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Temperature controls monthly variation in Ostracode valve Mg/Ca: *Cypridopsis vidua* from a small lake in Sonora, Mexico

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Abstract—The molar Mg/Ca ratio was measured in live-collected ostracodes from a small dammed body of water in northern Mexico. The species *Cypridopsis vidua* was collected every month throughout 1990. Four to ten specimens were measured from each month's collection. Monthly average Mg/Ca ratios range from 0.018 to 0.032 and are correlated with water temperature. An anomalously cool July is reflected in lower Mg/Ca ratios in that month's collection. The Mg/Ca ratio responds to temperature in this way: $T^{\circ} = (\text{Mg/Ca} - 0.0103)/0.00066$. The rapid valve chemistry response to temperature change in the lake can occur because the life span of *C. vidua* is very short (~30 d). The high variability in the data set shows that many measurements of single valves must be averaged to track temperature change, or that many valves must be combined. Valves must also be screened for incomplete calcification as Mg/Ca ratios are significantly higher in poorly calcified valves. If the Mg/Ca of valve is modeled as a temperature-dependant partition coefficient, the residuals on a linear regression are significantly larger. This implies that ostracode biology and temperature play a significant role in the elemental composition of the valve and that water chemistry is of minor importance. Copyright © 2001 Elsevier Science Ltd

1. INTRODUCTION

Ostracodes are small (0.3–3mm) crustaceans that produce and molt nine calcite shells during their lifetime. These calcite shells, made up of two valves, look similar to bivalve shells but are not the result of accretionary growth, rather they are precipitated in a matter of hours. In the last two decades a number of papers have reported on the use of the minor element composition of ostracode valves as indicators of paleoenvironmental conditions. The ratios of Sr and Mg to Ca in valves have been the primary focus. Our work addresses only Mg/Ca ratios, and we will limit our discussion to Mg. Chivas et al. (1983; 1986) investigated the relationship of Mg/Ca in valves with temperature, salinity, and Mg availability. Engstrom and Nelson (1991) showed that the chemistry of cultured *Candona rawsoni* valves can be explained using a partition coefficient (Kp) for Mg/Ca that increases with temperature. Xia et al. (1997), also working with *Candona rawsoni*, measured very different Kp values than that of Engstrom and Nelson (1991) and suggested that the partition coefficient of Mg decreases with increasing Mg/Ca ratios in the host water, complicating the application of a Kp for paleoenvironmental reconstructions. Other workers have shown that Kp is species dependant and that it can vary widely within the same genus and (as above) within different populations of the same species (Wansard, 1996; Wansard et al., 1998; De Deckker et al., 1999).

Palacios-Fest (1996) cultured *Limnocythere staplini* across a small range of ionic compositions (Mg/Ca of 6–8) and found that temperature was the dominant control on the valve Mg/Ca ratio. A regression model that did not use partition coefficients for [Mg] was developed. The model has been used in several case studies and has generated realistic temperature estimates

(Palacios-Fest, 1994; 1997; Cohen et al., 2000; Palacios-Fest et al., in press). Concerns for the effects of the artificial environment of the cultures have led to this study in which a natural setting is used to compare growth temperature and the chemistry of valves and waters. The specimens used here were collected from January to December 1990 from a small lake in the outskirts of Magdalena de Kino, Sonora, Mexico. The goal of this study was to document the effects of temperature and water chemistry on valve chemistry in a population of *Cypridopsis vidua* from a small lake in northern Mexico in hopes of using this relationship as a proxy for temperature in studies of ancient systems. Using the seasonal temperature cycle of a natural setting allows the effects of natural annual temperature variation to be studied and removes artificial stresses introduced by the culturing environment. We also test the validity of the Kp model in the explanation of the observed chemical variation in this setting. Finally these results are compared to the laboratory-derived regression for *L. staplini* (Palacios-Fest, 1996).

2. AREA OF STUDY

The Magdalena Basin is located in the Arizona Upland Subdivision of the Lower Sonoran Desert physiographic and biotic provinces, at an altitude of ~790 m above sea level (m asl). The mean annual temperature is 19.7°C (monthly mean summer: 27.5°C; winter: 11.8°C). The mean annual precipitation is 397.7 mm (Turner and Brown, 1994). Summer (June, July, August) rainfall accounts for 30 to 60% of the annual total with smaller proportions to the north and larger to the south (Turner and Brown, 1994). Winter rainfall ranges from 10 to 40% of the annual total. El Yeso Lake is an ephemeral body of water used for irrigation, created and controlled by a retaining dam. It lies 10 km southeast of Magdalena de Kino, Sonora, on the road to Cucurpe at an altitude of ~900 m asl (110°53' W; 30°38' N) (Fig. 1). At the time of this study it had an area of ~0.96 km², and a maximum depth of 13 m. It receives the runoff of several rain-fed streams from Sierra La Madera about 7.5 km to the east-northeast.

