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Geochemistry of ostracode calcite: Part 1. An experimental determination of oxygen isotope fractionation

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Abstract—Late-instar juveniles of the North American ostracode, *Candona rawsoni,* were cultured to maturity under controlled oxygen isotope composition and temperature (15°C and 25°C) to measure isotopic fractionation during shell calcification. The ostracode shells formed at experimental temperatures are not in isotopic equilibrium with water but had a constant offset from equilibrium based on the oxygen isotope fractionation of inorganic carbonates. The oxygen isotope composition of ostracode shells from 15°C cultures were higher by about 2‰ compared to that from 25°C cultures, a difference similar to that expected for inorganic calcite across a 10°C temperature range. The observed fractionations are expressed by the regression equations

$$25°C: \quad \delta^{18}O_{shell}^{PDB} = -0.47 + 0.97\delta^{18}O_{water}^{VSMOW}$$

$$15°C: \quad \delta^{18}O_{shell}^{PDB} = 1.12 + 1.07\delta^{18}O_{water}^{VSMOW}$$

The fractionation factors (α) are: 1.0305 at 25°C and 1.0322 at 15°C. The shells of *C. rawsoni* are elevated by about 0.8–1‰ in $\delta^{18}O$ compared to inorganic carbonates (O'Neil et al., 1969), but are close to marine biogenic aragonites (Grossman and Ku, 1986) with a slightly different temperature dependence.

1. INTRODUCTION

The application of oxygen isotopes in biogenic carbonates to studies of paleohydrology and paleotemperature was first suggested by Urey (1947). Shortly thereafter, Epstein et al. (1951, 1953) developed a paleotemperature scale for biogenic $CaCO_3$ that was later modified by Craig (1965)

$$t = 16.9 - 4.2\,(\delta^{18}O_c - \delta^{18}O_w) + 0.13\,(\delta^{18}O_c - \delta^{18}O_w)^2$$

where t is the isotopic temperature in Celsius, $\delta^{18}O_c$ is the corrected $\delta^{18}O$ of CO_2 obtained from the carbonate by reaction with phosphoric acid at 25°C with respect to the mass spectrometer working-standard gas, and $\delta^{18}O_w$ is the corrected $\delta^{18}O$ of CO_2 equilibrated isotopically at 25°C with the water from which the carbonate was precipitated, measured against the same mass spectrometer working-standard gas used for the carbonate analysis. Emiliani (1954, 1955, 1966) applied these equations for the first time to foraminifera in deep-sea cores and estimated the changes in ocean temperatures. Since then, stable isotope composition of foraminifera has been used in numerous studies to investigate Quaternary glacial-interglacial cycles.

Like foraminifera, ostracodes are another source of biogenic carbonate containing geochemical tracers of past environmental conditions. Ostracodes are small (typically <1 mm in length), environmentally sensitive, bivalved crustaceans that live in marine and nonmarine environments. Their low-Mg calcite shells are abundant microfossils in many sedimentary environments and may provide geochemical data on a variety of past aquatic conditions including temperature, salinity, and isotopic composition of water and dissolved inorganic carbon. Because ostracodes molt their shells eight to nine times before reaching maturity rather than grow them continuously like mollusks, the composition of a single shell represents a discrete set of hydrochemical conditions. Recent studies of ostracode shell chemistry have demonstrated the utility of trace element ratios, such as Mg/Ca and Sr/Ca, in reconstructing past salinity changes in marine (Carpenter et al., 1991) and lacustrine environments (Chivas et al., 1983, 1985, 1986a,b; Engstrom and Nelson, 1991; De Deckker et al., 1988). Furthermore, a combination of stable isotope and trace element analyses from the same ostracode sample has potential to identify both temperature and salinity changes (Chivas et al., 1986b) and the power to reinforce environmental reconstructions based on either proxy alone (Chivas et al., 1993; Curtis and Hodell, 1993; Palacios-Fest et al., 1993; Xia et al., 1997).

Although the oxygen isotope composition of ostracodes is now used as a paleoclimate proxy, isotope fractionation between ostracodes and water has not been studied experimentally. Without experimental verification, ostracode isotopic composition will remain a qualitative indicator of past conditions. Nonequilibrium fractionation induced by biological factors (vital effects) or variability in shell composition caused by physiological conditions within a population of ostracodes are possibilities that have not been investigated. In an attempt to resolve this problem, we cultured a single

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species of ostracode, *Candona rawsoni,* under controlled laboratory conditions to determine its isotopic fractionation behavior.

