



Oxygen and carbon isotope fractionation of marine ostracod calcite from the eastern Mediterranean Sea

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ARTICLE INFO

Article history:

Received 26 November 2011

Received in revised form 23 March 2012

Accepted 28 March 2012

Available online 5 April 2012

Keywords:

Marine ostracodes

Stable isotopes

Late Quaternary

Paleoceanography

ABSTRACT

Over the last two decades, non-marine ostracods have been intensively studied with respect to the stable isotopic composition ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) of their calcified valves, however, few data for marine taxa have been published so far. Here, we provide new data from recent and Pleistocene near-surface sediments of the Gulf of Taranto (recent) and the southern Aegean Sea (15 ka, both in the Mediterranean Sea) helping to improve our understanding of ostracod stable isotopes in palaeoceanography. Results are compared to those of certain benthic foraminiferal taxa for which the living habitat and the isotopic disequilibrium from ambient sea-water are known. In addition, monospecific size fractions of three common ostracod species (*Bairdia conformis*, *Bosquetina tarentina*, *Henryhowella sarsii*) have been studied from the Gulf of Taranto in order to test the existence of a size-dependent change in the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ composition of the valve calcite. Our results reveal positive average species-specific deviations from the $\delta^{18}\text{O}$ of calcite equilibrium for two ostracod taxa (*B. conformis* 0.31‰, *H. sarsii* 0.33‰), while *B. tarentina* shows a negative off-set of -0.41% . These values are substantially lower than those reported for most non-marine ostracods, which usually yield positive “vital effects” for $\delta^{18}\text{O}$ of more than 2‰. Furthermore, *B. tarentina* is thereby the only ostracod taxon so far for which a negative “vital effect” has been reported, apart from the non-marine *Eucypris mareotica*. $\delta^{13}\text{C}$ values cover a much larger range than $\delta^{18}\text{O}$ with a negative off-set from sea-water by -1.8 to -5% . Size-fraction data show no systematic change, although a statistically-significant positive covariance between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ has been observed, consisting of a slope similar to a kinetically controlled fractionation effect as has previously been documented for asymbiotic planktic foraminifera and corals. The documented interspecific offsets can be primarily attributed to differences in diet for $\delta^{13}\text{C}$ and for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ to fractionation processes related to different modes of calcification.

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1. Introduction

Ostracods are microcrustaceans and occupy virtually all known aquatic habitats on Earth showing a high diversity with more than 20,000 recent species (Horne et al., 2002). In the marine realm, ostracods represent one of the most important components of the metazoan meiobenthos ecosystems (e.g., Richardson et al., 1985). A carapace consisting of two calcified chitinous valves covers the whole body and has a high fossilization potential. Ostracods are known to precipitate low-Mg calcite and moult up to nine times (instars) before they reach adulthood (Kesling, 1951; Sohn, 1958). At their adult

stage, ostracods are usually between 0.5 and 2 mm large, sometimes showing a pronounced sexual dimorphism.

Assemblages of ostracods are widely used to reconstruct marine and non-marine environments as well as to study evolution through geologic time by investigating morphological features like size or ornamentation (see Holmes and Chivas, 2002a, and Park and Smith, 2003, for overviews; Hunt and Roy, 2006). Apart from these classical applications, it has been shown that chemical element uptake of the valves occurs directly from ambient water (Turpen and Angell, 1971; Chivas et al., 1983). In particular, changes of Mg/Ca and Sr/Ca ratios in ostracod calcite are widely used in palaeoenvironmental reconstructions (Dwyer et al., 2002; Holmes and Chivas, 2002b).

Formation of ostracod carapaces is a rapid process, which often takes place within hours to days (Turpen and Angell, 1971; Chivas et al., 1983; Roca and Wansard, 1997), however, it is still unknown to what extent factors like temperature, salinity, alkalinity or sea-water pH control the rate of calcite precipitation, e.g. Chivas et al. (1983) identified for the non-marine, saline ostracod *Mytilocypris henricae* that fully calcified adult valves took 13 ± 4 (1σ) days at

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15 °C and 7 ± 3 (1σ) at 25 °C. Due to the rapidity of valve production, the measured geochemical signal provides only a temporal snap-shot of the prevailing hydrological conditions. Multiple single-specimen measurements are expected to show, therefore, a much higher variability than benthic foraminifera, but may give a more complete picture of seasonal changes.

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of ostracod calcite are often thought to be ideal tracers in palaeolimnology, because they are believed to reflect ambient water mass characteristics and are, therefore, commonly used for reconstructions in aquatic environments (e.g., Fritz et al., 1975; Lister, 1988; Lister et al., 1991; Schwalb et al., 1994; Zhang et al., 1994; Holmes, 1996; Xia et al., 1997a,b; Ingram et al., 1998; Schwalb et al., 1999; von Grafenstein et al., 1999; Keatings et al., 2002; Von Grafenstein, 2002; Belis and Ariztegui, 2004; Wetterich et al., 2008; Gouramanis et al., 2010; Decrouy et al., 2011a,b). However, there is still ongoing research onto what extent these stable isotope values are controlled by so-called vital effects, which are indicated by detectable deviations from the isotopic equilibrium (Dettman et al., 1995; Xia et al., 1997a,b; von Grafenstein et al., 1999; Chivas et al., 2002; Holmes and Chivas, 2002b; Keatings et al., 2002; Simstich et al., 2004; Li et al., 2007; Wetterich et al., 2008; Li and Liu, 2010; Decrouy et al., 2011b). All these studies have been almost exclusively conducted on different non-marine taxa; up to now only one detailed stable isotope study exists for fully marine ostracods (Didié and Bauch, 2002).

In this paper, we present $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ostracod analyses from a recent near-surface sample from the Gulf of Taranto (off Southern Italy) and a Quaternary record from the southern Aegean Sea (15 ka, eastern Mediterranean Sea). Our results are compared to previously published data from the Iceland Plateau (Didié and Bauch, 2002) and to newly gained data on benthic foraminiferal taxa for which the living habitat and the isotopic disequilibrium from ambient sea-water are known. In addition, size fractions of mono-specific samples of common ostracod taxa have been studied from the Gulf of Taranto in order to test whether a size or mass-dependent change exists with respect to their $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ composition.

2. Materials and methods

The geographic position of the studied sites is shown in Fig. 1. Two samples from two selected offshore sites of recent and Pleistocene age have been investigated.

2.1. GeoB10749-3, P339, Station 719

During *Poseidon* cruise P339 in 2006, near surface sediments (muds) were recovered in the western Gulf of Taranto (GeoB10749-3; multicorer; 39°36.00'N, 17°10.99'E, water depth 279.3 m; Zonneveld et al., 2008). The sample from the depth interval between 3 and 5 cm below the sediment–water interface contains a diverse, well-preserved ostracod and benthic foraminifera fauna and is used as a recent analogue to compare recent and fossil data. Since the Gulf of Taranto is generally characterized by very high sedimentation rates with published data for the eastern part of the gulf of up to 70 cm/ky (Zonneveld et al., 2009), the studied sample can be considered to represent a very recent environment.

2.2. GeoTü SL123

One sample (178 cm) from the gravity core GeoTü SL123 (35°45.34'N, 27°33.34'E, 728 m water depth), which was recovered during *Meteor* cruise M51/3 in 2001 (Hemleben et al., 2003) in the southern most part of the Aegean Sea, was studied with respect to the isotopic composition of a few selected ostracod and benthic foraminiferal taxa. This sample contains an impoverished, but well-preserved ostracod fauna. The age is estimated to be about 15 ka,

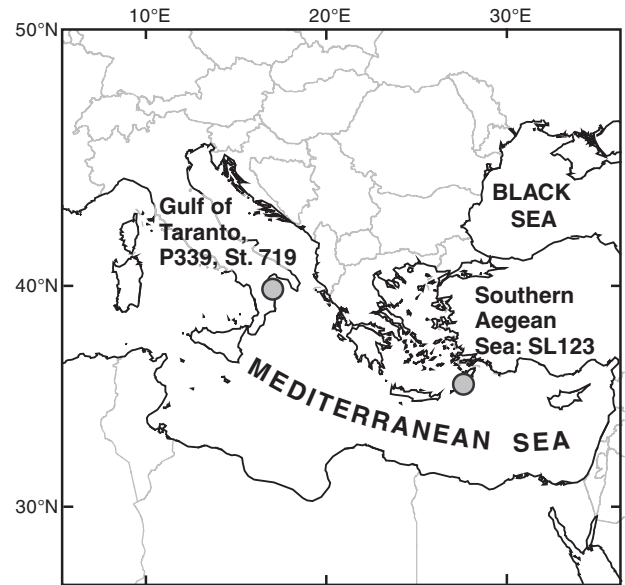


Fig. 1. Geographic map of the eastern Mediterranean region showing the position of the two localities investigated in this study.

based on the linear interpolation of ^{14}C ages (Kuhnt et al., 2007), directly post-dating the Last Glacial Maximum (LGM).

