

Comment on G. Wansard & F. Mezquita, The response of ostracode shell chemistry to seasonal change in a Mediterranean freshwater spring environment

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Abstract

In a study of the minor element chemistry of ostracode shells, Wansard and Mezquita (2001) concluded that the Mg/Ca and Sr/Ca of the ambient water controlled the respective ratios in ostracode calcite. Contrary to their conclusion that minor element chemistry is not influenced by temperature, we find a very strong statistical correlation ($r = 0.97$) between temperature and shell chemistry in their data. This discrepancy apparently arises due to their use of a partition coefficient model of shell chemistry that masks a number of strong correlations in their data. We argue here that the partition coefficient model is not appropriate for this biologically mediated carbonate, and that a broader range of possible controls on shell chemistry needs to be tested.

Introduction

Wansard and Mezquita (2001) presented an intriguing time-series study of ostracode shell chemistry and its relationship to the hydro-environment through the seasonal cycle. Using monthly collections of a rapidly growing ostracode *Herpetocypris intermedia*, they drew the following conclusions about the factors controlling the molar Sr/Ca and Mg/Ca ratios of ostracode shell calcite. (1) Both Sr/Ca_{shell} and Mg/Ca_{shell} are best correlated with elemental ratios in the water. (2) Both Sr/Ca_{shell} and Mg/Ca_{shell} are very sensitive to small changes in their respective elemental ratios in the water, i.e., water ratio changes are amplified in the shell chemistry. (3) Both Sr/Ca_{shell} and Mg/Ca_{shell} are negatively correlated with the ambient salinity for the pond they studied. (4) Mg/Ca_{shell} ratio does 'not depend, or only in a weak manner, on water temperature changes'.

While we do not question what is clearly a very high quality data set, we suggest that their interpretation is

not borne out by their data. Our statistical analysis of their data set considers a range of factors that may influence Sr/Ca_{shell} and Mg/Ca_{shell} that is wider than that of the original paper. Here we compare the shell chemistry to a number of factors: temperature, the concentration of the minor element in the water, Sr/Ca_{water}, Mg/Ca_{water} and salinity. We also test a multiple regression model to see if shell chemistry correlates with the interaction of two of these variables.

Partition coefficients

Prior work on ostracode shell chemistry has often assumed that a distribution coefficient or partition coefficient is the most appropriate way to model minor element concentrations. The partition coefficient for magnesium is:

$$D(\text{Mg}) = \text{Mg/Ca}_{\text{shell}} / \text{Mg/Ca}_{\text{water}} \quad (1)$$

Where $D(\text{Mg})$ the magnesium partition coefficient (or distribution coefficient if using the ratio of activities of cations in solution) and Mg/Ca is the molar ratio. It has been suggested that this partition coefficient is affected by temperature (Chivas et al., 1983, 1985, 1986a, 1986b) and perhaps changes significantly in different ranges of the $\text{Mg}/\text{Ca}_{\text{water}}$ spectrum (Engstrom & Nelson, 1991, DeDecker et al., 1999). The $D(\text{Sr})$ is thought to not be significantly affected by temperature (Chivas et al., 1983, 1986a).

The use of partition or distribution coefficients presupposes that changes in water molar ratios are reflected proportionally in the shell chemistry. We question whether this is the case in ostracode shells. The partition coefficient model has proven hard to verify in either the lab or the field. Chivas et al. (1986a) argued that $\text{Mg}/\text{Ca}_{\text{water}}$ had very little effect on the shell chemistry, showing that a 50-fold increase in $\text{Mg}/\text{Ca}_{\text{water}}$ led to only a factor of 2 increase in $\text{Mg}/\text{Ca}_{\text{shell}}$. Surprisingly, the same authors produced a second paper that year (Chivas et al., 1986b) modeling ostracode shell Mg as a partition coefficient. Engstrom and Nelson (1991) used a partition coefficient to explain the chemistry of cultured *Candona rawsoni* valves and showed a $D(\text{Mg})$ that increased with increasing temperature. Xia et al. (1997), also working with *Candona rawsoni*, measured very different $D(\text{Mg})$ 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. Other workers have argued that partition coefficients are species dependent, and can vary widely within the same genus and (as above) within different populations of the same species (Holmes, 1992; Wansard, 1996; Wansard et al., 1998; De Deckker et al., 1999).