2. OSTRACODE ECOLOGY AND SHELL COMPOSITION

Candona rawsoni is a common benthic ostracode of closed-basin lakes in the North American Great Plains. Hatching occurs in spring, and most individuals undergo eight molts before attaining maturity in late August or early September (Delorme, 1970), although our field data suggest some penultimate instars overwinter before attaining maturity in the following spring (Xia et al., 1997a). The adults of *C. rawsoni* range between 1.1 and 1.4 mm in length, and well-calcified shells weigh 60–100 μg (30–50 μg/valve). Its ecology and morphology are reviewed by Delorme (1970). *C. rawsoni* in North America has relatively broad environmental tolerance. Delorme (1969a) reports that it can withstand salinity up to 48‰, although this upper threshold is only attained in lakes where SO_4^{2-} is the dominant anion (Forester, 1986). Our own dataset of sixty-six lakes from the Dakotas and Saskatchewan suggests a much lower salinity optimum of 1–10‰ (TDS: 0.5–11 g/L; Engstrom and Nelson, 1991). An ostracode life cycle may be as short as 3–5 weeks or as long as a year or more (Delorme, 1978). It is not yet clear what triggers ostracodes to molt, but several factors may be considered: (1) temperature (Hiller, 1972), (2) daylight length, or (3) nutrition.

The mineralized portion of the shells of nearly all ostracodes consists of low-Mg calcite (Durazzi, 1975). In a few cases amorphous calcium carbonate has been reported, but there are no known shells of high-Mg calcite or aragonite. Sohn (1958) found the ostracode shell to consist of 80–90% calcium carbonate, 2–15% organic material (chitin plus protein), and various minor and trace elements. Calcium is evenly distributed through the shell, while phosphorous is concentrated near the shell margins (Sohn and Kornicker, 1969). Because magnesite is isomorphous with calcite, Mg is the dominant replacement cation occurring in concentration ranging from 2.6 ~ 6 mol% (Chave, 1954) depending on the water temperature. In addition to Mg, other potentially important minor or trace elements include Sr and Ba.

3. CULTURE METHODS

Candona rawsoni were collected with an Ekman dredge and a modified benthic trawl from Roslyn Lake, South Dakota, USA (45°48′N, 97°50′W) in September 1990. The mud-water samples were sieved to remove fine-grained sediment, and the ostracodes and coarse detritus were retained in lake water and stored on ice to induce torpor in the live specimens (Delorme, 1969b). Lake water was collected in 20 L polypropylene carboys for laboratory culture.

Live *C. rawsoni* were picked by syringe from the field collections under 10× magnification of a Zeiss dissecting microscope. The large populations of ostracodes recovered from Roslyn Lake served as stocks for the laboratory cultures. Five cultures were established at each of two temperatures 15°C and 25°C using Roslyn Lake water with or without the emendation of ^{18}O-rich water (20 atom% ^{18}O): one culture, W(I) and W(II) (duplicated), was established from native water; and four different cultures, Y(I), Y(II), R(I), and R(II), representing a spectrum of $\delta^{18}O$ values were created by emending Roslyn Lake water with ^{18}O-rich water. The $\delta^{18}O$ of water ranged from −2.23 to 6.63‰ in the 25°C experiment, and from −2.23 to 9.14‰ in the 15°C experiment. Roslyn Lake water is dominated by sodium-magnesium sulfate (Table 1) with $\delta^{18}O$ of −2.23‰, salinity of 3.2‰, and pH of 8.6. For each culture, fifty juveniles of *C. rawsoni* were placed in a 500 mL Erlenmeyer flask with the unfiltered lake water, and a filter paper was placed on the bottom of flask to provide a rough surface over which the ostracodes could crawl. Six flasks were placed in a 15°C ± 0.3°C incubator and six were placed in a 25°C ± 0.1°C water-bath. The temperature in the 15°C incubator was recorded continuously, and in the 25°C bath, was checked periodically. All flasks were covered with laboratory Parafilm™ to prevent evaporation of water during the experiment. The lighting arrangement consisted of a timer that provided 12 h of simulated daylight and 12 h of dark.

