Alkalinity control on the partition coefficients in lacustrine ostracodes from Australia

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ABSTRACT

The partition coefficients \( K_{\alpha} \) guiding the uptake of Mg and Sr in the low-Mg calcite valves of ostracodes in Australian saline lakes have been reviewed in line with new information on the bicarbonate content and the \( \alpha \)Mg/\( \alpha \)Ca of the ambient waters. Strongly alkaline and very high \( \alpha \)Mg/\( \alpha \)Ca \((>>20)\) waters cause the partition coefficients of ostracodes to differ significantly from those found in other lakes with lower \( \alpha \)Mg/\( \alpha \)Ca values. Water salinity does not affect the uptake of Mg or Sr in ostracode valves, whereas the \( \alpha \)HCO\(_3\) \(-\) of the water strongly correlates to \( K_{\alpha}[\text{Sr}] \), with high \( \alpha \)HCO\(_3\) \(-\) resulting in a significant \( K_{\alpha}[\text{Sr}] \) decrease.

INTRODUCTION

Trace metal substitution of Ca in the calcium carbonate system as proxies for reconstructing paleoenvironmental variables has been used wherever biogenic calcium carbonate is preserved. This technique has been used in studies of marine fossils to determine changes in temperature, salinity, terrestrial input, and many other factors, and has been utilized for a great number of calcium carbonate-secreting organisms, including foraminifera (for reviews see Eggins et al., 2003; Lea, 2003; Cusack and Freer, 2008), coccolithophores, mollusces, brachiopods (Cusack and Freer, 2008), corals (for reviews see Lea, 2003; Corrège, 2006; Cusack and Freer, 2008), fish otoliths (Bath et al., 2000), ostracodes (Corrège and De Deckker, 1997; Dwyer et al., 2002; for a review see Lea, 2003), and others. Trace metal substitution for calcium in calcite has been utilized in lacustrine environments using ostracodes (for reviews see Holmes and Chivas, 2002; Ito and Forester, 2009).

The uptake of bivalent cations replacing some Ca atoms during the calcification process in ostracodes is only beginning to be understood. The pioneering work of Turpen and Angell (1971) showed, using \( ^{40}\text{Ca} \) as a tracer, that ostracodes obtain Ca for their valves directly from the ambient water, and do not utilize Ca from old (molted) valve material. Following this, Chivas et al. (1983, 1985, 1986a, 1986b) and De Deckker et al. (1988) developed the use of trace metal substitution of Ca in the calcitic lattice as a tool for determining environmental change from limnic ostracodes.

Chivas et al. (1986b) showed that Mg incorporation into ostracode valves is primarily driven by the Mg/Ca\(_{\text{water}}\) and ambient water temperature, and that Sr incorporation is only related to the Sr/Ca\(_{\text{water}}\). However, De Deckker et al. (1999) showed that there may be a slight temperature effect guiding the uptake of Sr in ostracode valves, and concluded that water salinity is not the controlling factor in trace element uptake.

Assuming that ostracode calcite forms in thermodynamic equilibrium from a large volume of solution containing low concentrations of trace metals (Katz et al., 1972), then trace metal (Mg, Sr) incorporation at a given temperature \( T \) is dictated by the partition coefficient \( K_{\alpha}[\text{Me}] \) between the molar trace metal \( ([\text{Me}] = \text{any divalent cation} [\text{Mg}, \text{Sr}]) \) to Ca ratio \( (\text{Me}/\text{Ca}) \) of the water and the valves (Chivas et al., 1986a). However, in highly saline water, the ions bond temporarily, forming ion complexes that are not available for carbonate production (Hem, 1985). Consequently, it is assumed that the true concentration of ions available is the concentration of the active ions in the solution (activities, \( \alpha \)), and follows the relationship

\[
K_{\alpha}[\text{Me}]_T = (\text{Me}/\text{Ca})_{\text{water}}/[\alpha \text{Me}/\alpha \text{Ca}]_{\text{water}}. \tag{1}
\]

Several \( K_{\alpha}[\text{Mg}] \) and \( K_{\alpha}[\text{Sr}] \) have been determined for several lacustrine, estuarine, and marine ostracode species (for summary, see Holmes and Chivas, 2002), but only the thermodependence with respect to Mg was established for one species, Cyberideis australiensis (De Deckker et al., 1999). Other cations have been used variously to reconstruct environmental variables such as Fe and Mn (see Holmes, 1998) and U (see Ricketts et al., 2001).