Even in inorganic calcite the determination of partition coefficients for Mg into calcite has proven to be highly problematic in naturally occurring carbonates (Given & Wilkinson, 1985) and carefully controlled studies of inorganic calcites have shown that this system is extremely complex, strongly influenced by other ions in solution (summarized in Morse & Bender, 1990; see also Huang & Fairchild, 2001). We have argued elsewhere that great caution should be used in applying a partition coefficient model to a biologically-mediated calcite (Palacios-Fest, 1996, Palacios-Fest & Dettman, 2001). In ostracodes biological processes seem to play a large role in the addition of Mg to shell calcite. The strong influence of biological 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, calcium content increases until the fully calcified valve has a Mg/Ca molar ratio that is typically less than 0.04. Chivas et al. (1986a) report values as high as 400,000 and 152,000 ppm Mg in poorly calcified valves, representing a Mg/Ca molar 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.

Biological controls?

Unusually elevated (Mg) in the earliest calcite suggests that metabolic fluids play a role in the formation of ostracode valve and that these fluids seem to be enriched in Mg. Fassbinder (1912) was able to culture fully-calcified *Cypridopsis vidua* 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 prior to molting (Mann & Pieplow, 1938). In at least one crustacean species, the crayfish *Procambarus clarkii*, temperature strongly affects the Mg concentration in body fluids (de Legarra et al., 1985). Researchers favoring a partition coefficient model of shell chemistry have pointed to the study of Turpen and Angell (1971) who concluded 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. It also demonstrated the importance of biological processes in shell formation, where outer lamellar cells played an active role in triggering and driving calcification. Because Turpen and Angell did not monitor minor elements, such as Mg or Sr, we suggest that this paper adds little weight to those who wish to model minor element distributions based on a simple aqueous partitioning into calcite.

Finally, we note that ostracode valves typically fall into the 0.01–0.04 range of molar Mg/Ca ratios, and that 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 ratio covers more than 3 orders of magnitude. A partition coefficient model would predict a similar 3 order of magnitude range in shell chemistry. Hence the Mg/Ca ratio of water cannot be a significant factor in determining the Mg/Ca ratio of ostracode valves.

Testing environmental factors

Therefore, given that biological effects may play a significant role in the elemental composition of ostracode valves, we argue that a wider array of factors should be considered as possible controls. Wansard and Mezquita (2001) tested shell chemistry against the Sr/Ca and Mg/Ca ratios of the water and against salinity. Although they described the use of partition coefficients to model shell chemistry, they did not try to calculate partition coefficients from their data. Given the importance of biological processes, we suggest that testing shell chemistry against temperature and the availability of Mg or Sr in the water, $[Mg]$ $[Sr]$, would also be appropriate. We therefore compare shell chemistry to T , Mg/Ca_{water} or Sr/Ca_{water} , partition coefficients, $[Mg]$ or $[Sr]$, and salinity. We will limit our discussion here to adult valves, in keeping with many other calibration and paleoenvironmental studies. In performing some of these comparisons, Wansard and Mezquita (2001) found that the correlations were improved by averaging water conditions at the time of shell collection with the prior month's conditions. This seems appropriate because the shells may have been produced at any time during the prior month, given the rapid development of this species (Mezquita, 1998). Table 1 shows the Pearson correlation coefficient (r) for Mg/Ca_{shell} and Sr/Ca_{shell} in adults against the above variables at the time of collection, and for the average of the collection time and the previous month. Note that correlations are significantly improved for all comparisons when using the averaged water data.