Table 1 Cation composition of waters used for the culture experiments*

	Na ppm	K ppm	Mg ppm	Ca ppm	Sr ppm	Ba ppm	Si ppm
15°C							
W(I)	639.4	52.58	211.1	108.49	1.357	0.0862	26.04
W(II)	658.9	66.80	212.0	108.33	1.359	0.0759	25.71
Y(I)	644.6	52.23	212.9	136.63	1.394	0.0911	29.54
Y(II)	635.2	52.79	205.6	104.34	1.309	0.0706	19.15
R(I)	632.2	52.36	206.4	103.68	1.290	0.0644	21.44
R(II)	623.1	52.02	207.0	103.31	1.268	0.0483	15.74
25°C							
W(I)	na	na	na	na	na	na	na
W(II)	639.2	53.21	209.3	107.56	1.351	0.0936	37.75
Y(I)	619.1	53.10	208.4	106.83	1.328	0.0937	39.69
Y(II)	636.0	53.54	211.5	106.92	1.345	0.0826	34.12
R(I)	624.6	52.04	204.7	103.52	1.262	0.0335	14.49
R(II)	634.8	52.92	205.6	106.23	1.291	0.0710	29.44

*Anions were analyzed only once immediately after field collection and gave the following results; Cl: 419.34 ppm, SO_4: 1344 ppm, and Total inorganic carbon: 96.74 ppm. Cations were measured at the completion of the culture experiments.

The small juvenile ostracodes were left to undergo successive molts and calcify new shells for three months (adults could be seen crawling on the bottom of the flasks after about three weeks), after which time the culture setups were dismantled, and adults picked and stored in 99% ethanol for isotope and chemical analyses. One culture was monitored for possible changes in its $\delta^{18}O$ and was found to change by 0.03‰ and 0.20‰ over 17 and 50 days, respectively.

4. ANALYTICAL METHODS

The shells of individual adults were separated from soft tissues with a dissecting needle, cleaned for 15 min in hot (80°C) 5% H_2O_2, rinsed with triply-distilled water on a polycarbonate membrane filter, and air dried in a laminar-flow hood. Any chemical cleaning method will likely etch the surface of the ostracode shell and may alter its composition. Our cleaning method results in small (0.1–0.3‰) nonsystematic shifts in both $\delta^{18}O$ and $\delta^{13}C$ and a generally small decrease in trace element ratios (0.001 for Mg/Ca; $2 \cdot 10^{-5}$ for Sr/Ca) between uncleaned and cleaned samples (Haskell et al., unpubl. data).

Extraction of CO_2 from ostracode shells used a method modified from McCrea (1950). Individual cleaned ostracodes (both valves) were reacted at 80°C for 30 min with 104% H_3PO_4 made from ultra pure P_2O_5 and triply-distilled H_2O. Evolved CO_2 was passed over a dry-ice bath twice to remove water before being sealed in a Pyrex tube. The isotope composition of the evolved CO_2 was measured using a Finnigan MAT delta E mass spectrometer equipped with triple collectors for simultaneous determination of masses 44, 45, and 46. The results are reported in permil (‰) deviations relative to the PDB standard. The overall analytical accuracy for $\delta^{18}O$ was ±0.2‰ based on thirty-one analyses of NBS-19. Most of the uncertainty arises from the extraction process.

For analysis of the oxygen isotope composition of culture water, 5 mL water samples were equilibrated overnight with instrument-grade CO_2 (99.99%) at 25°C (Epstein and Mayeda, 1953). The equilibrated CO_2 was measured by the mass spectrometer described above. The results are reported in permil deviations relative to the

V-SMOW standard. The analytical accuracy for this method is ±0.1‰. The reported shell weights are nominal values calculated stoichiometrically from the Ca content of the residue from the isotopic extraction (Xia et al., 1997b).

5. RESULTS AND DISCUSSION

The number of ostracodes that survived to adulthood varied among the different cultures. There were higher rates of survival for the 25°C cultures (10–25%) than for the 15°C cultures (5–15%). Specimens cultured at 25°C also attained maturity in shorter time (1.5 months) than those at 15°C (3 months). Adult ostracodes from the 15°C cultures also had lower shell weight (20–25 μg/valve) than those from 25°C cultures (35–40 μg/valve). Our field data (Xia et al., 1996a) showed that 25°C is the optimum molting and calcification temperature for *C. rawsoni*, and our culture data suggest that growth at 15°C occurred under a stressful condition, 15°C being barely above the temperature that induces torpidity in *C. rawsoni*. The shell weight of the 25°C group is only slightly lower than the weight of field-collected adults (~40 μg/valve). Ostracodes from 25°C cultures had sufficiently well-calcified shells so that one individual ostracode (i.e., both valves) was adequate for isotopic analysis, whereas two ostracodes from 15°C cultures were needed for each isotopic analysis.