2.3. Methods

The samples were freeze dried, weighed and washed with tap water through a 63 μm mesh sieve.

Isotope analyses were performed on well-preserved ostracod and foraminifera specimens of the sieve size fraction larger than 180 μm . For size fraction analyses from P339 Station 719, all valves of adult and juvenile ostracods were picked and the maximum length and height was measured using an image analysis system (Zeiss Axiovision) with a digital camera connected to a trinocular microscope. Valves were ultrasonically cleaned in distilled water. The shell carbonate was reacted with 100% phosphoric acid at 75 °C using a Kiel III online carbonate preparation line connected to a ThermoFinnigan 252 mass spectrometer at the University of Erlangen, Germany. Reproducibility was checked by replicate analysis of laboratory standards and was better than ± 0.05 and 0.06% (1σ) for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively. All values are reported in ‰ relative to VPDB by assigning a $\delta^{13}\text{C}$ value of +1.95‰ and a $\delta^{18}\text{O}$ value of -2.20% to NBS19. Results of all measurements are documented in Table 1.

As a reference system, we used the $\text{CaCO}_3\text{-H}_2\text{O}$ fractionation curve according to Friedman and O'Neil (1977), which is situated between the 5 mM Ca^{2+} and 15 mM Ca^{2+} solutions based fractionation curves of Kim and O'Neil (1997). Considering that the modern ocean has an average of 8 to 10 mM Ca^{2+} (Nimer et al., 1996; Stoll and Schrag, 1998) we assume that the position of the Friedman and O'Neil curve might, despite its high temperature calibration, better approximate a fully marine system than the Kim and O'Neil (1997) equation which is based on solutions that strongly deviate from sea-water. Moreover, the Friedman and O'Neil (1977) equation has been more frequently used in marine and non-marine environmental studies for both ostracods and foraminifera (e.g., McCorkle et al., 1997; von Grafenstein et al., 1999; Chivas et al., 2002; Didié and Bauch, 2002; Schmiiedl et al., 2004; Li and Liu, 2010) allowing for a direct comparison of previously published data. Determination of $\delta^{18}\text{O}$ equilibrium calcite values ($\delta^{18}\text{O}_{\text{EC}}$) followed McCorkle et al.'s (1997) procedure using the $\text{CaCO}_3\text{-H}_2\text{O}$ fractionation curve of Friedman and O'Neil (1977). Fractionation factors, VPDB–SMOW conversion and $\delta^{18}\text{O}$ of equilibrium calcite were calculated employing the following

Table 1
Summary of all data discussed in this publication. For the size fraction data, the mean sizes are given. Abbreviation: O: ostracods, BF: benthic foraminifera, PF: planktic foraminifera, (A) = adult specimens, (A-x) = the x-th pre-adult moulting stage.

Sample	Species		No. valves (O) –specimens (BF, PF)	Ø max. length [µm]:	δ ¹³ C [‰] VPDB	δ ¹⁸ O [‰] VPDB
P339, St. 719	<i>Cibicides lobatulus</i>	BF	3	–	0.82	1.26
P339, St. 719	<i>Cibicides lobatulus</i>	BF	3	–	1.19	1.62
P339, St. 719	<i>Globobulimina affinis</i>	BF	5	–	–0.86	2.25
P339, St. 719	<i>Globobulimina affinis</i>	BF	5	–	–0.93	2.59
P339, St. 719	<i>Planulina ariminensis</i>	BF	3	–	1.44	1.36
P339, St. 719	<i>Planulina ariminensis</i>	BF	3	–	1.72	1.61
P339, St. 719	<i>Uvigerina mediterranea</i>	BF	5	–	0.74	2.09
P339, St. 719	<i>Uvigerina mediterranea</i>	BF	5	–	0.51	1.69
P339, St. 719	<i>Bairdia conformis</i> (A)	O	2	1315	–1.80	2.27
P339, St. 719	<i>Bairdia conformis</i> (A)	O	3	1237	–1.52	2.41
P339, St. 719	<i>Bairdia conformis</i> (A)	O	3	1217	–1.10	2.51
P339, St. 719	<i>Bairdia conformis</i> (A-1)	O	3	1020	–0.69	2.75
P339, St. 719	<i>Bairdia conformis</i> (A-1)	O	5	942	–1.25	2.71
P339, St. 719	<i>Bairdia conformis</i> (A-2)	O	6	767	–1.76	2.53
P339, St. 719	<i>Bairdia conformis</i> (A-2)	O	6	807	–1.15	2.78
P339, St. 719	<i>Bairdia conformis</i> (A-3)	O	13	638	–1.46	2.61
P339, St. 719	<i>Bairdia conformis</i> (A-4)	O	13	524	–1.01	2.74
P339, St. 719	<i>Bairdia conformis</i> (A)	O	5	–	–1.31	2.52
P339, St. 719	<i>Bairdia conformis</i> (A)	O	5	–	–1.45	2.51
P339, St. 719	<i>Bairdia conformis</i> (A-2?)	O	5	–	–0.82	2.62
P339, St. 719	<i>Bosquetina tarentina</i> (A)	O	2	1200	–3.37	1.87
P339, St. 719	<i>Bosquetina tarentina</i> (A)	O	2	1225	–3.12	1.86
P339, St. 719	<i>Bosquetina tarentina</i> (A-1)	O	4	953	–4.02	1.68
P339, St. 719	<i>Bosquetina tarentina</i> (A-2)	O	6	737	–3.37	1.67
P339, St. 719	<i>Bosquetina tarentina</i> (A-3)	O	7	617	–1.43	2.15
P339, St. 719	<i>Bosquetina tarentina</i> (A)	O	5	–	–3.05	1.78
P339, St. 719	<i>Bosquetina tarentina</i> (A)	O	5	–	–2.94	1.71
P339, St. 719	<i>Bosquetina tarentina</i> (A-1)	O	5	–	–3.44	1.95
P339, St. 719	<i>Henryhowella sarsii</i> (A)	O	3	793	–2.13	2.43
P339, St. 719	<i>Henryhowella sarsii</i> (A-1)	O	5	676	–1.38	2.65
P339, St. 719	<i>Henryhowella sarsii</i> (A-1)	O	5	662	–1.27	2.60
P339, St. 719	<i>Henryhowella sarsii</i> (A-1)	O	5	526	–1.51	2.47
P339, St. 719	<i>Henryhowella sarsii</i> (A-1)	O	4	570	–1.60	2.51
P339, St. 719	<i>Henryhowella sarsii</i> (A-1/A-2)	O	5	494	–2.65	2.05
P339, St. 719	<i>Henryhowella sarsii</i> (A-2)	O	8	372	–2.45	2.48
P339, St. 719	<i>Henryhowella sarsii</i> (A)	O	5	–	–1.00	2.50
P339, St. 719	<i>Henryhowella sarsii</i> (A)	O	5	–	–1.17	2.70
P339, St. 719	<i>Henryhowella sarsii</i> (A-2?)	O	5	–	–1.80	2.40
P339, St. 719	<i>Henryhowella sarsii</i> (A-2?)	O	5	–	–1.49	2.58
P339, St. 719	<i>Henryhowella sarsii</i> (A-2?)	O	5	–	–2.61	2.03
P339, St. 719	<i>Globigerinoides ruber</i> - pink	PF	6	–	1.60	0.32
P339, St. 719	<i>Globigerinoides ruber</i> - pink	PF	5	–	3.81	3.53
P339, St. 719	<i>Globorotalia truncatulinoides</i>	PF	1	–	0.03	1.78
P339, St. 719	<i>Orbulina universa</i>	PF	5	–	1.47	0.80
P339, St. 719	<i>Orbulina universa</i>	PF	6	–	1.72	0.71
SL123	<i>Cibicides pachydermus</i>	BF	2	–	1.72	2.88
SL123	<i>Cibicides pachydermus</i>	BF	1	–	1.57	2.81
SL123	<i>Cyroidinoides neosoldanii</i>	BF	4	–	–0.88	3.24
SL123	<i>Planulina ariminensis</i>	BF	3	–	1.84	3.17
SL123	<i>Uvigerina mediterranea</i>	BF	3	–	0.88	3.46
SL123	<i>Uvigerina mediterranea</i>	BF	3	–	0.82	3.13
SL123	<i>Aurila</i> sp. (A)	O	4	–	–3.17	2.55
SL123	<i>Cistacythereis</i> sp. (A)	O	3	–	–2.40	1.85
SL123	<i>Cytherella</i> sp. (A)	O	4	–	–1.33	1.44
SL123	<i>Parakosta</i> sp. (A)	O	4	–	–2.49	2.76
SL123	<i>Parakrithe</i> sp. (A)	O	12	–	–0.28	2.58
SL123	<i>Xestoleberis</i> sp. (A)	O	2	–	–0.89	1.44

equations (Eqs. (2) and (3) are based on Friedman and O'Neil, 1977):