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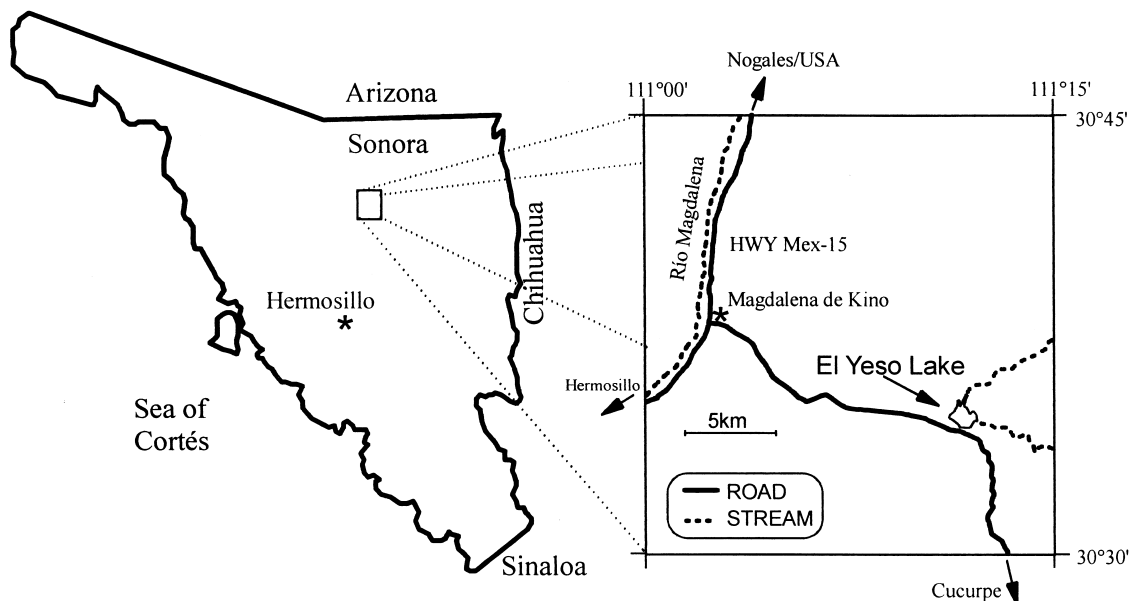


Fig. 1. Study area.

The vegetation is dominated by Palo Verde (*Cercidium* spp.) and cacti (*Opuntia* spp.) associated with ironwood (*Olneya tesota*), mesquites (*Prosopis* spp.) and cat-claw (*Acacia greggii*). The arboreal nature of this desert subdivision indicates that this is the least desert-like deserts in North America. Agricultural vegetation along the irrigation belt consists of alfalfa, oat, wheat, cotton, sugar beat, rye grass, sorghum and sunflower: all species tolerant of high salinity (1500–2000 ppm total dissolved solids).

The Magdalena Basin is part of the upper plate of the Magdalena core complex (Miranda-Gasca and DeJong, 1992). It is a topographic depression surrounded by the Magdalena, La Madera, El Torreon and La Ventana Ranges. Quaternary sediments and pre-Quaternary volcanics fill the basin. The oldest rocks are fossiliferous Lower Cretaceous rocks (Bisbee Group) that occur northwest of Magdalena and locally along the southwestern part of Sierra La Madera. The Cuesta and Magdalena Formations underlie the Quaternary alluvium. Alkaline basalts, andesites and ignimbritic rhyolites of the El Torreon Formation unconformably underlie the Cuesta and Magdalena Formations (Miranda-Gasca et al., 1998). This rock assemblage is the source of ions to the host water of El Yeso Lake.

3. MATERIAL AND METHODS

3.1. Field Work

Cypridopsis vidua, a small cypridacean ostracode, was used for this study because it is a cosmopolitan, eurythermic species. Optimal hatching temperature for this species is greater than 13°, although it may hatch and live at lower and higher temperatures (<2°C to >32°C) (Taylor, 1992). Like *Limnocythere staplini* (to which we will make a comparison), this species tolerates a wide range of aquatic environments from ephemeral to permanent systems. In contrast to *L. staplini*, its salinity tolerance is limited to the lower range of the spectrum (10–10000 ppm) (Delorme, 1989).

Delorme (1970; 1989) has reviewed the taxonomy and ecological requirements of *C. vidua* in North America. As with many other *Cypridopsis* species, *C. vidua* lives in oligo- to slightly hypersaline, Ca²⁺/HCO₃⁻-enriched waters (streams, ponds, lakes). Large variations in pH, dissolved oxygen, as well as in Mg²⁺, Na⁺, SO₄²⁻ and Cl⁻ concentrations are tolerated by this species (Delorme, 1989; Taylor, 1992). This allows these organisms to live in waters ranging from Type I (Ca²⁺, (Mg²⁺)/HCO₃⁻) to Type II (Ca²⁺-enriched) of Eugster and

Hardie (1978). However, unlike some other *Cypridopsis* species, *C. vidua* cannot tolerate high HCO₃⁻ and CO₃²⁻ concentrations (Delorme, 1989; Taylor, 1992).

From January to December of 1990, sediments, water and living ostracodes were collected from the northwest shoreline of El Yeso Lake (Fig. 1). The locality was sampled once a month, very near the beginning of each month. At the sampling station physical and chemical parameters were measured (Tables 1 and 2) using a conductivity meter for conductivity and water temperature and a pH meter. Major ions were measured in the field using a Hach digital titrator (model 16900-01 with portable test kit), with a precision of ± 2ppm for [Ca] and [Mg]. The concentration of Sr could not be measured in the field. Monthly mean temperatures, precipitation, evaporation rates, usage discharge and lake level information was obtained from El Yeso weather station data sheets of the Secretaria de Agricultura y Recursos Hidráulicos de Mexico (SARHM).

Sediments with water were collected in 500 mL wide mouth nalgene bottles, labeled, sealed and stored in an ice chest at 4°C. Because of the possibility of recovering live ostracodes in the sediments these samples were not acidified or fixed in any way. Sediments were collected with a bottom net gently removing the uppermost sediment layer at a water depth of 35 cm. In addition, living ostracodes were collected using a small (fine mesh) aquarium net gently passed around aquatic vegetation. The organisms were placed in a 150 mL glass jar and fixed with 70% ethanol.