Analytical results for $\delta^{18}O$ in ostracodes and water are shown in Table 2. The variation of ostracode $\delta^{18}O$ within any one culture was very small: 0.2‰ at 25°C and 0.3‰ at 15°C, values equal or close to the analytical error (0.2‰). The only exception is for one 15°C culture with the heaviest isotopic composition of water. Two samples (each with two individuals) from that culture gave results that differed by about 5‰. The reason for this 5‰ difference is unknown but may be related to the weight of the analyzed shells: the weight of the sample that gave higher $\delta^{18}O$ was nearly twice that of the other. The possible relationship between shell weight and calcification is discussed later in this section. Both data points were retained on the graph (Fig. 1), but the lower value was treated as an outlier and excluded from the calculation of the isotopic fractionation factors.

Table 2 Oxygen isotope values of *Candona rawsoni* shells and water in laboratory culture

Cultures	Sample	Ostracode $\delta^{18}O$ (VSMOW)	Water $\delta^{18}O$ (VPDB)	Cultures	Sample	Ostracode $\delta^{18}O$ (VSMOW)	Water $\delta^{18}O$ (VPDB)
15°C				25°C, continued			
W(I)	1	-0.43	-2.23	Y(I)	2	0.64	1.04
W(I)	2	-0.28	-2.23	Y(I)	3	0.21	1.04
W(II)	1	-0.46	-2.23	Y(II)	1	2.22	2.94
W(II)	2	-0.90	-2.23	Y(II)	2	1.84	2.94
Y(I)	1	1.60	0.81	Y(II)	3	1.63	2.94
Y(I)	2	1.25	0.81	Y(II)	4	1.81	2.94
Y(II)	1	3.41	2.44	Y(II)	5	2.20	2.94
Y(II)	2	2.89	2.44	R(I)	3	6.11	5.87
R(I)	1	11.24	9.14	R(I)	5	5.63	5.87
R(I)	2	6.44	9.14	R(I)	6	5.62	5.87
				R(I)	7	5.87	5.87
25°C				R(I)	8	6.22	5.87
W(I)	1	-2.43	-2.23	R(I)	9	5.65	5.87
W(I)	2	-2.34	-2.23	R(I)	10	5.39	5.87
W(I)	3	-2.49	-2.23	R(II)	1	5.88	6.63
W(I)	4	-2.05	-2.23	R(II)	2	4.76	6.63
W(I)	5	-2.12	-2.23	R(II)	3	5.71	6.63
W(I)	6	-2.22	-2.23	R(II)	4	5.74	6.63
W(II)	1	-2.74	-2.23	R(II)	5	5.96	6.63
W(II)	2	-2.51	-2.23	R(II)	6	5.58	6.63
W(II)	3	-2.77	-2.23	R(II)	7	5.64	6.63
Y(I)	1	0.26	1.04	R(II)	8	5.70	6.63

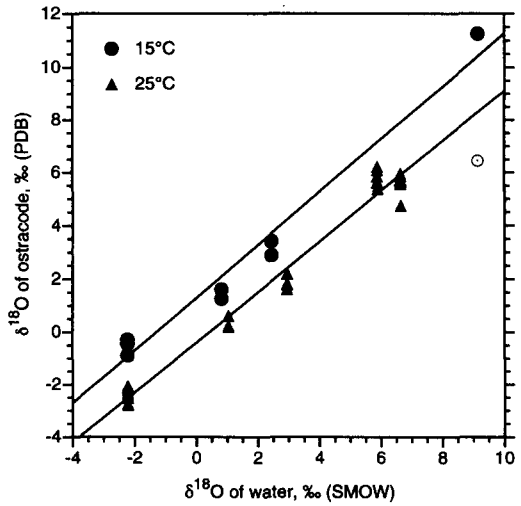

Fig. 1. $\delta^{18}O$ values in *Candona rawsoni* shells vs. $\delta^{18}O$ of the water in which the ostracodes were cultured. Filled circles are from 15°C cultures and triangles are from 25°C cultures. The lines represent best fit by least-squares regression for the data from 15°C and 25°C cultures, and the unfilled circle is an outlier omitted from the 15°C regression (see text).