$$\alpha_{\text{CaCO}_3-\text{H}_2\text{O}} = \left(\delta^{18}\text{O}_{\text{CaCO}_3(\text{SMOW})} + 1000 \right) / \left(\delta^{18}\text{O}_{\text{SW}} + 1000 \right) \quad (1)$$

$$\delta^{18}\text{O}_{\text{VPDB}} = 0.97006 \times \delta^{18}\text{O}_{\text{SMOW}} - 29.94 \quad (2)$$

$$1000 \ln \alpha = 2.78 \times 10^6 / T^2 - 2.89 \quad (3)$$

A bottom water temperature of approximately 13 °C at P339 St. 719 (Gulf of Taranto) has been extrapolated from temperature

profiles obtained by Sellschopp and Alvarez (2003) and Zonneveld et al. (2008). These two data sets represent measurements of winter (February 1999, Sellschopp and Alvarez, 2003) and summer temperatures (June/July 2006, Zonneveld et al., 2008), showing values at ~300 m water depth between 12.5 and 14 °C. This suggests that the water temperatures are relatively stable over the seasons with a variability of about ±1 °C. Estimates of bottom water δ¹⁸O_{SW} (1.55‰ SMOW) and δ¹³C_{DIC} (DIC: dissolved inorganic carbon; 1.05‰ VPDB) in the Gulf of Taranto are based on data from nearby stations (Pierre, 1999; Grauel and Bernasconi, 2010). The values reported for both δ¹⁸O_{SW} and δ¹³C_{DIC} from the larger Gulf of Taranto area from water depths between 200 and 400 m are relatively constant (<±0.05‰).

3. Results

3.1. Preservation of ostracod valves

Carbonate preservation of ostracod valves is crucial for interpreting geochemical data. In both samples, ostracod and foraminiferal calcareous shells are pristinely preserved, displaying primary morphological features like ornamentation and pores without any signs of recrystallization (Plate 1). Rotaliid foraminifera and juvenile ostracods have a “glassy” appearance. The adult ostracods are thicker and therefore usually not translucent. This observed pristine carbonate preservation ought to provide reliable stable isotope data.

3.2. Size measurements (Gulf of Taranto, P339 Station 719)

The sample from the Gulf of Taranto has been intensively studied with respect to three common ostracod species: *Henryhowella sarsii*, *Bairdia conformis* and *Bosquetina tarentina*. For these taxa, size measurements of single valves (length and height) have been performed to identify different molting stages and to gain taphonomic information. The 46 measured specimens of *H. sarsii* cover a size range from 318 to 800 μm for lengths, and from 212 to 515 μm for heights. For *B. conformis*, 96 specimens have been measured revealing a length ranging between 413 and 1343 μm , and a height between 252 and 913 μm . For the third taxon *B. tarentina*, 34 valve sizes have been determined showing values between 396 and 1310 μm , and between 229 and 681 μm for length and height, respectively. The distribution of the data is displayed in Fig. 2. The length–height plots display for all three species that the size data are concentrated in certain clusters: three for *H. sarsii*, and five for *B. conformis* and *B. tarentina*, representing discrete growth stages as shown in Fig. 2.

3.3. Isotope data (Gulf of Taranto, P339 Station 719)

Numerous planktic and benthic foraminiferal taxa have been analyzed for a comparison with the three studied ostracod taxa from this sample. All data are reported in Table 1 and are graphically shown in Fig. 3A.

The planktic foraminifers *Orbulina universa* and *Globigerinoides ruber* show the lowest $\delta^{18}\text{O}$ values between 0.3‰ and 0.8‰, and high $\delta^{13}\text{C}$ values around 1.5‰. Similar $\delta^{13}\text{C}$ values are recorded in the epibenthic foraminifer *Planulina ariminensis*, and somewhat lower values for *Cibicides lobatulus* and shallow infaunal *Uvigerina mediterranea*, all these $\delta^{13}\text{C}$ values are close to $\delta^{13}\text{C}_{\text{DIC}} = 1.05\text{‰}$. More negative $\delta^{13}\text{C}$ values are observed in subsurface dwelling planktic foraminifer *Globorotalia truncatulinoides* (0‰) and deep infaunal *Globobulimina affinis* (−1‰). The latter also shows the highest foraminiferal $\delta^{18}\text{O}$ values (2.2 and 2.6‰).

Ostracod $\delta^{13}\text{C}$ values are generally lower compared to foraminifera with values between −4‰ and −1.1‰. Here, *B. conformis* and *H. sarsii* cover nearly the same range for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, whereas *B. tarentina* displays much lower values for both isotope systems (Fig. 3A). The results vary strongly with size for all taxa analyzed (Fig. 4A). For *B. conformis* $\delta^{13}\text{C}$ fluctuates between −1.8‰ and −0.7‰, for *H. sarsii* −2.7‰ and −1.3‰, and for *B. tarentina* −4.0‰ and −1.4‰. For the latter two taxa, the values of small valves strongly deviate from those of larger sizes (Fig. 4A). The $\delta^{18}\text{O}$ of *B. conformis* ranges from 2.3‰ to 2.8‰ showing the lowest values for the largest valves (Fig. 4B). For *H. sarsii*, the $\delta^{18}\text{O}$ covers the range from 2.0‰ to 2.7‰ and 1.7‰ and 2.1‰ for *B. tarentina*. *B. tarentina* displays its lowest values for the smallest valves. For all three taxa and both isotope systems and no systematic trend with size has been observed (Fig. 4A). In addition a linear relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is revealed for *B. conformis* and *H. sarsii*, the one observed for *B. tarentina* is statistically not robust and might be an artefact due to one outlier (Fig. 4C).

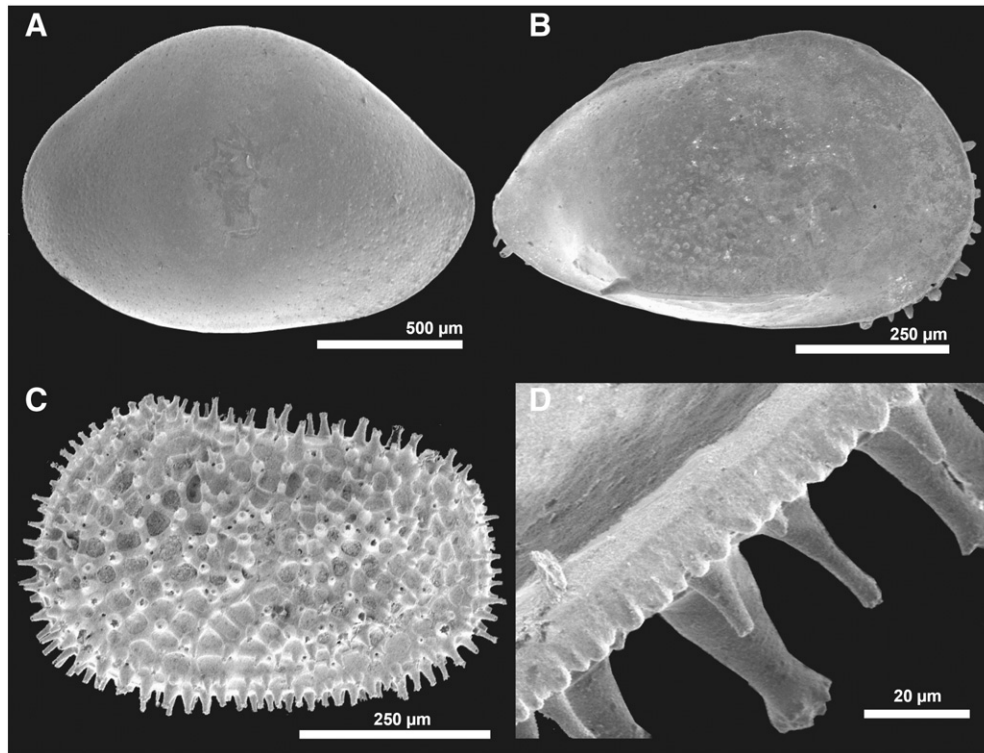


Plate 1. Scanning electron microscope photographs showing the taxa studied herein and document their state of preservation. (A) *Bairdia conformis* (external view of left valve), (B) *Bosquetina tarentina* (A-2 instar, external view of right valve), (C) *Henryhowella sarsii* (A-1 instar, external view of left valve), (D) close up of *H. sarsii* showing inner view of the valve rim and protruding external ornamentation (P339, Station 719, 3–5 cm, Gulf of Taranto).