Chivas et al. (1986a) proposed that cogenic species have identical \( K_{\alpha}[\text{Sr}] \), and that closely related genera, such as Australocypris and Mytilocypris from Australian lacustrine environments, share a similar \( K_{\alpha}[\text{Sr}] = 0.208 \); however, they found that \( K_{\alpha}[\text{Sr}] \) for Australocypris robusta in Lake Keilambete, a volcanic maar lake in western Victoria, has a very different \( K_{\alpha}[\text{Sr}] = 0.082 \) (Chivas et al., 1985).

Wansard (1996) and Wansard et al. (1998) showed that Cyberideis torosa from European lakes have very different \( K_{\alpha}[\text{Sr}] \) with a high degree of variation \((0.602–0.83)\) from the cogenic \( C. \) australiensis \((K_{\alpha}[\text{Sr}] = 0.475)\) from Australian waters (De Deckker et al., 1988). De Deckker et al. (1999) showed some variation in the \( K_{\alpha}[\text{Sr}] \) of \( C. \) australiensis \((K_{\alpha}[\text{Sr}] = 0.438)\) from their previous work (Chivas et al., 1986a). Wansard et al. (1999) showed that in Herpetocypris intermedia, a freshwater ostracode, the \( D(\text{Mg}) \text{ and } \text{D(Sr)} (\text{D(\text{Me}) implies a constant solution composition during mineral precipitation}) \) varied with respect to the Mg/Ca of the water. Ito and Forester (2009) urged caution in using ostracode partition coefficients in paleoenvironmental reconstructions, stating a range of hydrological and physiological issues that affect the uptake of both Mg and Sr in ostracode valves.

Our investigation seeks to clarify the Chivas et al. (1985, 1986a) paradox between invariant cogenic Australian lacustrine ostracode partition coefficients and the very different partition coefficients of conspecifics in terms of hydrochemical variability. We reanalyze the Chivas et al. (1985, 1986a) partition coefficients from southeastern Australia (SEA) in light of new data from southwestern Western Australia (SWA) lakes.

METHODS

Because the methods presented in the paper are standard procedures, the methods are presented in the GSA Data Repository.\(^1\)

RESULTS

The \( K_{\alpha}[\text{Mg}] \) and \( K_{\alpha}[\text{Sr}] \) for the ostracode species belonging to the nektonic Australocypris, Mytilocypris, Diacypris, and Reticypris collected from SEA and SWA lakes are presented in Table DRI in the Data Repository.

For all Australocypris and Diacypris species collected from SWA and SEA lakes (Table DR1), the \( K_{\alpha}[\text{Mg}] \) from the SWA lakes is larger, as is the variation in \( K_{\alpha}[\text{Mg}] \). Most Mytilocypris species, however, have similar \( K_{\alpha}[\text{Mg}] \) values and variation in both SEA and SWA lakes (Table DR1), with the exception of \( M. \) mytiloides. The \( K_{\alpha}[\text{Mg}] \) values of Reticypris spe-

\(^{1}\)GSA Data Repository item 20100901, a description of the sites sampled and the methods used, and Table DRI (the \( K_{\alpha}[\text{Mg}] \) and \( K_{\alpha}[\text{Sr}] \) determined from a number of nektonic ostracode species from southeastern and southwestern Australian lakes), is available online at www.geosociety.org/pubs/ft2010.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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cies do not vary at all between regions, and have similar means and variances (Table DR1).

Determination of species $K_{i}[\text{Sr}]$ for SEA and SWA demonstrates that there is a regional difference in the $K_{i}[\text{Sr}]$ between A. insularis collections (Table DR1). Little variability occurs between Western Australia species of Mytilocypris, although a high variability occurs within species from SEA lakes (Table DR1). The overall means of $K_{i}[\text{Sr}]$ for all Mytilocypris species in the two regions are very similar (SEA $K_{i}[\text{Sr}] = 0.3045 \pm 0.2309$ and SWA $K_{i}[\text{Sr}] = 0.2924 \pm 0.113$).