The relationship between $\delta^{18}O$ of the ostracode shells and that of the culture water shows a clear and consistent temperature dependence of oxygen isotope fractionation during biological calcification by *C. rawsoni* (Fig. 1). Linear regression fit of the data give

$$25°C: \quad \delta^{18}O_{shell}^{PDB} = -0.47 + 0.97\delta^{18}O_{water}^{VSMOW}$$

$$15°C: \quad \delta^{18}O_{shell}^{PDB} = 1.12 + 1.07\delta^{18}O_{water}^{VSMOW}$$

The regression line from the 15°C cultures is nearly parallel to the line from the 25°C cultures and is shifted upward by about 2‰. A 2‰ difference would be expected for inorganic carbonate from a temperature difference of 10°C. It is clear that $\delta^{18}O$ in ostracode shells is well defined by $\delta^{18}O$ and temperature of the water from which the shells are formed. The oxygen isotope fractionation factors (α) are calculated for both 15°C and 25°C cultures based on the definition

$$\alpha = \frac{\delta^{18}O_{shell} + 1000}{\delta^{18}O_{water} + 1000}$$

where $\delta^{18}O_{shell}$ and $\delta^{18}O_{water}$ relative to the same standard. The results are: $\alpha = 1.0322$ at 15°C and $\alpha = 1.0305$ at 25°C.

The temperature dependence of oxygen isotope fractionation between ostracode shells and water is shown in Fig. 2, along with the results for inorganic calcite (O'Neil et al., 1969) and some marine biogenic aragonites (Grossman and Ku, 1986) that are known to incorporate more ^{18}O than calcite. The oxygen isotope composition of *Candona rawsoni* is about 0.8–1‰ higher relative to inorganic calcite

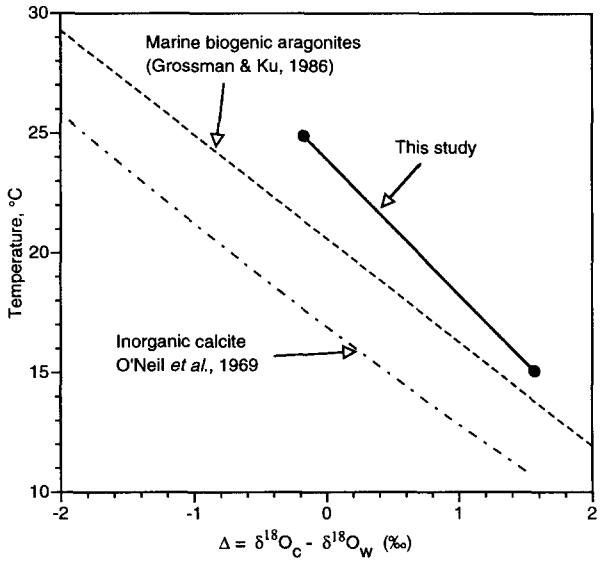

Fig. 2. Comparison of temperature dependence of oxygen isotope fractionation in *Candona rawsoni* with that of inorganic carbonates (O'Neil et al., 1969) and marine biogenic aragonites (Grossman and Ku, 1986).

and is similar to the oxygen isotope composition of marine biogenic aragonite but with a slightly different temperature dependence, incorporating more ^{18}O relative to inorganic calcite at 25°C than at 15°C. The fractionation factors of the ostracodes (1.0305 at 25°C and 1.0322 at 15°C) are thus higher than those of inorganic calcite (1.0283 at 25°C and 1.0306 at 15°C). Ostracodes were cultured at only two different temperatures, so that the slope of temperature dependence is currently defined by just two points. The equation relating temperature to ostracode $\delta^{18}O$ is t (°C) = 22.04 − 5.59 ($\delta^{18}O_c - \delta^{18}O_w$), with $\delta^{18}O_c$ and $\delta^{18}O_w$, defined the same as in the standard paleotemperature scale (Epstein et al., 1953).