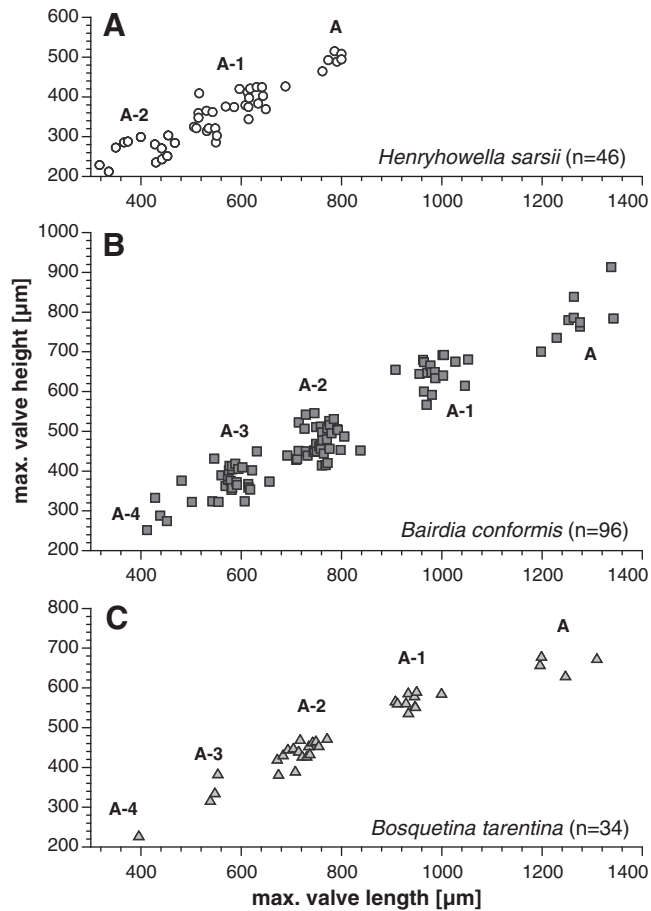


Fig. 2. Size measurements: maximal length and maximal height of ostracod valves, and suggested moulting stages (instars: A = adult, A-1 to A-4: juveniles) of three common taxa: (A): *Henryhowella sarsii*; (B): *Bairdia conformis*; (C): *Bosquetina tarentina* from P339 Station 719 (Gulf of Taranto).

Considering only adult (A) and ultimate juvenile instar (A-1) specimens (Table 2), positive species-specific deviations from the $\delta^{18}\text{O}_{\text{EC}} = 2.22\%$ and thereby a higher $\delta^{18}\text{O}$ fractionation factor $\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$ for two ostracod taxa with average values for *B. conformis* of 0.31% (min = 0.05, max = 0.53, $\alpha = 1.0319$ for 13 °C, $n = 7$) and for *H. sarsii* of 0.33% (min = 0.21, max = 0.48, $\alpha = 1.0319$ for 13 °C, $n = 7$) have been observed. By contrast, *B. tarentina* exhibits a negative off-set of -0.41% (min = -0.54 , max = -0.28 , $n = 6$) and the lowest fractionation factor ($\alpha = 1.0311$ for 13 °C) (Table 2).

3.4. Isotope data (Aegean Sea, SL 123)

For the sample from the southern Aegean Sea, spot measurements of benthic foraminifera and ostracods (Fig. 3B; Table 1) have been performed in order to compare the recent Gulf of Taranto data with those from a time interval influenced by the LGM. Benthic foraminifera show $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values between 2.8‰ and 3.5‰, and between 0.8‰ and 1.8‰, respectively. Epifaunal taxa (*Cibicidoides pachyderma*, *P. ariminensis*) show significantly higher $\delta^{13}\text{C}$ values than infaunal ones (*U. mediterranea*), but slightly lower $\delta^{18}\text{O}$ values. By contrast, the Gulf of Taranto ostracod $\delta^{18}\text{O}$ values are lower compared to the foraminifera covering a range from 1.4‰ to 2.7‰, and $\delta^{13}\text{C}$ values between -3.2% and -0.3% are also lower than those reported for the foraminifera. Documented $\delta^{13}\text{C}$ values for smooth valved ostracods (*Cytheridea*, *Parakriella*, *Xestoleberis*) are higher than those for reticulated, ornamented species (*Aurilla*, *Cytherella*, *Paracosta*), however, both groups cover a similar range of $\delta^{18}\text{O}$ values.

4. Discussion

4.1. Taphonomic implications based on ostracod size distributions

Length–height plots of ostracod valves (Fig. 2A–C) from the Gulf of Taranto (P339, St. 719) reveal several distinctive clusters, which obviously represent different ontogenetic stages (Fig. 2). The distribution patterns suggest that the valves analyzed for the size fraction study cover the last moulting stages, presumably A-4 to A for both *B. conformis* and *B. tarentina*, and A-2 to A for *H. sarsii* (A: adult stage, A-1: the ultimate juvenile stage, A-2 the penultimate juvenile stage, and so on). It cannot be ruled out that this attribution to different instars is slightly biased by sexual dimorphism, though sexual dimorphism is known for many ostracod taxa, which is generally expressed in a lower length/height-ratio in females (Kornicker, 1961). The presence of adult ostracods and an extended range of instars suggests that the studied assemblage represents a low to moderate energy autochthonous thanatocoenosis, which is only weakly biased by size sorting induced through transportation processes (Boomer et al., 2003).

4.2. Calcification of ostracod carapaces

So far, little is known about the mechanisms of biomineralization of ostracod carapaces, whereas calcification of foraminifera tests, which is substantially different from ostracods, are somewhat better understood (e.g., Erez, 2003; Keyser and Walter, 2004; de Nooijer et al., 2009). Rotaliid foraminifera vacuolize sea-water before calcite formation and increase the intracellular pH in order to force precipitation of low-Mg calcite (de Nooijer et al., 2009). They calcify their test more or less continuously and the measured isotope data represent an average of their full ontogeny. On the contrary, ostracod isotope compositions can provide only a snapshot of the prevailing palaeoceanographic conditions, because the formation and calcification of ostracod carapaces is a rather rapid process, which is accomplished within hours or days (Turpen and Angell, 1971; Chivas et al., 1983; Roca and Wansard, 1997). However, there are also observations suggesting that ostracod growth and calcification continues after moulting (Herman and Heip, 1982; Chivas et al., 1983).

Ostracod valves consist of tiny calcitic crystallites embedded in matrix made of chitin and proteins, e.g. for Cytheroidea, they completely consist of calcite crystals, whereas Bairdioidea and Cypridoidea exhibit parallel layers made of chitin and calcite, respectively (Keyser and Walter, 2004). According to observations by Keyser and Walter (2004), ostracods start producing their carapace prior to moulting by storing calcium phosphate granules together with chitin precursors in the outer epidermal cells. The granules release their contents extracellularly outside the epidermal cells and are transformed into small platelets. These platelets now consist of CaCO_3 and disintegrate into small granular structures, which appear to consist of amorphous calcite, which forms the ostracod shell together with chitin and proteins. However, in shells of adult specimens of most genera, the entire amorphous material will have crystallized and no amorphous material is left, whereas, in early juvenile stages, crystallization is sometimes incomplete.

4.3. Stable isotope compositions of benthic foraminifera tests and ostracod valves

Stable isotope analyses of foraminiferal calcite have been an indispensable tool in palaeoceanography since the 1960s (e.g., Shackleton, 1967; Shackleton and Opdyke, 1977). They are used to reconstruct changes in ocean's $\delta^{18}\text{O}$ sea-water composition in response to glacial–interglacial cycles (Shackleton, 1967, 1968), changes in evaporation and precipitation balance (e.g., Railsback