3.2. Laboratory Work

In the Laboratory of Paleolimnology of the Department of Geosciences, live-collected specimens were removed from the 70% ethanol solution. When available, ten adults were analyzed for Ca²⁺ and Mg²⁺. The carapaces were separated from the soft body using a surgical needle and a fine brush (000) under a low power stereoscopic microscope. Valves were immersed in a 5% H₂O₂ solution at room temperature for 30 min to remove organic remains, then rinsed three times with distilled water (18 MΩ). Right valves were selected, weighed in a Cahn 29 (± 0.002 μg) electronic balance, and dissolved in 3 mL 2% distilled HCl solution for elemental (Ca²⁺ and Mg²⁺) analysis using a Turner TS SOLA inductively coupled plasma mass spectrometer (ICP-MS). Detection limit for Mg²⁺ was 0.001 ppb and 10 ppb for Ca²⁺–2σ above background. All analyses were run against multi-element stan-

Table 1. El Yeso Lake physical and hydrological environment.

Month	Collection Date	Time	Precipitation* (mm)	Evaporation* (mm)	Lake Level [#] (m ASL)	Water Storage [#] (1000m ³)	Temp (°C)* minimum*	Temp (°C)* maximum*	Air Temp (°C) this study	Water Temp this study
J	1-5-90	10:00	14	55.6	893.2	306	1.77	19.75	14	13
F	1-27-90	10:15	12	56.2	893.1	288	2.08	18.57	18	14
M	3-3-90	09:45	0	92.8	893.0	274	6.33	24.67	21	16
A	3-24-90	09:30	0	180.8	892.9	274	9.43	28.43	25	24
M	5-5-90	09:15	0	270.7	892.6	273	12.38	32.41	32	32
J	6-4-90	10:30	21.5	366.1	894.6	278	19.61	37.35	36	32
J	7-7-90	10:15	212	338.9	898.8	849	19.79	34.03	26	23
A	8-3-90	10:00	82	335.3	898.9	1884	17.95	31.59	26	26
S	9-1-90	09:30	77	327.4	899.5	2121	16.75	33.36	25	25
O	10-2-90	09:30	30	223.1	899.9	2290	10.48	29.95	26	21
N	11-1-90	09:45	30	108.1	899.4	2091	5.30	24.43	22	16
D	12-5-90	09:15	70	38.8	899.0	1935	2.79	17.08	18	14

* Monthly Average values from SARHM.

[#] 1990 data from SAHRM.

dards prepared from Spex™ stock solutions. To obtain good counting statistics four scans were made per sample, with four passes per scan, consuming the whole sample. Precision is 3% of signal for Mg²⁺ and 6% of signal for Ca²⁺ (2σ).

4. RESULTS

Table 1 summarizes the physical parameters obtained from El Yeso weather station logs of the SARHM and air and water temperatures obtained during sample collections. Some major features deserve consideration, for example, precipitation remained low during the first six months of 1990. Heavy rains occurred from July to mid September and moderate rains continued through December. The annual precipitation was almost 200 mm higher than the mean reported in the literature (Turner and Brown, 1994). In addition, evaporation increased between March and June and began to decline in October. As a result of the heavy summer rains the lake level rose ~6 m from May to July and the lake's surface area rose from 0.15 km² to 0.49 km². Water withdrawals for irrigation were low from January to July, achieved a maximum in October and were low again in November and December. Changes in lake volume were primarily the result of irrigation discharge and not evaporation. Therefore, ionic concentration showed only moderate variation through the year.

El Yeso water is dominated by Na⁺, Mg²⁺, Cl⁻ and (presumably) SO₄²⁻; it is Ca²⁺-enriched and HCO₃⁻-depleted (Ta-

ble 2). Conductivity rose from January to May, declined during the summer rains, and increased again starting in October. pH remained stable throughout the year. Alkalinity decreased after May. Cl⁻ increased during the dry season and decreased with the monsoon rains. Sulfate was not measured in the field. While the concentration of calcium and magnesium both decreased with the beginning of the monsoon, change in Mg was proportionally less. The molar Mg/Ca ratio of the water was moderately variable at 0.34 ± 0.03 for the first 8 months of the year, then increased gradually to 0.46 in December.

Table 3 presents the chemical composition of *Cypridopsis vidua* in El Yeso Lake by month. One hundred and two full-size adult specimens were selected for spectrometric analysis. The Mg/Ca molar ratios of the valves range from 0.010 to 0.048. The ratio increases with increasing temperature (Fig. 2a). The life span of *C. vidua* is very short, on the order of one month (Kesling, 1951; Anderson et al., 1998) and in a subtropical setting, where temperature does not limit growth, the valves are contemporaneous with the measurements of the lake environment. This is shown in the significant difference in Mg/Ca ratios from month to month, suggesting that the valves respond to the ambient environment on roughly that time scale. The monthly trend in temperature is very closely paralleled by the trend in valve chemistry (Fig. 2b). Valve Mg/Ca responds quickly to temperature change as is seen in the anomalous

Table 2. El Yeso lake chemical parameters.