Disequilibrium fractionation of biogenic carbonates has been reported and discussed in many papers. Most of the disequilibrium values have been reported for planktonic foraminifera (e.g., Shackleton et al., 1973; Kahn, 1979; Van Donk, 1977; Fairbanks et al., 1980; Kahn and Williams, 1981; Erez and Honjo, 1981; Duplessy et al., 1981; Erez and Luz, 1983). Erez and Luz (1983) suggested several possible explanations for observed disequilibria: (1) authors have made incorrect assumptions regarding water temperature and water isotopic composition, (2) most isotopic analyses of planktonic foraminifera are made on materials containing large quantities of organic matter that are difficult to totally remove, and (3) nonequilibrium values in planktonic foraminifera occur only in the earlier stages of growth when metabolic activity is more intense (Berger et al., 1978). Metabolic (growth) rates are known to be generally faster at higher temperatures within reasonable temperature limits (Moberly, 1968), and this could also contribute to disequilibrium.

A high metabolic rate during initial shell calcification may explain the observed nonequilibrium oxygen isotope fractionation in our ostracode cultures. Preferential uptake of Mg during the early stages of calcification, observed by Chivas et al. (1983, 1986b) for *Mytilocypris henricae,* has been inferred for *C. rawsoni* from laboratory determinations of Mg partitioning by Engstrom and Nelson (1991). The cause appears to be more rapid (less discriminating) calcification during the early stages of shell formation. If early stages of calcification are characterized by less effective discrimination against ^{16}O as is the case for Mg, then we would expect shells that are not completely calcified to show lower $\delta^{18}O$. We cannot measure the mass ratio of early- and late-calcified portions of an ostracode shell. If these mass ratios varied among cultured ostracodes, and if the disequilibrium effects during the early calcification were measurably large, we would expect to see a larger scatter in their $\delta^{18}O$ composition, but such scatter was not observed except in one culture (Fig. 1). The much lower weight of that particular sample grown at 15°C may mean that at least one of the two individuals in that sample was not completely calcified. Indeed, Chivas et al. (1983, 1986b) found shell weight to be a good proxy for the degree of calcification. The $\delta^{18}O$ value of the sample whose individual shell weight was about half that of the other sample is 5‰ lower than the other, i.e., these shells show lower $\delta^{18}O$ value than inorganic calcites.

The rate of ostracode shell calcification is higher at 25°C resulting in more robust shells with weights similar to those of field-grown individuals in less time. Thermodynamically, ^{18}O is preferred by calcite over ^{16}O by ~30‰ relative to the water from which it precipitates in the temperature range of interest, but increased departure from thermodynamic equilibrium behavior (e.g., faster calcification) should decrease the discrimination between ^{18}O and ^{16}O. Indeed, De Villiers et al. (1995) observed that more ^{18}O than expected is incorporated (i.e., stronger discrimination against ^{16}O) by coralline aragonite, *Pavona clavus,* at slow extension (growth) rates. However, results from this study show the opposite effect. The steeper slope shown in Fig. 2 suggests that the discrimination against ^{16}O is more effective at 25°C (i.e., larger departure from equilibrium fractionation) than at 15°C. Slower or less robust calcification, whether due to lower temperature or some other factor, seems to result in less discrimination against ^{16}O by ostracodes.

The observed behavior is contrary to our expectation of vital effects that increase with growth rate and discriminate against the incorporation of heavier isotopes of carbon and oxygen (in the case of oxygen it may be more accurate to characterize it as less effective discrimination against ^{16}O) (e.g., McConnaughey, 1989). Nevertheless, such unexpected behavior has been noted for other carbonate-secreting organisms (reviewed by Vizer, 1983). All we can surmise from our data is that ostracodes in the 15°C experiment grew more slowly under stress, and that slower growth rate led to a closer approach to equilibrium fractionation.

Sohn (1958) found ostracode shells to consist of 80–90% calcium carbonate and 2–15% organic material. However, if organic matter is the cause for the disequilibrium, the $\delta^{18}O$ values of ostracode shells in the cultures should be lower rather than higher as we found, because most organic matter

is depleted in ^{18}O. Other environmental and biogenic factors, such as the rate of metabolism, food quantity, photosynthetic activity of symbionts, light penetration, and ionic composition of the water may affect oxygen isotope fractionation in ostracode shells. Our experiments point to two possible factors affecting oxygen isotope fractionation: (1) temperature-dependent rate of calcification, with faster calcification at higher temperature leading to more incorporation of ^{18}O relative to inorganic calcite; and (2) environmental stress during calcification leading to incomplete calcification and more incorporation of ^{16}O. Experiments that explore how these factors indirectly control rates of shell calcification should shed additional light on the cause(s) of nonequilibrium isotope fractionation by ostracodes.

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