The $K_{i}[\text{Sr}]$ values of Diacypris species determined from SWA lakes are systematically higher than those from SEA lakes (Table DR1). Individual species comparisons show that D. spinosa differs significantly between regions; however, there is no significant regional difference in D. compacta $K_{i}[\text{Sr}]$ (Table DR1). The reverse is true of the Reticypris species analyzed between the two regions, the specimens analyzed from SEA lakes (Table DR1). The overall means of $K_{i}[\text{Sr}]$ for all Reticypris species of $\text{Mg}/\text{Ca}$ increased with higher Sr/Ca of water.

DISCUSSION

The variation in $K_{i}[\text{Mg}]$ and $K_{i}[\text{Sr}]$ suggests that the mechanism of trace metal incorporation in ostracodal calcite may vary between SEA and SWA. Several authors (Xia et al., 1997, for Candona rawsoni; Wansard et al., 1998, for several other Candona species and Cyprideis torosa; Wansard et al., 1999, for Herpetocypris intermedia) found that the $K_{i}[\text{Mg}]$ and $K_{i}[\text{Sr}]$ varied with water chemistry. Xia et al. (1997) found that Mg/Ca of C. rawsoni varied most with respect to temperature and that $K_{i}[\text{Sr}]$ increased with higher Sr/Ca of water and Mg/Ca of water. Wansard et al. (1998), however, showed that $K_{i}[\text{Mg}]$ decreased as Mg/Ca of water increased for three Candona species, and that the $K_{i}[\text{Sr}]$ for Cyprideis torosa differed significantly from De Deckker et al.’s (1999) work on Cyprideis australiensis. Wansard et al. (1999) also showed that the $K_{i}[\text{Mg}]$ of Herpetocypris intermedia (a freshwater species) was constant as Mg/Ca of water increased above 1, and that the variability and value of $K_{i}[\text{Sr}]$ increased when Mg/Ca of water decreased. De Deckker et al. (1999) clearly showed that the $K_{i}[\text{Mg}]$ and $K_{i}[\text{Sr}]$ of C. australiensis did not vary as a function of salinity.

Chivas et al. (1985, 1986a) suggested that the unique water chemistry of Lake Keilambete in SEA with high salinity (ranging from 71.5 to 74 g/L), high Mg/Ca of water (89), high HCO$_3$ (2180 meq/L), and negligible SO$_4$ may be related to the lower $K_{i}[\text{Sr}]$ of A. robusta found in this lake (0.082 ± 0.0051) compared with the $K_{i}[\text{Sr}]$ of Australocypris and Mytilocypris species found in other SEA lakes (0.208 ± 0.048).

Figure 1 shows the variation in water chemical parameters for both SWA and SEA lakes, with very little variation in $\alpha$Mg/$\alpha$Ca of water (Figs. 1A and 1B) and $\alpha$Sr/$\alpha$Ca of water (Figs. 1C and 1D), with salinity for both regions. Similarly, comparison of Mg/Ca of valve (Figs. 1E and 1F) and Sr/Ca of valve (Figs. 1G and 1H) with salinity shows no significant relationship. This confirms that, for Australian lacustrine ostracodes, De Deckker et al.’s (1999) suggestion for C. australiensis that Sr/Ca of valve is not a function of salinity, but is in fact a function of $\alpha$Sr/$\alpha$Ca of water (Figs. 1K and 1L); similarly, Mg/Ca of valve is not a function of salinity, but is weakly a function of $\alpha$Mg/$\alpha$Ca of water (Figs. 1I and 1J) and the high variability is due to the temperature effect on Mg incorporation (Chivas et al., 1986a, 1986b).

As mentioned previously, however, the $K_{i}[\text{Mg}]$ and $K_{i}[\text{Sr}]$ of ostracodes vary in both value and amplitude for both species and genera.
between SWA and SEA. Figure 2 shows combined $K_d[\text{Mg}]$ and $K_{\text{Sr}}$ for both SWA and SEA versus salinity (g/L), $\alpha\text{Mg/\alphaCa_{water}}$ and $\alpha\text{HCO}_3^-$ (Figs. 2C–2F). Both $K_d[\text{Mg}]$ and $K_{\text{Sr}}$ for all Australian lacustrine species examined here show a weak decrease at first as salinity increases (Figs. 2A and 2B). At low salinity values (<20 g/L), the variability in partition coefficients is high (Figs. 2A and 2B), but then values are scattered. The variability in $K_d[\text{Mg}]$ and $K_{\text{Sr}}$ is relatively uniform above a salinity of 20 g/L. This suggests that uniform $K_d[\text{Mg}]$ and $K_{\text{Sr}}$ can be applied to reconstruct paleoenvironmental variables from ostracode valve chemistry (Chivas et al., 1986a). However, the values and variability of $K_d[\text{Mg}]$ decrease as $\alpha\text{Mg/\alphaCa_{water}}$ increases (Fig. 2C).