Month	Water temp. (°C)	pH	COND. μmMHOS	ALK (mg/l)	Cl- (mg/l)	Ca (mg/l)	Mg (mg/l)	Mg/Ca (molar ratio)
J	13	8.26	740	222	33.2	258	48	0.307
F	14	8.37	750	234	35.8	258	56	0.358
M	16	8.40	780	234	42.2	256	56	0.361
A	24	8.35	800	242	43.6	238	52	0.360
M	32	8.31	850	220	48.3	226	50	0.365
J	32	8.31	850	140	52.0	221	41	0.306
J	23	8.33	750	120	38.4	208	40	0.317
A	26	8.31	710	100	25.6	186	38	0.337
S	25	8.35	710	102	32.0	146	34	0.384
O	21	8.43	740	140	24.4	140	36	0.424
N	16	8.37	765	156	20.3	146	39	0.440
D	14	8.30	780	144	25.1	136	38	0.461

Table 3. Ostracode valve chemistry.

Month	Water Temp. (°C)	Valve Wt. (µg)	Ca in Valve (µg)	Mg in valve (µg)	Mg/Ca molar ratio	Average Mg/Ca*	Calculated T (eqn. 1)	Average calc. T*
Jan	13	8.9	3.58	0.0324	0.0149	0.0186	7.00	12.61
		6.1	2.42	0.0281	0.0191		13.36	
		13.8	5.45	0.0584	0.0177		11.24	
		7.7	3.07	0.0313	0.0169		10.03	
		10.0	3.95	0.0346	0.0145		6.39	
		6.5	2.58	0.0281	0.0179		11.55	
		7.4	2.92	0.0452	0.0256		23.21	
		7.5	2.99	0.0296	0.0163		9.12	
		6.2	2.43	0.0372	0.0253		22.76	
		7.0	2.78	0.0303	0.0180		11.70	
Feb	14	6.5	2.57	0.0337	0.0217	0.0211	17.30	16.39
		7.0	2.75	0.0320	0.0192		13.52	
		7.4	2.93	0.0362	0.0203		15.18	
		6.2	2.46	0.0371	0.0249		22.15	
		6.5	2.59	0.0315	0.0201		14.88	
		3.8	1.50	0.0225	0.0247		21.85	
		6.5	2.55	0.0313	0.0202		15.03	
		6.2	2.44	0.0289	0.0196		14.12	
		6.6	2.61	0.0304	0.0192		13.52	
		6.9	2.74	0.0348	0.0210		16.24	
Mar	16	4.6	1.82	0.0282	0.0255	0.0212	23.06	16.55
		6.8	2.69	0.0338	0.0208		15.94	
		7.1	2.82	0.0337	0.0197		14.27	
		6.7	2.63	0.0316	0.0198		14.42	
		6.3	2.47	0.0347	0.0232		19.58	
		6.7	2.65	0.0363	0.0226		18.67	
		5.0	1.99	0.0270	0.0224		18.36	
		8.0	3.17	0.0299	0.0156		8.06	
		3.9	1.52	0.0266	0.0288		28.06	
		4.3	1.69	0.0235	0.0229		19.12	
Apr	24	7.2	2.87	0.0289	0.0166	0.0272	9.58	25.64
		4.1	1.62	0.0274	0.0279		26.70	
		3.1	1.22	0.0237	0.0319		32.76	
		3.6	1.39	0.0296	0.0350		37.45	
		3.8	1.50	0.0267	0.0293		28.82	
		4.2	1.64	0.0254	0.0256		23.21	
		3.8	1.48	0.0276	0.0308		31.09	
		4.4	1.75	0.0249	0.0236		20.18	
		4.9	1.91	0.0418	0.0361		39.12	
		4.2	1.66	0.0297	0.0296		29.27	
May	32	3.8	1.50	0.0269	0.0296	0.0318	29.27	32.61
		4.6	1.79	0.0377	0.0346		36.85	
		3.5	1.36	0.0282	0.0343		36.39	
		5.1	2.02	0.0328	0.0268		25.03	
		2.3	0.89	0.0204	0.0377			
		4.0	1.58	0.0372	0.0390		43.52	
		4.5	1.77	0.0411	0.0383		42.45	
		3.8	1.49	0.0267	0.0295		29.12	
		6.9	2.70	0.0419	0.0256		23.21	
		3.9	1.52	0.0226	0.0246		21.70	
Jun	32	2.7	1.06	0.0285	0.0442	0.0314		32.00
		5.6	2.21	0.0286	0.0213		16.70	
		5.7	2.26	0.0295	0.0215		17.00	
		4.4	1.75	0.0292	0.0276		26.24	
		5.0	1.98	0.0295	0.0247		21.85	
		3.3	1.29	0.0240	0.0308		31.09	
		7.3	2.89	0.0388	0.0222		18.06	
		5.3	2.08	0.0325	0.0258		23.52	
		5.8	2.29	0.0323	0.0233		19.73	
		4.8	1.91	0.0299	0.0258		23.52	
Jul	23	5.0	1.96	0.0301	0.0253	0.0248	22.76	22.00
		4.9	1.93	0.0307	0.0262		24.12	
		4.2	1.66	0.0264	0.0263		24.27	
		3.8	1.51	0.0261	0.0285		27.61	
		3.2	1.27	0.0217	0.0282		27.15	
		2.8	1.12	0.0205	0.0303			
		2.2	0.85	0.0224	0.0432			
		2.6	1.00	0.0224	0.0369			
		5.8	2.29	0.0323	0.0233		19.73	
		4.8	1.91	0.0299	0.0258		23.52	
Aug	26	5.0	1.96	0.0301	0.0253	0.0262	22.76	24.12
		4.9	1.93	0.0307	0.0262		24.12	
		4.2	1.66	0.0264	0.0263		24.27	
		3.8	1.51	0.0261	0.0285		27.61	
		3.2	1.27	0.0217	0.0282		27.15	
		2.8	1.12	0.0205	0.0303			
		2.2	0.85	0.0224	0.0432			
		2.6	1.00	0.0224	0.0369			