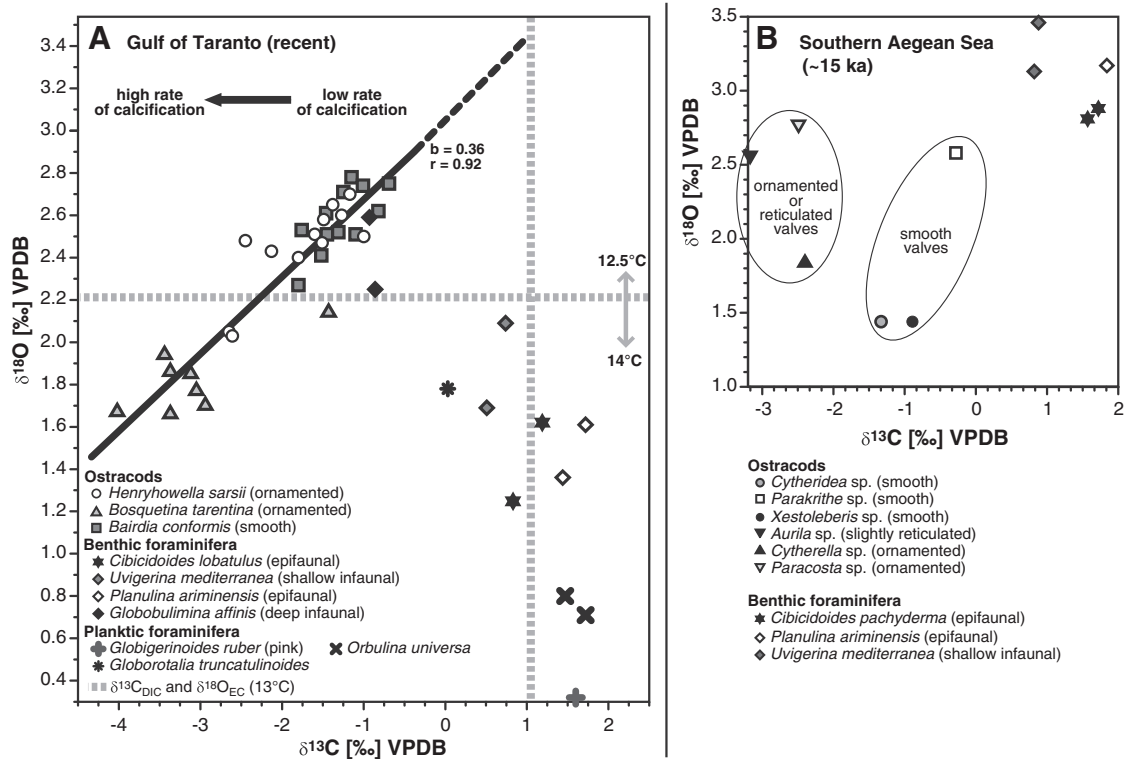


Fig. 3. (A) $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ cross plot from a near surface sample (3–5 cm) from the Gulf of Taranto showing selected ostracod taxa, benthic and planktic foraminifera. Greyish dotted lines indicate values for $\delta^{13}\text{C}_{\text{DIC}}$ (dissolved inorganic carbon in sea-water) and $\delta^{18}\text{O}_{\text{EC}}$ (equilibrium calcite). (B) $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ cross plots of data from the southern Aegean Sea (15 ka, ^{14}C age interpolation following Kuhn et al., 2007). Thickness of the greyish vertical bar represents the range of values taken from the literature for $\delta^{13}\text{C}_{\text{DIC}}$, temperature dependence of calculated $\delta^{18}\text{O}_{\text{EC}}$ are indicated by vertical arrows.

et al., 1989; Roche et al., 2004) and are widely employed to estimate water temperature changes on various timescales (e.g., Shackleton, 1967; Zachos et al., 2008). $\delta^{13}\text{C}$ is often used to reconstruct bottom water circulation patterns, primary productivity at the sea-surface and the microhabitat of benthic foraminifera (e.g., Kroopnick, 1985; McCorkle and Keigwin, 1994; Sarnthein, 1994; Mackensen et al., 2000). Stable isotope applications of ostracods in palaeoceanography have been largely neglected, while elemental analyses like Mg/Ca ratio have been increasingly employed during the last two decades in particular in areas with a scarce benthic foraminifera fauna (e.g., Corrège, 1993; Dwyer et al., 1995; Corrège and De Deckker, 1997; Cronin et al., 2002; Dwyer et al., 2002).

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements performed on ostracod valves from the Gulf of Taranto and the Aegean Sea are accompanied by additional analyses of different foraminiferal taxa representing different habitats in order to directly compare the data of these two microfossil groups. Certain *Cibicides* and *Uvigerina* species are believed to precipitate their calcite close to the $\delta^{18}\text{O}$ composition of sea-water (Shackleton, 1974; Lynch-Stieglitz et al., 1999; Schmiedl et al., 2004). A higher variability exists with respect to $\delta^{13}\text{C}$ due to their food preference, organic matter flux rate and their preferred microhabitat within and on the sediment (predominantly epibenthic: *Cibicides lobatulus*, *Cibicides pachyderma*, *Planulina ariminensis*; endobenthic: *Uvigerina mediterranea*, *Globbulimina affinis*; Schmiedl et al., 2004; Kuhnt et al., 2007). In order to characterize the entire water column range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, the data are supplemented by several measurements from surface dwelling planktic foraminifera (*Orbulina universa*, *Globigerinoides ruber* pink, *Globigerinoides sacculifer*) and one sub-thermocline taxon (*Globorotalia truncatulinoides*) (Schiebel and Hemleben, 2005).

Foraminiferal analyses reveal that all epibenthic or shallow endobenthic taxa show $\delta^{13}\text{C}$ values close to $\delta^{13}\text{C}_{\text{DIC}}$ of sea-water, only the deep endobenthic *Globbulimina affinis* shows an expected strong negative off-set from $\delta^{13}\text{C}_{\text{DIC}}$. *Cibicides lobatulus* and

Planulina ariminensis show on average a negative deviation of -0.65‰ from the $\delta^{18}\text{O}$ of equilibrium calcite (calculated using the Friedman and O'Neil, 1977, fractionation equation), whereas *Uvigerina mediterranea* is rather close to the equilibrium value or slightly below and two measurements of *Globbulimina affinis* exhibit slightly positive offsets from equilibrium calcite values of less than 0.4‰ (Fig. 3A). These observations are largely in agreement with previous studies from the Mediterranean region (e.g., Schmiedl et al., 2004) (Fig. 3A).

From the Gulf of Taranto sample, three different podocypid ostracod species belonging either to the superfamily Cytheroidea (family Trachyleberididae: *H. sarsii* and *B. tarentina*) or to the superfamily Bairdioidea (family Bairdiidae: *B. conformis*) have been intensively studied herewith. These species are typical components of bathyal Mediterranean ostracod assemblages (Bonaduce et al., 1983; Ertekin and Tunoglu, 2008). Based on their morphology, the genera *Henryhowella* and *Bosquetina* are considered as epibenthic taxa due to their strong ornamentation and the development of ventral alae, respectively, following the arguments of Elofson (1941), Benson (1981) and Didié and Bauch (2002). By contrast, little is known on the microhabitat of the genus *Bairdia*, but laboratory observations mentioned by Kornicker (1961), and our observations herein suggest that they have an epibenthic lifestyle.

The Gulf of Taranto sample represents modern conditions so that the analyzed ostracods can be directly compared to the $\delta^{18}\text{O}$ of equilibrium calcite ($\delta^{18}\text{O}_{\text{EC}}$) and sea-water $\delta^{13}\text{C}_{\text{DIC}}$ (DIC: dissolved inorganic carbon) values (Pierre, 1999; Grauel and Bernasconi, 2010). Moreover, compared to lakes or the study of glacial–interglacial cycles, relatively stable conditions can be expected for the Gulf of Taranto and the Aegean Sea samples, because of the bathyal position, the rather uniform isotopic composition of eastern Mediterranean sea-water (Pierre, 1999) and the short period of time represented by single samples.