Based on the correlation results in Table 1, we can see that both Mg/Ca_{shell} and Sr/Ca_{shell} are best correlated with temperature. Although temperature is widely acknowledged as an important factor in Mg/Ca_{shell} , Sr/Ca_{shell} is often described as being temperature independent (Chivas et al., 1983, 1985, 1986b). Wansard and

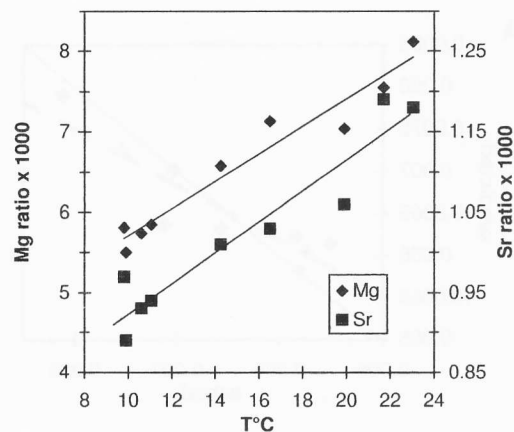


Figure 1. Both Mg/Ca_{shell} and Sr/Ca_{shell} are highly correlated with temperature.

Mezquita (2001) argued that the close correlation of Mg/Ca_{shell} with the presumed temperature independent Sr/Ca_{shell} implied that Mg/Ca_{shell} is not affected by temperature change, a conclusion clearly not borne out by the data, where both elemental ratios in the shell correlate with temperature. Mg/Ca_{shell} is highly correlated with temperature (Figure 1).

It is not clear if Wansard and Mezquita (2001) are comparing Mg/Ca_{shell} to temperature or $D(Mg)$ to temperature when they state "the observed variations in the mean Mg/Ca ratios for the Maiques *H. intermedia* specimens do not depend, or only in a weak manner, on water temperature changes". It is possible that they are arguing that there is no temperature dependence in the partition coefficients for magnesium and strontium. The correlation of temperature and calculated partition coefficient is relatively weak ($Mg: r = 0.594$ $Sr: r = 0.650$) and $D(Sr)$ has a slightly greater temperature dependence than $D(Mg)$. Nor does a single partition coefficient for either Mg or Sr predict the measured shell chemistry very well; in Figure 2 we have predicted shell chemistry using the average calculated partition coefficients: $D(Mg) = 0.0156 \pm 0.0010$ (1σ) and $D(Sr) = 0.220 \pm 0.017$ (1σ). In the case of Mg, the slope of the best fit line is 0.66 and the slope for Sr is 0.40. Using a single partition coefficient to predict shell chemistry from water chemistry or to back calculate water chemistry from shells would introduce significant errors. That these slopes deviate from 1 suggests that other factors play a role in controlling shell chemistry. By limiting discussion of these data to only the partition

Table 1. Pearson correlation coefficient for shell chemistry vs. hydro-environment of collection date

	M/Ca_{water}	$[M]$	$T^{\circ}C$	salinity
Time of collection conditions				
Mg/Ca_{shell}	0.640	-0.843*	0.932**	-0.885*
Sr/Ca_{shell}	0.243	-0.866*	0.834*	-0.755
Collection conditions averaged with prior month				
Mg/Ca_{shell}	0.906**	-0.888*	0.973***	-0.962***
Sr/Ca_{shell}	0.670	-0.934**	0.951**	-0.943**

[†]M is either Sr or Mg. *Significance: $p < 0.01$; ** $p < 0.001$; *** $p < 0.0001$.