(Continued)

Table 3. (Continued)

Month	Water Temp. (°C)	Valve Wt. (μg)	Ca in Valve (μg)	Mg in valve (μg)	Mg/Ca molar ratio	Average Mg/Ca*	Calculated T (eqn. 1)	Average calc. T*
Sep	25	5.5	2.16	0.0388	0.0296	0.0279	29.27	26.70
		5.6	2.20	0.0351	0.0263		24.27	
		5.7	2.25	0.0350	0.0256		23.21	
Oct	21	5.9	2.30	0.0418	0.0300	0.0238	29.88	20.48
		7.4	2.92	0.0314	0.0177		11.24	
		6.7	2.64	0.0342	0.0213		16.70	
		4.7	1.84	0.0269	0.0241		20.94	
		4.2	1.66	0.0319	0.0316		32.30	
		5.1	2.00	0.0335	0.0276		26.24	
		6.0	2.36	0.0297	0.0208		15.94	
		4.3	1.69	0.0284	0.0277		26.39	
		5.4	2.13	0.0280	0.0217		17.30	
		6.4	2.53	0.0380	0.0247		21.85	
Nov	16	5.0	1.98	0.0252	0.0211	0.0213	16.39	16.70
		7.0	2.76	0.0291	0.0174		10.79	
		7.1	2.81	0.0340	0.0200		14.73	
		7.4	2.94	0.0325	0.0182		12.00	
		4.9	1.92	0.0252	0.0217		17.30	
		6.3	2.49	0.0320	0.0212		16.55	
		7.0	2.78	0.0334	0.0198		14.42	
		4.9	1.94	0.0337	0.0287		27.91	
		5.6	2.21	0.0298	0.0223		18.21	
		6.4	2.51	0.0319	0.0209		16.09	
Dec	14	5.2	2.07	0.0288	0.0230	0.0180	19.27	11.70
		5.4	2.14	0.0238	0.0184		12.30	
		5.2	2.07	0.0279	0.0223		18.21	
		5.9	2.33	0.0261	0.0185		12.45	
		6.3	2.48	0.0323	0.0215		17.00	
		10.9	4.31	0.0296	0.0113		1.55	
		7.4	2.93	0.0293	0.0165		9.42	
		11.5	4.58	0.0289	0.0104		0.18	
		3.9	1.52	0.0231	0.0251		25.45	
		6.9	2.72	0.0292	0.0177		11.24	
		2.0	0.79	0.0228	0.0476			

* Excluding valves $<3 \mu\text{g}$.

month of July. The beginning of the monsoon rains led to cooling of the ambient temperatures and to a parallel offset in the Mg/Ca ratio for the month of July. Many of the anomalously high ratios relative to the mean values for each temperature are from valves weighing less than $3 \mu\text{g}$. These may be incompletely calcified and are not included in the regression of Figure 2a as discussed below.

5. DISCUSSION

The relationship between Mg/Ca ratio in ostracode valve and temperature has primarily been modeled as a simple temperature-dependant partition coefficient between valve and ambient water (e.g., De Deckker et al., 1999; Engstrom and Nelson, 1991; Xia et al., 1997). Both these data and a number of other observations suggest that this is not appropriate. The determination of partition coefficients for Mg into calcite has proved to be highly problematic in naturally occurring carbonates (Given and Wilkinson, 1985) and carefully controlled study of inorganic calcites have shown that this system is extremely complex, strongly influenced by other ions in solution (see summary in Morse and Bender, 1990). Thus in a biologically-mediated calcite, caution should be used in trying to apply a simple partition coefficient.

The strong influence of biologic processes is clear in the Mg/Ca ratio of the initial carbonate which forms on the chitinous exoskeleton of the ostracode immediately after molting. Initially, the animal comes very close to precipitating magnesite, and as calcification continues the fully calcified valve becomes calcite with less than 4 mole% Mg. Chivas et al. (1986) reports values as high as 400000 and 152000 ppm Mg in poorly calcified valves, representing a Mg/Ca ratio of 1.64 and 1.32. Cadot et al. (1975) showed significant gradients across marine ostracode valves with the highest [Mg] usually at the interior. Our data also show the influence of degree of calcification (expressed as μg valve mass) on the Mg/Ca ratio (Fig. 2c). All the valves analyzed for this study are the adult stage and full sized for this population, but light valves with lower total Ca have significantly higher Mg/Ca ratios. The average ratio for valves less than $3 \mu\text{g}$ is 0.40, much higher than the average value at our warmest temperature, we would therefore argue that this group of shells are not fully calcified and reflect the high Mg/Ca ratios of early valve calcification. Valves between 2 and $3 \mu\text{g}$ (open triangles in Fig. 2a) are therefore excluded from our calculations. High ratios may also be partly explained by the much higher uncertainties in low mass specimens.