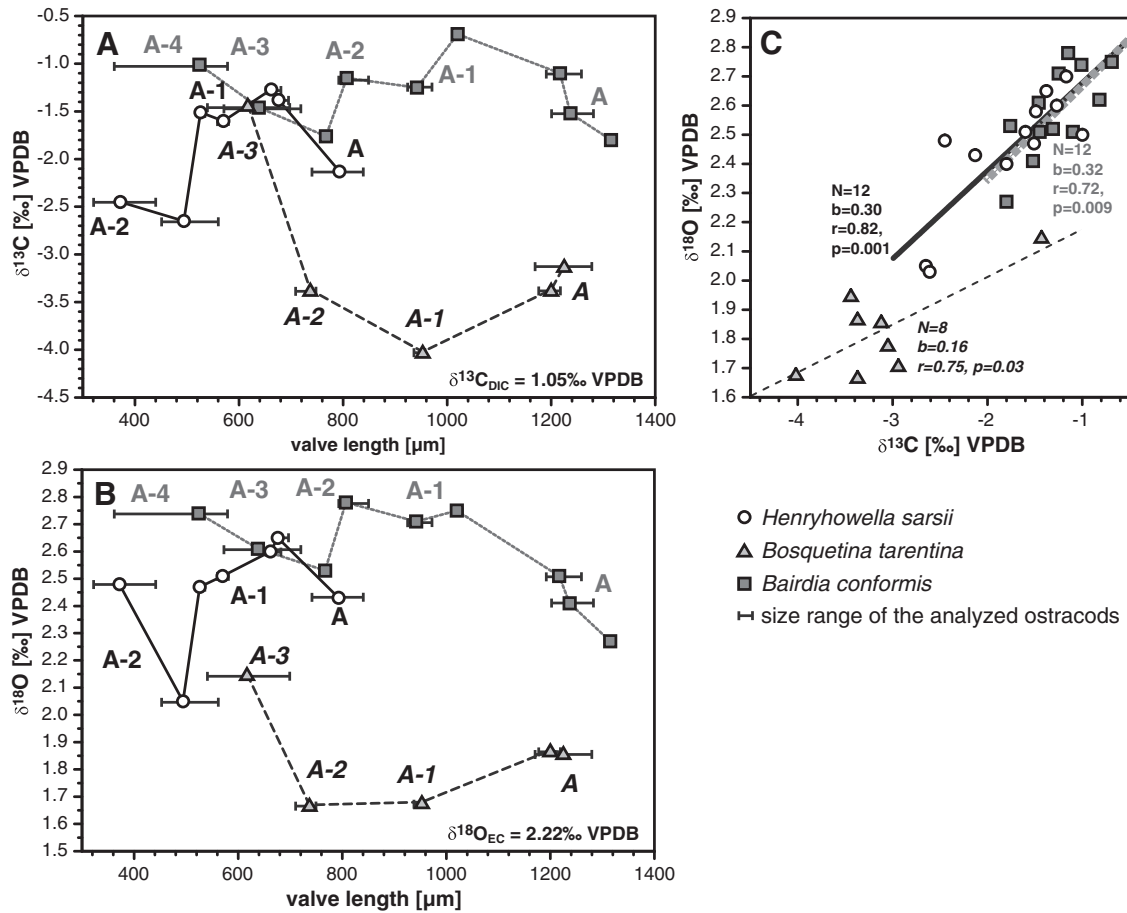


Fig. 4. Size fractionation data of $\delta^{13}\text{C}$ (A) and $\delta^{18}\text{O}$ (B). (C) Cross plot of $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ of all data available for the three taxa (incl. size fractionation data) showing a statistically significant positive correlation with a slope (= b) of about 0.3 which might reflect kinetic isotope fractionation. However, the observed correlation for *B. tarentina* is due to a potential outlier, which makes this correlation less robust. Isotopic composition of sea-water has been adopted from Pierre (1999) for $\delta^{13}\text{C}$ and from Grauel and Bernasconi (2010) for $\delta^{18}\text{O}$.

The studied oyster species reveal distinctive clusters for the three taxa with *B. conformis* showing the highest, whereas *H. sarsii* has somewhat lower and *B. tarentina* substantially lower isotope

Table 2

Mean values for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for the three oyster taxa intensively studied from the Gulf of Taranto (P339, St. 719), the species-specific off-sets from equilibrium calcite assuming a water temperature of 13 °C and the $\delta^{18}\text{O}$ fractionation factors α are listed. For these calculations only adult (A) or ultimate juvenile instars (A-1) have been used. In addition, calculated fractionation factors for two marine oyster genera studied by Didié and Bauch (2002) are shown. $\delta^{13}\text{C}_{\text{EC}}$ considers a positive correction by $1 \pm 0.2\text{‰}$ of the calcite as a consequence of $\delta^{13}\text{C}$ fractionation between the host dissolved inorganic carbon and calcite for temperatures between 10 and 40 °C (Romanek et al., 1992).

	$\delta^{13}\text{C}$ [‰] VPDB	$\delta^{18}\text{O}$ [‰] VPDB	n=	$\delta^{13}\text{C}_{\text{DIC}}$ [‰] VPDB	$\delta^{18}\text{O}_{\text{SW}}$ [‰] SMOW	$\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$
<i>Bairdia conformis</i> (A, A-1, 13 °C)	-1.30	2.53	7	1.05	1.55	1.0319
<i>Bosquetina tarentina</i> (A, A-1, 13 °C)	-3.32	1.81	6	1.05	1.55	1.0311
<i>Henryhowella sarsii</i> (A, A-1, 13 °C)	-1.44	2.55	7	1.05	1.55	1.0319
equil. calcite (EC, 13 °C)	2.05 ^a	2.22	-	1.05	1.55	1.0315
$\Delta B. conformis\text{-EC}$	-3.35	0.31	-	-	-	-
$\Delta B. tarentina\text{-EC}$	-5.37	-0.41	-	-	-	-
$\Delta H. sarsii\text{-EC}$	-3.49	0.33	-	-	-	-
<i>Henryhowella</i> (A, A-1, -0.9 °C; Didié and Bauch, 2002)	-2.04	4.96	5	-	0.22	1.0357
<i>Krithe</i> (A, A-1, -0.9 °C; Didié and Bauch, 2002)	-0.7	5.91	3	-	0.22	1.0367

values for all individuals and both isotope systems (Figs. 3A and 4C). Our oyster results for ultimate juvenile (A-1) and adult specimens reveal positive species-specific deviations from the $\delta^{18}\text{O}$ of equilibrium calcite and, thereby, a higher fractionation factor $\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$ for two oyster taxa with mean values for *B. conformis* of 0.31‰ ($\alpha = 1.0319$ for 13 °C) and for *H. sarsii* of 0.33‰ ($\alpha = 1.0319$ for 13 °C) (Table 2). The latter value is in good agreement with the vital effect of +0.4‰ reported in Didié and Bauch (2002) for the same genus. By contrast, *B. tarentina* shows a negative off-set of -0.41‰ ($\alpha = 1.0311$ for 13 °C) and is, thereby, the first marine oyster taxon found so far with a negative "vital effect" using the Friedman and O'Neil (1977) fractionation equation as reference. Only for *Eucypris mareotica*, a freshwater species, has a fractionation factor below the one for inorganic calcite been reported (Li and Liu, 2010) (Fig. 5). According to the compilation of Holmes and Chivas (2002b) and data by Decrouy et al. (2011b), calcite of non-marine and marine oysters usually displays a positive species-specific deviation from the $\delta^{18}\text{O}$ of equilibrium inorganic calcite between 0.3‰ and 4.1‰ and consequently higher fractionation factors (Fig. 5). The superfamily Cytheroidea, to which nearly all marine taxa shown in Fig. 5 belong to, is known to show $\delta^{18}\text{O}$ values closer to equilibrium than other oyster groups. Based on a study by Kim et al. (2006) for inorganic aragonite, Decrouy et al. (2011b) suggest that deprotonation of HCO_3^- may be a dominant factor for the general positive vital effect on $\delta^{18}\text{O}$, because $\alpha_{\text{HCO}_3\text{-H}_2\text{O}}$ is higher than $\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$, the $\delta^{18}\text{O}$ of calcite rapidly precipitated from a large DIC pool in a closed system should be thereby higher than for equilibrium calcite. In addition, the same authors suggest a "salt effect" on $\delta^{18}\text{O}$ for Cypridoidea that have not been studied here.