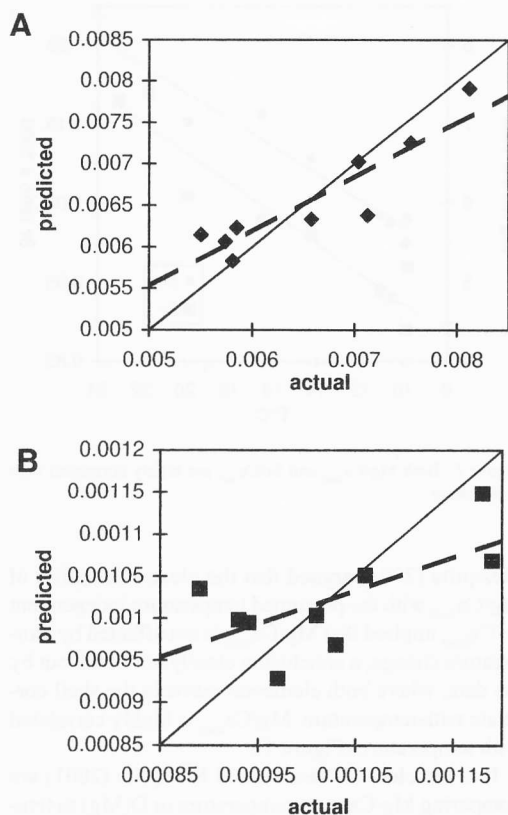


Figure 2. (A) A comparison of shell chemistry predicted from the average partition coefficient for Mg with the measured shell chemistry. See text for discussion. Solid line is where predicted = measured. Dotted line is the linear regression of predicted vs. measured. (B) The same comparison for Sr.

coefficient model for Mg/Ca_{shell} a very strong and potentially very valuable relationship is lost. The correlation between temperature and Mg/Ca_{shell} is clearly the strongest in this data set (Figure 1).

The Sr/Ca_{shell} results are puzzling in light of other studies that show little variation with temperature and the best correlation with Sr/Ca_{water} . The relationship to Sr/Ca_{water} here is relatively weak. Table 1 also shows a relatively good correlation of Sr/Ca_{shell} with [Sr] and salinity, although this is an inverse relationship. We do not know of other studies that have shown an increase in Sr/Ca_{shell} tracking a decrease in [Sr].

The primary conclusion of Wansard and Mezquita (2001) that shell chemistry is best correlated with Mg/Ca_{water} or Sr/Ca_{water} is also problematic. In both cases temperature correlates better with the variation in shell

chemistry. Because many of the components of the water chemistry in this study correlate with temperature, it is not possible to easily separate their influence on shell chemistry. In an attempt to statistically test the possible interaction of temperature and the other variables listed in Table 1 as controls on shell chemistry we ran a step-wise multiple regression model to describe Mg/Ca_{shell} and Sr/Ca_{shell} . In both cases, even with a significance probability threshold of 0.25, the only significant factor was temperature. The addition of other variables to the regression, even those very highly correlated with shell chemistry, did not significantly improve the description of shell chemistry.

Conclusions

In conclusion we have presented an alternative interpretation of the very useful data set of Wansard and Mezquita (2001). Our interpretation emphasizes the likelihood that biology, and especially the likely effect of temperature on metabolic rates and ionic uptake, plays a major role in controlling the minor element composition of ostracode valve calcite. A statistical examination of a wide variety of potential controlling factors shows that temperature explains almost all the variation in Mg/Ca_{shell} and Sr/Ca_{shell} . The salinity of the water was also inversely and highly correlated with both Mg/Ca_{shell} and Sr/Ca_{shell} . The elemental ratios of the water, Mg/Ca or Sr/Ca , do not explain the variability in the valves nearly as well as other factors. Auto-correlation between possible influencing factors in the data of Wansard and Mesquita (2001) makes it impossible to identify a single factor that is controlling shell chemistry. Temperature-invariant partition coefficients do a poor job of predicting shell chemistry (Figure 2). The correlation of temperature with calculated partition coefficient is relatively weak for both Mg ($r = 0.594$) and Sr ($r = 0.650$).

In two recent calibration studies of rapidly developing ostracode species, Wansard and Mezquita (2001) and Palacios-Fest and Dettman (2001), the magnesium content of ostracode shell is best correlated with water temperature. This suggests that, although the relationship must be calibrated for different taxa, Mg/Ca_{shell} has the potential to be a powerful paleothermometer, one that is independent of water chemistry. We have argued elsewhere, based on both culturing studies (Palacios-Fest, 1996; Cohen et al., 2000) and calibrations in natural systems (Palacios-Fest & Dettman, 2001), that Mg/Ca ratios can be used as a proxy for temperature.

Clearly more work needs to be done in this area of biologically mediated carbonates. Natural experiments, like the one under discussion here, are the best way to avoid the stresses and problems of an artificial culturing environment, but they are often prone to autocorrelation of environmental variables. In order to determine the dominant controls on ostracode minor element chemistry, systems must be found where temperature, water chemistry and salinity are statistically separable. The results of such studies, however, must not be forced into models of shell chemistry that have proved to be highly problematic.

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