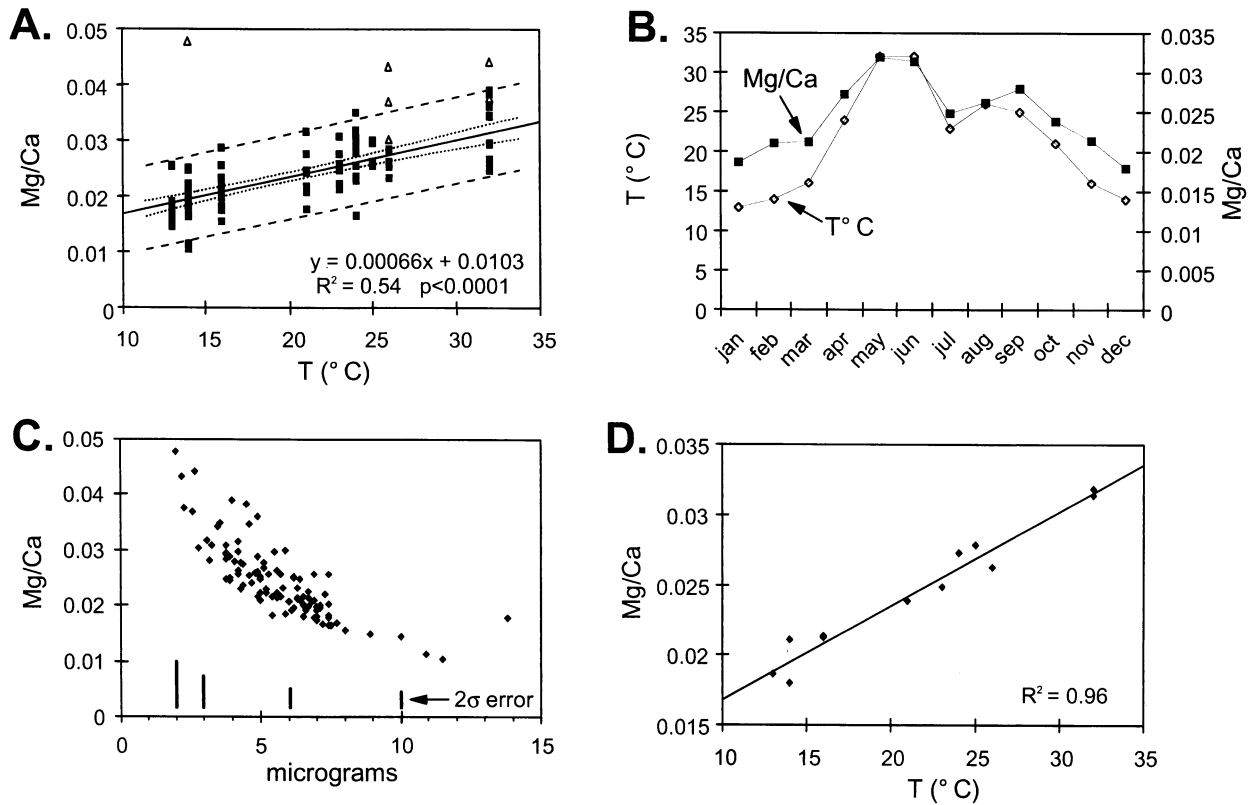


Fig. 2. **A.** The Mg/Ca ratio of *C. vidua* valves in monthly collections from El Yeso lake in 1990. Triangles are poorly calcified valves ($<3 \mu\text{g}$) and are not included in the linear regression. Dotted line is 95% confidence interval for the regression line. Dashed line is the 95% confidence interval for a single measurement's relationship to temperature. **B.** Mg/Ca ratio of well calcified valves and measured water temperature by month (Jan. to Dec. 1990). **C.** Valve mass and Mg/Ca ratio. Maximum error in Mg/Ca ratio arising from analytical uncertainty ($\pm 2\sigma$) for typical shell masses is also shown. **D.** Average Mg/Ca ratio for each monthly collection compared to temperature.

Unusually elevated [Mg] in the earliest calcite suggests that metabolic fluids play a role in the formation of valve and that these fluids seem to be enriched in Mg. The role of metabolic fluids was disputed by Turpen and Angel (1971), who showed that, in *Heterocypris*, the Ca in the valve is derived from the ambient waters. Their study, however, only demonstrated that some of the Ca had to be derived from ambient waters, not that the sole source was ambient water; metabolic sources of Ca, particularly food, may have played a role in the calcification of the valves. They noted that Fassbinder (1912) was able to culture fully-calcified *Cypridopsis vidua* (the subject of our study) in Ca free waters. In this case metabolic Ca must have been the source of the calcite in the valves. Other crustaceans have the ability to virtually decalcify their valves and store Ca in gastroliths and elevated blood Ca concentrations immediately before molting (Mann and Pieplow, 1938). In at least one crustacean species, *Procambarus clarkii*, temperature strongly affects the Mg concentration in body fluids of this crayfish (De Legarra et al., 1985). We speculate that a similar process may occur in ostracodes leading to valve enriched in Mg at higher temperatures.

Finally, we note that Mg/Ca ratios greater than 0.05 are extremely rare in the valves of fully-calcified adult ostracodes of any species. Yet these animals thrive in most natural waters,

where the range of Mg/Ca ratios cover more than 3 orders of magnitude. In this study the Mg/Ca ratio of the water ranged from 0.30 to 0.46 and calcite ranged from 0.01 to 0.038 for well calcified valves. The range of Mg/Ca ratios measured for this study is the same as the range reported by others who analyzed ostracodes that grew in waters with much higher Mg/Ca ratios. In fact, the ratio of 0.01 to 0.04 is the typical range reported for ostracodes whether they grew in dilute waters with low Mg/Ca (<1 as in this study) or in saline waters with Mg/Ca as high as 305 (Chivas et al., 1986; De Deckker et al., 1999). Hence Mg/Ca ratio of water cannot be a factor in determining the Mg/Ca ratio of ostracode valves. In our data a 50% change in the Mg/Ca ratio of the water had no effect on valve chemistry. A multiple regression model of the valve chemistry indicated that the only significant factor was temperature ($F = 97.6$; $p < 0.0001$), water chemistry was not a significant variable ($F = 0.1558$; $p = 0.6939$).