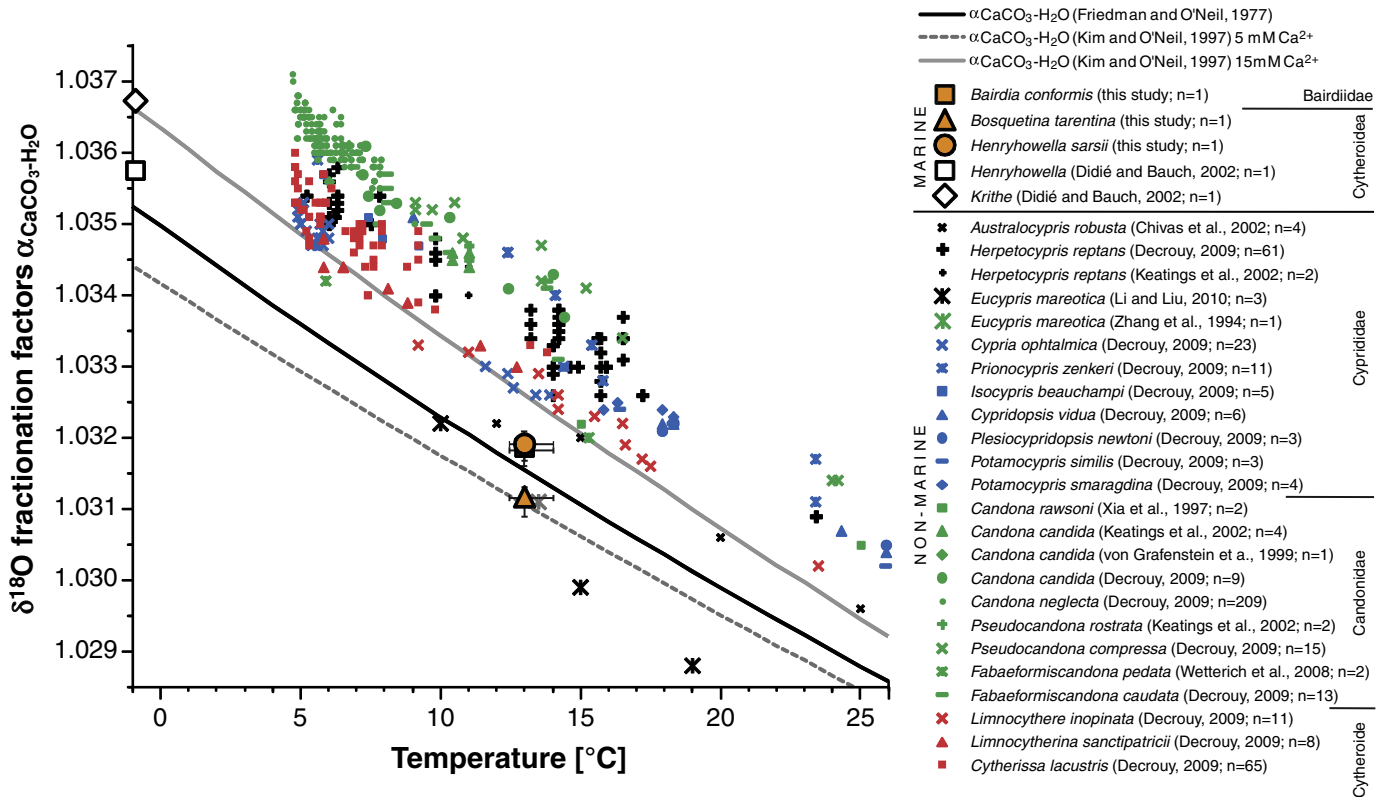


Fig. 5. This fractionation factor α -temperature plot shows all published fractionation factors for marine and non-marine ostracods (n : total number of α values plotted). As a reference the $\text{CaCO}_3\text{-H}_2\text{O}$ fractionation curve according to Friedman and O'Neil (1977) is shown, which is situated between the 5 mM Ca^{2+} and 15 mM Ca^{2+} fractionation curves of Kim and O'Neil (1997) considering that the modern ocean has an average between 8 and 10 mM Ca^{2+} (Nimer et al., 1996; Stoll and Schrag, 1998) the position of the Friedman O'Neil curve might better approximate this level, despite its high temperature calibration. Error bars present the total range covered by all analyses of adult and ultimate juvenile instars and considered a $\delta^{18}\text{O}_{\text{sw}}$ variability of $1.55 \pm 0.05\%$ SMOW (Decrouy, 2009).

$\delta^{13}\text{C}$ values from our study cover a much larger range than $\delta^{18}\text{O}$ with a negative off-set from sea-water DIC by -1.8 to -5% . The off-set increases by about 1% if we calculate $\delta^{13}\text{C}$ of equilibrium calcite due to calcite-bicarbonate fractionation during inorganic calcite precipitation (Romanek et al., 1992) and is substantially larger than the expected natural variability in $\delta^{13}\text{C}_{\text{DIC}}$ (Pierre, 1999). The overall intraspecific variability of adult or ultimate juvenile instars is less than 0.5% for $\delta^{18}\text{O}$ for *B. conformis* and 0.27% for both *H. sarsii* and *B. tarentina*. For $\delta^{13}\text{C}$ the value is up to 1.13%, but is becoming substantially larger for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ if earlier instars are included (see size fraction data below, Figs. 2 and 4) suggesting that values for both isotope systems are rather variable throughout all instars analyzed. The isotopic values of ostracods are rather different from those of benthic foraminifera. Only the deep endobenthic globobuliminids which feed on degraded organic matter (Corliss, 1985; Schmiedl et al., 2000) show similar values to *H. sarsii* and *B. conformis*, and this contrasts with the assumed epibenthic habitats for the studied ostracod taxa. The observed pattern with smooth valved ostracods generally displaying higher isotope values resembles that of Didié and Bauch (2002) from the Iceland Plateau and those of Palaeogene taxa by Bornemann et al. (in press). Didié and Bauch (2002) observed that there are offsets with respect to both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ between the smooth-shelled *Krithe* and the ornamented *Henryhowella*. The latter genus shows lower values for both isotope systems compared to *Krithe*. This shift cannot be explained by the living habitat of ostracods since *Krithe* is usually viewed as an endobenthic taxon based on its slender, smooth shell and direct observations (Coles et al., 1994; Majoran and Agrenius, 1996), whereas *Henryhowella* is considered to live on the sediment as it has a spinose carapace. It is therefore expected that *Henryhowella* would display higher $\delta^{13}\text{C}$ values than the endobenthic *Krithe*,

because pore-water $\delta^{13}\text{C}$ is lower than $\delta^{13}\text{C}$ of sea-water due to the oxidation of ^{12}C -enriched organic matter within the sediment (e.g., McCorkle et al., 1997). Since an opposite trend has been observed for *Krithe* and *Henryhowella* by Didié and Bauch (2002), it can be assumed that other factors than the microhabitat are controlling the isotopic composition of ostracod calcite, specifically for $\delta^{13}\text{C}$.

Decrouy et al. (2011b) pointed out that there are systematic differences with respect to $\delta^{18}\text{O}$ fractionation in non-marine ostracods, e.g. Candoninae showing a consistently higher degree of fractionation than the Cytheroidea or Cyprididae, whereas the latter shows the highest variability of these groups. However, the taxonomic affiliation to a specific family alone cannot explain the pattern observed in this study. *Bairdia* and *Henryhowella* belong to different superfamilies and consist of different valve ultrastructures (Keyser and Walter, 2004), but both show very similar values and ranges in Gulf of Taranto sample, while *Bosquetina* which is closely related to *Henryhowella* (both belong to the family Trachyleberidae) shows totally different values. This suggests that the systematic affiliation or the valve ultrastructure alone cannot explain the isotope differences for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ between *B. conformis*/*H. sarsii* and *B. tarentina* reported herein.

Similar to Didié and Bauch (2002), our measurements of Pleistocene ostracods from the Aegean Sea show that ornamented taxa (*Aurila*, *Cistacythereis*, *Paracosta*) are about 2% lower for $\delta^{13}\text{C}$ (range: -3.2% to -2.4%) than ostracods consisting of a smooth carapace (*Cytherella*, *Xestoleberis*, *Parakrithe*) (range: -1.4% to -0.2%). No clear offset with respect to the $\delta^{18}\text{O}$ composition (range: 1.4% to 2.8%) of the carapaces is apparent between the two groups. This might be due to the low number of measurements or that the analyzed taxa are different from those studied in the Gulf of Taranto. The ostracod $\delta^{18}\text{O}$ data cover exactly the same range as those from the recent Gulf of

Taranto sample, while the benthic foraminifera show a prominent positive $\delta^{18}\text{O}$ shift expected for the early stage of deglaciation after the Last Glacial Maximum (15 ka; Fig. 2B), so it seems that the response to the glacial $\delta^{18}\text{O}$ effect is not unequivocally recorded in ostracod calcite. This contrasts with the observation in Didié and Bauch (2002), and the hypothesis of a direct dependence between $\delta^{18}\text{O}$ of the ambient waters as proposed in many studies on non-marine ostracods (e.g., Xia et al., 1997a,b; von Grafenstein et al., 1999; Chivas et al., 2002; Decrouy et al., 2011b).

4.4. Size fraction isotope data

A further objective of this study was to test whether changes in the isotope composition depend on the valve size and, thereby, of different development stages of the studied ostracod species. In general, no systematic change with ontogeny for stable isotope data has been observed in this study (Fig. 4). Values of $\delta^{18}\text{O}$ show an overall variability of $\leq 0.6\%$, $\delta^{13}\text{C}$ values cover a broader range of up to 1.1‰ for *B. conformis*, 1.4‰ for *H. sarsii* and 2.6‰ for *B. tarentina*. For $\delta^{13}\text{C}$ the early moulting stages of *H. sarsii* and *B. tarentina* display the largest deviation from the larger specimens, maybe due to a lower degree of calcite crystallization during the juvenile stage (Keyser and Walter, 2004), a different mode of calcification compared to later moults or differences in diet or microhabitat for specific instars (Xia et al., 1997a; von Grafenstein et al., 1999; Didié and Bauch, 2002). In comparison to a size fraction study based on cultured non-marine species by Li et al. (2007), the variability in our data is somewhat larger and lacks any systematic change in $\delta^{13}\text{C}$. However, the size range studied herein covers a broader range than the one investigated by Li et al. (2007), so the extreme values are possibly not recorded in their culture study.

Values for the instars A–2 to A for *B. conformis* and *B. tarentina*, and A–1 to A for *H. sarsii* show rather similar values, even if the variability is much larger than those expected for benthic foraminifera (cf. Schmiedl et al., 2004; Friedrich et al., 2006). This suggests that the choice of a full adult stage is not strictly necessary, if absolute abundances of ostracods are low, to receive reliable stable isotope results within the general limits of uncertainty and variability in ostracod calcite.