The decrease in $K_d[\text{Mg}]$ with increasing $\alpha\text{Mg/\alphaCa_{water}}$ suggests that the physiological mechanism for secreting low-Mg calcite in Australian lacustrine ostracodes is a tradeoff between the physiological control of Mg uptake in high $\alpha\text{Mg/\alphaCa_{water}}$ and the thermodependence on the Mg uptake in low $\alpha\text{Mg/\alphaCa_{water}}$. This implies that the influence of temperature on Mg uptake diminishes as $\alpha\text{Mg/\alphaCa_{water}}$ increases, and is replaced by physiological control. A similar result has been found for the freshwater species *Herpetocypris intermedia* in low (<4) Mg/Ca water cultures (Wansard et al., 1999) and *Candona* species in a range of Mg/Ca water values (Wansard et al., 1998).

The value and variability of $K_{\text{Sr}}$ also decrease with increased $\alpha\text{Mg/\alphaCa_{water}}$ as $\alpha\text{Mg/\alphaCa_{water}}$ approaches 110 (Fig. 2D). In the two lakes with $\alpha\text{Mg/\alphaCa_{water}} > 110$ (Lake Purdigulac $\alpha\text{Mg/\alphaCa_{water}} = 115$; Lake Coragulac $\alpha\text{Mg/\alphaCa_{water}} = 316$, both in western Victoria, SEA), both of which have highly evolved waters, the $K_{\text{Sr}}$ increases substantially ($K_{\text{Sr}} = 0.566 \pm 0.06$ for Lake Purdigulac and $K_{\text{Sr}} = 0.956 \pm 0.092$ for Lake Coragulac). This suggests that $\alpha\text{Mg/\alphaCa_{water}}$ is not the primary controlling factor in the variability in $K_{\text{Sr}}$. Wansard et al. (1998) examined $K_{\text{Sr}}$ variability with respect to Mg/Ca water and found no systematic variation; however, they only analyzed waters with Mg/Ca < 15. Australian lacustrine ostracodes show a similar non-relationship for $\alpha\text{Mg/\alphaCa_{water}} < 15$.

Figures 2E and 2F show that with increasing $\alpha\text{HCO}_3^-$, the variability in $K_d[\text{Mg}]$ and $K_{\text{Sr}}$ decreases. SWA analyses are all from waters with a low $\alpha\text{HCO}_3^-$ and display very high variability, whereas SEA analyses vary from low to high $\alpha\text{HCO}_3^-$ and the variability decreases with increasing $\alpha\text{HCO}_3^-$. Exceptions to this are the analyses of $K_d[\text{Mg}]$ and $K_{\text{Sr}}$ of *M. splendida* in very shallowLesser Twin Lake in SEA ($\alpha\text{HCO}_3^- = 0.045$) that show a high degree of variability. East Basin Lake and Lake Keilambete in SEA also recorded high $\alpha\text{HCO}_3^-$ concentrations on two of the three sampling occasions (East Basin Lake = 0.0195 and 0.0247; Lake Keilambete = 0.018 and 0.0232), and the $K_{\text{Sr}}$ variability was low in both lakes. This suggests that if the $K_{\text{Sr}}$ analyses of Lesser Twin Lake are ignored, the $\alpha\text{HCO}_3^-$ water appears to influence the $K_{\text{Sr}}$. Lesser Twin Lake had only 10 cm of water at the time of collection and the water’s ionic ratio may have varied between the time of ostracode calcification and water and ostracode collection.