The temperature-Mg/Ca ratio relationship resulting from close monitoring of the *C. vidua* population at El Yeso lake is:

$$T^{\circ}\text{C} = \frac{(\text{Mg/Ca}) - 0.0103}{0.00066} \quad (1)$$

for all shells with mass $> 3 \mu\text{g}$ ($R^2 = 0.54$, $n=96$); where

Mg/Ca is the molar ratio in the valve carbonate. The variance of these data is large, as indicated by the 95% confidence interval for single measurements (dashed lines in Fig. 2a), which shows that most individual measurements could be associated with any temperature from 10 to 35°C. However, if we regress the mean values of fully calcified adults of each monthly collection the R^2 is 0.96 (Fig. 2d) and the 95% confidence interval for the regression is relatively small (dotted lines in Fig. 2a). Note that analytical error contributes to significant error in the estimated temperature. The error bars in Figure 2c, which represent the maximum ratio change resulting from the $\pm 2\sigma$ uncertainties in [Ca] and [Mg], yield the following uncertainties on calculated temperature: at $3\mu\text{g} \pm 4.3^\circ\text{C}$, at $6\mu\text{g} \pm 2.65^\circ\text{C}$, and at $10\mu\text{g} \pm 2.0^\circ\text{C}$. Nonetheless, a comparison of measured vs. mean calculated temperature shows a relatively low level of noise (Fig. 3).

If the variation in valve Mg/Ca ratio is modeled as a temperature-dependant partition coefficient (Kp), a linear regression of all well calcified shells ($>3\mu\text{g}$) shows a slightly lower R^2 (0.53), suggesting that the variance is approximately the same around these regressions and that linear regressions are equally appropriate. However, mean monthly Kp vs. temperature has a significantly lower R^2 (0.79) in comparison to mean Mg/Ca vs. temperature (Fig. 4). Average shell Mg/Ca is therefore highly correlated with temperature and this relationship is degraded when water chemistry is incorporated as a partition coefficient (the ratio of $\text{Mg}/\text{Ca}_{\text{valve}}/\text{Mg}/\text{Ca}_{\text{water}}$). Note that when fall and spring temperatures are the same the valve Mg/Ca ratios are very similar (Fig. 2b), but because the Mg/Ca ratio of the water changed late in the year (Table 2) calculated partition coefficients would be notably different. This reinforces our argument that temperature and metabolic processes play the major role in the control of valve Mg/Ca ratio and that ambient fluid chemistry is not significant in this study. It is clear however that more work on *C. vidua* needs to be done over a wider range of water Mg/Ca ratios. We argue that this thermometer can be applied in similar waters and that it may be applicable to a broad range of water chemistries, although the latter has not yet been verified.

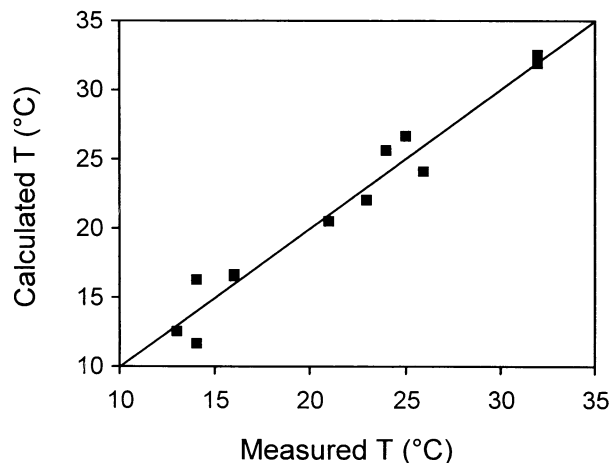


Fig. 3. Measured temperature vs. temperature calculated from mean Mg/Ca ratios for each month. Diagonal line is where $T_{\text{measured}} = T_{\text{calculated}}$.

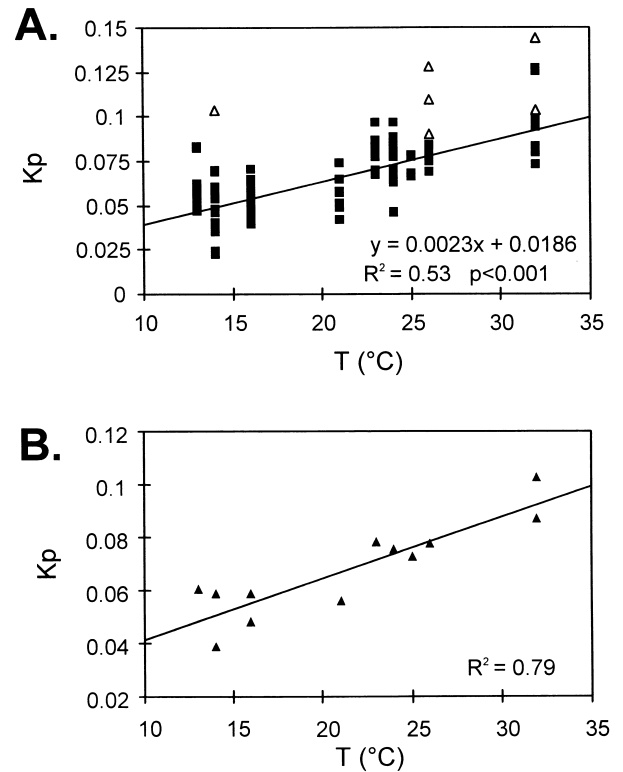


Fig. 4. **A.** Temperature vs. Kp for well calcified shells (triangles are poorly calcified valves and not included in linear regression). **B.** Temperature vs. monthly average Kp.