A statistically significant positive covariance between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ has been observed, consisting of a slope $b \approx -0.3$ for both *B. conformis* and *H. sarsii* (Fig. 4C). These values are similar to those previously reported from asymbiotic planktic foraminifer (*Globigerina bulloides*) as well as corals, and have been interpreted to result from kinetic fractionation effects during the calcification process (e.g., McConnaughey, 1989a,b; Wefer and Berger, 1991; Spero and Lea, 1996; McConnaughey et al., 1997). Spero and Lea (1996) demonstrated that this slope is independent of $\delta^{18}\text{O}_{\text{SW}}$, temperature and $\delta^{13}\text{C}_{\text{DIC}}$ for *G. bulloides*. The observed $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ relationship allows us to tentatively assume that "kinetic" disequilibria may to some extent control isotope fractionation in ostracod calcite. For $\delta^{18}\text{O}$ McConnaughey (1989b) proposed that respired CO_2 is incorporated into CaCO_3 before full isotopic equilibration with ambient sea-water is accomplished, which usually takes place within 10^4 seconds. This CO_2 is depleted in $\delta^{18}\text{O}$ by about 13‰ relative to the $\delta^{18}\text{O}$ of CO_2 equilibrated with sea-water (Spero and Lea, 1996), i.e. $\delta^{18}\text{O}$ disequilibrium increases with calcification rate. Since we see strongly depleted ^{13}C values in ostracod calcite compared to the $\delta^{13}\text{C}_{\text{DIC}}$ we can assume that there is a mixed $\delta^{13}\text{C}$ composition with a large contribution of diet and respired CO_2 together with HCO_3^- the dominant DIC component in sea-water. Spero and Lea (1996) were able to show that changes in diet affect the carbon isotopic composition of the asymbiotic foraminifer *G. bulloides*. Turner (1982) showed that higher calcification rates result in more negative $\delta^{13}\text{C}$ values of inorganic calcite; however, this finding has been questioned by Romanek et al. (1992). We propose that depletion of

both ^{18}O and ^{13}C is particularly pronounced during rapid calcification processes as can be expected for ostracod valve formation (Turpen and Angell, 1971). In the case of ostracods, the influence of photosynthesis as apparent in photosymbiont-bearing organisms can be ignored, therefore metabolic factors like respiration and the digested diet may cause $\delta^{13}\text{C}$ deviations from an ideal "kinetic" $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ relationship based on simple mass considerations.

Even if there is no direct relationship between valve size and thereby a given development stage and isotope values, differences in the rate of calcification might be a possible explanation for the presumed kinetic disequilibria. Until now, the rapidity of calcite precipitation and the factors controlling ostracod size and calcification, in particular, of marine taxa is poorly documented and understood. Results from culture experiments of non-marine ostracods suggest increased ostracod growth rates, calcification and shortened intermoulting times at higher temperatures (e.g., Chivas et al., 1983; Martens, 1985; Mezquita et al., 1999; Li and Liu, 2010). Based on culture studies, Xia et al. (1997b) suggested two alternative explanations for $\delta^{18}\text{O}$ disequilibria. These authors inferred that (1) the calcification rate depends on temperature, and faster calcification at higher temperatures may lead to more incorporation of ^{18}O relative to inorganic calcite, while (2) environmental stress leads to a lower degree of calcification and more incorporation of ^{16}O . Keatings et al. (2002) also proposed the existence of slightly acidic conditions in the inner lamellae where calcification is believed to take place in order to explain the $\delta^{18}\text{O}$ off-set, whereas Decrouy et al. (2011b) suggest that deprotonation of HCO_3^- leads to more positive $\delta^{18}\text{O}$ values in ostracods as mentioned above. However, these studies focused exclusively on the ontogenetic changes in size and degree of calcification, but do not provide any information about how fast the carapace has calcified (e.g. μg calcite per hour), which would be of interest in order to evaluate the effect of kinetic fractionation on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ at different temperatures and valve sizes. Further, the calcification rate must not necessarily be related to the instar development.

Intriguingly, a similar slope value occurs for a $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ covariance if we include all ostracod measurements from the Gulf of Taranto sample (Fig. 2A). Based on this observation we tentatively hypothesize that a species-specific degree of kinetic fractionation exists with *B. tarentina* showing the lowest values, followed by *H. sarsii* and *B. conformis* as the least fractionated taxon. This hypothesis may also explain the general clustering with somewhat lighter values of both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for ornamented taxa compared to ostracods forming smoother valves (Didié and Bauch, 2002; Bornemann et al., in press; partly this study). This would imply that in particular smooth valved taxa are less affected by kinetic fractionation, probably due to slower calcification during their moulting and calcification phase than ornamented ostracods, or alternatively simply by different ways of calcification (Keyser and Walter, 2004). A different mode of calcification has been documented by Yamada et al. (2005), for the formation of ridges on the carapace of the marine taxon *Semicytherura kazahana*, which supports the idea that the mode of calcification may also play a role for the recorded geochemical composition. Finally ongoing growth and calcification during the post-moulting phase seems to take place at least in some species and are known to influence Mg/Ca ratios of ostracod calcite (Chivas et al., 1983), therefore it cannot be ruled out that this process also influences isotope values.

In contrast to trace metal incorporation into ostracod calcite it is directly taken up from sea-water (e.g., Chivas et al., 1983) carbon pathways and fractionation processes of both carbon and oxygen isotopes are considered to be more complex. It is generally accepted that the $\delta^{13}\text{C}$ values are strongly influenced by metabolic effects, ingested diet and DIC, whereas studies on non-marine ostracods suggest that the $\delta^{18}\text{O}$ of their valve calcite correlates well with the $\delta^{18}\text{O}$ of the ambient water mass and temperature, even if they usually exhibit a constant vital effect as documented for numerous species (e.g., Xia et al., 1997a,b; von Grafenstein et al., 1999; Chivas et al.,

2002; Li and Liu, 2010; Decrouy et al., 2011b). The magnitude of $\delta^{18}\text{O}$ changes in non-marine settings is usually much larger than those in fully marine environments, because they are largely controlled by run-off and seasonal precipitation-evaporation changes, whereas in deeper marine conditions, bottom water temperatures and glacial effects are the dominant factors. Consequently, the factors usually controlling non-marine environments are outpacing any potential vital or kinetic effect so that they are identifiably recorded in the $\delta^{18}\text{O}$ of ostracod calcite. In the deep-sea, $\delta^{18}\text{O}$ changes rarely exceed a magnitude of 1.2‰ and the isotope value is thereby more prone to overprinting by vital and kinetic effects.

5. Conclusions

This study of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of marine ostracod valves from the Mediterranean Sea has revealed the following results:

- Our $\delta^{18}\text{O}$ data of marine ostracod calcite are rather different to those of equilibrium calcite (according to the Friedman and O'Neil, 1977, $\text{CaCO}_3\text{-H}_2\text{O}$ fractionation curve). The fractionation factors calculated for marine taxa are usually substantially lower than those of non-marine ostracods and independent from their taxonomic affiliation. For two ostracod taxa, positive deviations from equilibrium calcite (*Bairdia conformis*: 0.31‰; *Henryhowella sarsii*: 0.33‰) and a negative off-set of -0.41% for *Bosquetina tarentina* are reported. The latter is the only marine ostracod taxon so far for which a negative “vital effect” has been reported.
- $\delta^{13}\text{C}$ values comprise a large range with an off-set from $\delta^{13}\text{C}_{\text{DIC}}$ of sea-water by -1.8 to -5% . This large off-set cannot be explained by $\delta^{13}\text{C}_{\text{DIC}}$ changes, because this value is very constant in the study area, or differences in their microhabitat. More likely is a metabolic control on $\delta^{13}\text{C}$ or differences in diet.
- The intra-specific variability of adult and ultimate juvenile instars (A, A-1) is less than 0.3‰ for $\delta^{18}\text{O}$ of *B. tarentina* and *H. sarsii*, but nearly 0.5‰ for *B. conformis*, and about 1.1‰ for $\delta^{13}\text{C}$ of all three taxa. Variability of isotope values increases if earlier instars are included.
- Size-fraction data from the Gulf of Taranto reveal no systematic change in isotopic values, although a statistically significant positive covariance between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ has been observed consisting of a slope of about 0.3. This suggests that “kinetic” disequilibria may also control isotope fractionation in ostracod calcite to some extent, which would not be unusual for rapid calcification processes as they take place during carapace formation.
- The general tendency of ornamented and alar-bearing ostracods to show lighter values for both isotope species compared to taxa with a simple, smooth carapace might be explained by different calcification mechanisms with higher calcification rates for the ornamented taxa causing possibly a kinetic fractionation effect with a depletion of heavier isotopes.
- Previous studies on non-marine ostracods suggest that the $\delta^{18}\text{O}$ of their valve calcite correlates well with the $\delta^{18}\text{O}$ of the ambient water mass. By contrast, our limited dataset from the southern Aegean Sea does not show the prominent “late glacial” positive shift in sea-water $\delta^{18}\text{O}$ from 15 ka compared to today as recorded in the benthic foraminiferal data. Time series data for marine ostracods are rather scarce, but necessary to better evaluate the applicability of stable isotopic composition of marine ostracod calcite in palaeoceanography and should be accompanied by trace element ratio analysis like Mg/Ca to better constrain the temperature and glacial effects on the $\delta^{18}\text{O}$ of ostracod calcite.

Acknowledgements

The paper greatly benefited from very constructive comments by two anonymous reviewers. G. Schmiedl (Hamburg) and T. Kuhnt (Frankfurt) are thanked for providing sample material from SL123

and P339. M. Joachimski (University of Erlangen) is thanked for stable isotope analyses and J. Lenzner (University of Leipzig) helped with the SEM photography. Financial support for this project was provided by Research Foundation Flanders (FWO) and K.U. Leuven Research Fund to RPS and DFG BO2505/5 to AB.

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