**Mechanism for HCO$_3^-$-Induced Partition Coefficient Variability**

A mechanism behind the systematic variation in $K_d[\text{Mg}]$ with $\alpha\text{HCO}_3^-$ water documented here was presented by Paquette and Reeder (1995), who described a model of calcite growth in which crystal growth occurs on the [10T4+] face by the spiral mechanism. The spiral mechanism causes a microtopographic relief with randomly distributed pyramidal hillocks that comprise two characteristically similar pairs (a and b, a′ and b′) of vicinal faces that vary slightly in orientation (±1°) from the [10T4+] face; Paquette and Reeder (1995) found that Mg enrichment always occurred on the a′ and b′ vicinal faces, and Sr enrichment on the a and b vicinal faces. This enrichment in trace metals of each vicinal face is related to kink structures that are caused by the Ca$^{2+}$ and CO$_3^{2-}$ coordination in the crystal structure. Paquette and Reeder (1995) also found that the degree of supersaturation of calcite in the precipitating solution (ranging from 8 to 20 times calcite saturation) and, more important, the $\alpha\text{Ca$^{2+}$/\alphaCO}_3^{2-}$ of the precipitating solution (ranging from 100 to 30,000 in their experiments) influenced the shape of these hillocks, with increasing $\alpha\text{CO}_3^{2-}$ in the precipitating solution resulting in less differentiation between the pairs of vicinal faces. The $\alpha\text{CO}_3^{2-}$ increase in the solution also caused a decrease in the relative growth of a′ and b′ vicinal faces, thus reducing the uptake of Sr. All of the Paquette and Reeder (1995) experiments were conducted at 28 ± 2 °C, and so comment on the temperature influences of Mg uptake into the a′ and b′ vicinal faces cannot be made.

This microstructural analysis of trace metal incorporation in calcite has fundamental implications for ostracodal $K_d[\text{Mg}]$ in lacustrine systems in SEA lacustrine systems. In pH-buffered lacustrine systems with elevated $\alpha\text{HCO}_3^-$, such as SEA lakes (Radke et al., 2003), increases in $\alpha\text{CO}_3^{2-}$ are expected, and as Paquette and Reeder (1995) found, elevated $\alpha\text{CO}_3^{2-}$ suppresses trace metal, in particular Sr, incorporation into the calcitic lattice during crystal growth. The implication for ostracodal $K_d[\text{Mg}]$ is that as $\alpha\text{HCO}_3^-$ increases, trace metal incorporation into ostracode calcitic valves will be suppressed, regardless of the $\alpha\text{Me/\alphaCa}$ water. This results in decreased $K_d[\text{Mg}]$ in $\alpha\text{HCO}_3^-$-enriched waters.

The biominalization of several ostracode species was investigated by Keysel and Walter (2004); they showed that calcium mobilization from inside epidermal cells into the calcite valves changed morphology and that calcium underwent at least one chemical transformation, from calcium phosphate to calcium carbonate. The microenvironment in which these chemical and morphological transformations occur must be the result of

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**Figure 2. Plots of combined southeastern Australia and southwestern Western Australia data showing relationship between ostracode $K_d[\text{Mg}]$ (on left) and $K_{\text{Sr}}$ (on right). A, B: Against TDS (total dissolved solids equivalent to salinity, g/L), C, D: Against $\alpha\text{Mg/\alphaCa_{water}}$. (Inset in C enlarges 0–30 $\alpha\text{Mg/\alphaCa_{water}}$ range), E, F: Against $\alpha\text{HCO}_3^-$ water.**
subtle chemical variations. Comprehension on how ostracodes secrete their valves and the biophysical and biochemical changes during this calcification is still in its infancy and more research is required before a holistic system-based understanding is gained.

CONCLUSION

The K_α[Mg] and K_α[Sr] of several Australian saline lacustrine ostracode species are shown to vary between southeast Australia and southwest Australia, both in terms of mean values and in the degree of variability. As the αMg/αCafractions increases above ~50, the Mg uptake by ostracodes has a reduced thermodependence, and so K_α[Mg] can be utilized as an indicator of αMg/αCafrac. When αMg/αCa < 50, K_α[Mg] depends both on αMg/αCa and temperature at the time of calcification. In low αHCO_3 water, the K_α[Sr] is higher and more variable than in waters with high αHCO_3. This suggests that at low αHCO_3 water, the K_α[Sr] does not accurately reflect the αSr/αCafrac. At the opposite, at greater αHCO_3 water, the K_α[Sr] variability decreases, suggesting that it can be used as an accurate indicator of αSr/αCafrac. Across all salinities, the Sr/Cafrac is clearly a poor indicator of salinity in Australian lacustrine ostracodes.

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