In applying this thermometer to natural systems we would suggest the following procedure. Only adult valves should be included in the study. We have not tested the chemistry of juvenile *C. vidua*. Valves should be weighed to screen out incompletely calcified valves because these usually have anomalously high Mg/Ca ratios (as discussed above). There is also considerable variability in each month's collection. Given that these animals calcify their valves in a matter of hours (Turpen and Angell, 1971), part of this may be attributable to diurnal variation in water temperature. Another untested cause of variability in this study may be secondary encrustations of calcite on the valve. This can be very hard to see, especially if it occurs in the enclosed vestibule of the valve. Finally, there is significant noise inherent in the measurement of elemental ratios in such small amounts of carbonate (Fig. 2c). Therefore combining a number of valves into a single measurement will better document the mean, reduce analytical error, and in a study of core or other ancient material, may allow the removal of significant seasonal or diurnal variability from overall trends in average temperatures through time. The advantage of combining many valves into a single analysis of Mg/Ca is that the errors associated with the measurement should be reduced. The disadvantage is the inability to examine the variance of each sample set.

Some culturing studies of ostracodes have reported a strong effect of the water Mg/Ca ratio on valve ratios (Engstrom and Nelson, 1991; De Deckker et al., 1999). It may be that severely limited food intake and removal of all non-aqueous sources of Mg from the environment created a strong response in the valve

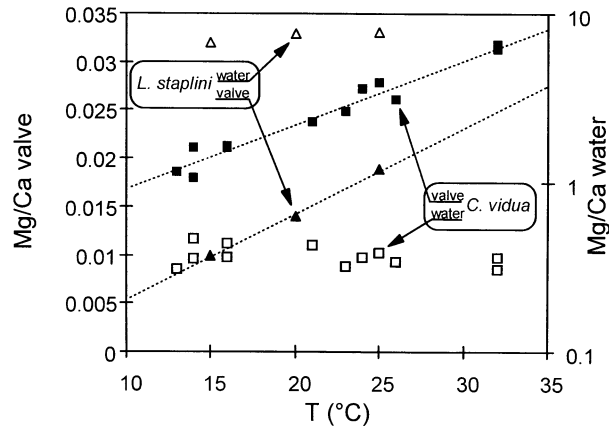


Fig. 5. Temperature — Mg/Ca ratio relationships for *C. vidua* and *L. staplini* (solid symbols). The Mg/Ca ratio of the water in which each set grew is also shown (open symbols).

chemistry. It is not clear how these animals respond when given access to both solid and aqueous sources of Mg and Ca. De Deckker et al. (1999) suggested that the valve may respond to water chemistry in different ways in different regions of the Mg/Ca spectrum. At low Mg/Ca ratios the valves enrich Mg over that predicted by a simple Kp, at high ratios Mg is excluded, but in a middle range, perhaps 1 to 20 the Mg/Ca of the valve follows a simple Kp. Although this may be valid in some cases, there are still many questions about the response of these organisms in natural settings, and it is quite possible that this suggested pattern does not pertain to all taxa of ostracode. Biology may also play a role in the different responses of different ostracode taxa to water chemistry. One study of the freshwater gastropod *Melanopsis* (Rosenthal and Katz, 1989) showed that the two species studied control the Mg/Ca ratio of their body fluids independent of water chemistry. In contrast, Sr and Ba concentrations were not metabolically controlled and followed simple partition coefficients. Many taxa of molluscs seem to be able to control [Ca] and [Mg] in their body fluids (Wilbur and Saleuddin, 1983).

Finally we compare the temperature — Mg/Ca ratio relationship of *C. vidua* from a natural setting to that of *L. staplini* from a cultured growth experiment (Palacios-Fest, 1996) (Fig. 5). The Mg/Ca — temperature relationship from the *L. staplini* experiment is:

$$T^{\circ}C = \frac{(Mg/Ca) + 0.0035}{0.00089} \quad (2)$$

where Mg/Ca is the molar ratio in the valve carbonate. The regressions have slightly different slopes. The latter experiment used waters with Mg/Ca ratios of 6 to 8. Note that the partition coefficients calculated for any one temperature would differ for the two species by a factor of 60 or 70. This again suggests that temperature is the primary controlling factor on valve chemistry and that large variations in the Mg/Ca ratio of water do not play a significant role in the Mg/Ca ratio of the valve in these species. We would predict from these data that *L. staplini* with ratios of greater than 0.03 will not be found in bodies of water at normal surface temperatures (<40°C) and that ratios lower

than 0.01 or greater than 0.04 would not occur in the valves of *C. vidua*. If populations of these species are located with average ratios beyond the above limits, it would point to greater influence of the water chemistry than we have proposed here.

6. CONCLUSIONS

1. Temperature is the dominant control on the Mg/Ca ratio of *C. vidua* valve and the ratio can be used as a proxy of temperature in waters of low Mg/Ca ratio (0.3 to 0.5). The relationship of Eqn. 1 may be applicable to a broader range of water chemistries, but that has not been tested.
2. Extreme caution is needed in the application of partition coefficients for Mg in biomineralized calcite. This is particularly the case when reported partition coefficients for Mg/Ca range over almost 2 orders of magnitude.
3. Much more work is needed on the Mg/Ca ratios of ostracode populations in natural settings.

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