary the influx of isotopically light meltwater led to a decrease in $\delta^{18}\text{O}_{\text{water}}$ value, that is why it is extremely difficult to estimate such signal in dynamics, given simultaneous temperature changes. Thus, any attempts aimed at calculating paleotemperature values for the CS during the Quaternary using $\delta^{18}\text{O}$ data may lead to false results.

Conclusions

This study determined the environmental factors that influence calcite stable oxygen isotope values for six common Caspian ostracod species. Besides bottom T and S, the major impact on $\delta^{18}\text{O}_{\text{ost}}$ values of water depth and the distance from freshwater sources (proximity of rivers) was determined. An additional contribution can be made by the seasonal changes in the characteristics of water masses. The temperature signal has a strong negative correlation with the sea depth, while for the other factors correlation is positive. The oxygen isotope composition of ostracod shells is generally heavier for those specimens that formed in water masses of the higher salinity, and it does not depend on the taxonomic affiliation. The depth stratification of the water masses plays a significant role in the spatial distribution of measured $\delta^{18}\text{O}_{\text{ost}}$ in the CS. The changes of $\delta^{18}\text{O}_{\text{ost}}$ in shallow waters can be explained by the high-amplitude temperature variations during the year, while deeper waters are homothermic regardless of season. The depth factor in modern samples concealed a climatic (temperature) signal. Obtained results allows to successfully identify the properties of the water mass, where the carapace has been formed. It also enables to use $\delta^{18}\text{O}_{\text{ost}}$ values in paleoenvironmental reconstructions by recognizing the climatical signal in the $\delta^{18}\text{O}$ records.

Our research determined vital offset for the six most common ostracods species in the modern CS, which is generally about +1‰ from the expected equilibrium calcite formation values. The offset of the mixed ostracod samples is equal to the mean value, +1‰ (± 0.5). By correcting $\delta^{18}\text{O}_{\text{ost}}$ for vital effect, we are able to detect a climatic signal in the isotopic record. This could be a base for further oxygen isotope paleoreconstructions in the CS.

We conclude that $\delta^{18}\text{O}_{\text{ost}}$ values of common species can be reliable recorders of changes in water temperature and isotopic composition for the lake-type steady-state water basin. Our results allow to conclude that the predicted temperature correspond to the actual temperature at the sampling sites. The average predicted temperature exceeded the measured temperature by only 0.45 °C. The most significant difference between the measured and the calculated temperature is determined for the mixed ostracod samples (-1.72 °C). Therefore, it is preferable to use monospecies samples for paleotemperature reconstructions.

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Competing Interest declaration

The authors declare no competing interests.

Author Contribution declaration

Conceptualization: A. Tkach and N. Tkach; formal analysis: A.T., N.T., M. Zenina; investigation: A.T. and N.T.; resources: A.T.; data curation: A.T.; writing – original draft preparation: A.T.; writing – review and editing: A.T., A.N., M.Z.; visualization: N.T.; supervision: A.T.; project administration: A.T.; funding acquisition: A.T.

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