

The response of ostracod shell chemistry to seasonal change in a Mediterranean freshwater spring environment

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Abstract

We established the relationships between water chemistry changes in a pool fed by a permanent spring and seasonal variations in trace-element contents (Sr & Mg) in the shells of the ostracod species *Herpetocypris intermedia*, based on monthly collections of ostracod and water samples. The water chemistry of the investigated pool (Maïques, València, Spain) was dominated by calcium and bicarbonate, and showed marked seasonal variation in alkalinity, Ca²⁺ content, Sr/Ca and Mg/Ca ratios. Although the variability in the water chemistry was relatively low (~10% relative standard deviation over the entire period), the trace-element contents in the ostracod shells tracked the seasonal change in the water chemistry of Maïques pool. Moreover, due to the rapid renewal of *H. intermedia* population, this species is able to record in its shells the evolution of the water chemistry at a monthly time scale. Our results also showed that, in the Maïques pool system, ostracod Sr/Ca and Mg/Ca ratios increased with the decrease in water salinity.

To our knowledge, this is the first geochemical study of ostracods dwelling in spring environments. The results of this study may be applied to paleohydrological reconstruction using ostracods preserved in sediments deposited around springs (i.e., travertine and tufa deposits).

Introduction

Trace-element geochemistry of ostracod shells is a recently developed method, increasingly used to infer past environmental conditions in diverse water bodies (e.g., Dwyer et al., 1995; Holmes, 1996; Corrège & De Deckker, 1997; Xia et al., 1997b; Hu et al., 1998). The interest in this method was initiated by the works of Chivas et al. (1983, 1985, 1986a,b) who showed quantitative relationships between trace-element contents (i.e., Sr/Ca and Mg/Ca) of lacustrine ostracod shells and the chemistry and temperature of the host water.

Ostracods are microscopic crustaceans that are characterised by a bivalved carapace made of low-Mg calcite. They live in marine and continental waters depicting a wide range of salinity, aquatic composition

and temperature conditions. Ostracods moult their shell up to eight times before reaching adulthood. Immediately after each moult, they calcify rapidly new shells, over a period of a few hours (Turpen & Angell, 1971) to a few days (Roca & Wansard, 1997). The calcium, and trace-elements such as Sr and Mg, are taken directly from the host water at the time of shell formation (Turpen & Angell, 1971; Chivas et al., 1983). Consequently, trace-element contents recorded in ostracod shells may be related to environmental changes that occur at a very short time scale (i.e., seasonal). Thus, a knowledge of the life history of the studied species is required to enhance the palaeo-environmental interpretation of trace-element contents in ostracod shells (Xia et al., 1997a).

The study of links between geochemistry of freshwater ostracod shells and environmental parameters has only

rarely been undertaken on animals moulting in the field, following a seasonal sampling programme (Xia et al., 1997a). Moreover, to our knowledge, no detailed geochemical study has been undertaken on ostracods dwelling in spring environments despite the fact that sediments deposited around springs (i.e., travertine and tufa deposits) are important archives of the Holocene hydrological change (Goudie et al., 1993).

In this paper, the relationships between water chemistry and temperature changes in a pool fed by a permanent spring and variations in ostracod trace-element ratios for *Herpetocypris intermedia* Kaufmann 1900, a common inhabitant of bicarbonate-rich springs, are discussed. The work is based on monthly collections (from December 1995 to September 1996) of ostracods living in the Maïques spring (València, Spain).

The freshwater ostracod *H. intermedia* inhabits pools, springs and rivers (Mezquita et al., 1999 a,b). Extensive collection of ostracods in a wide variety of springs in the València area provided the following ecological preferences for *H. intermedia* (Mezquita et al., 1999 a): average water temperature of 15 °C (5–20 °C range), alkaline waters with conductivity less than 1 mS cm⁻¹, water Mg/Ca ratios ranging from 0.1 to 1, and pH values ranging from 7.2 to 8.5.

In Maïques pool, Mezquita (1998) showed that the population of *H. intermedia* was renewed in nearly a half yr. This feature of its population dynamic offers the opportunity to test the response of shell chemistry to rapid environmental changes occurring in the studied pool.

Site description

The Maïques spring is located in eastern Spain (38 ° 55' 49" N; 0 ° 24' 37" W) at an altitude of 180 m a.s.l. The area has a Mediterranean climate with average

annual rainfall of 601 mm (Pérez, 1994). Average monthly temperature recorded during the study period at the observatory of La Pobla del Duc (close to Maïques) ranged from 8.7 °C in February to 24.2 °C in August.

The Maïques spring is a permanent helocrene freshwater spring. Just beyond (< 0.5 m) the water source, the spring is artificially transformed in three consecutive rectangular rock pools. Ostracods were collected from pool 3 (dimensions: 82 × 1230 × 58 cm) which is 6 m far from the spring discharge. This pool is characterised by the development of characae and filamentous algae.

Materials and methods

Ostracods and water samples were collected monthly, from December 1995 to September 1996. Ostracod samples were taken at the centre of the pool with a 100 µm mesh size hand net over an approximate area of 0.075 m². The material collected was fixed in 70% ethanol. In the laboratory the ostracods were picked up from the field collections and identified under a binocular microscope.

Water temperature, pH, conductivity, alkalinity and dissolved oxygen were measured *in situ*. The collected water samples were analysed for sulphate and chloride contents following standard methods (APHA, 1985), and for Ca²⁺, Mg²⁺ and Sr²⁺ contents by DCP spectrometry.

Trace-element analyses were performed on adult and A-1 (i.e., the last juvenile stage) shells of the *H. intermedia* species. Shells were washed in a 10% H₂O₂ solution heated at 80 °C during a maximum of 10 min to eliminate organic materials, rinsed in de-ionised water and air dried. The carapace (= two valves) of each specimen (adult or juvenile) was subsequently dissolved in 5 ml of tri-distilled water mixed with 50 µl

Table 1. Chemistry of Maïques pool water from monthly collections

Sampling Date	Ca ²⁺	Mg ²⁺	Sr ²⁺	Cl ⁻	SO ₄ ²⁻	Alk.	Sr/Ca	Mg/Ca	Cond.	Oxygen	pH	CSI	Temp.
			Mg l ⁻¹					meq l ⁻¹	molar	molar	µS cm ⁻¹	%	°C
95/12/20	135	32.35	1.39	48	151	6.80	0.00472	0.395	933	93	7.77	0.72	9.9
96/01/21	136	31.73	1.30	48	143	6.80	0.00439	0.384	652	90	7.82	0.80	11.3
96/02/21	147	32.59	1.31	47	124	7.60	0.00409	0.365	967	85	8.02	1.03	8.3
96/03/21	126	33.26	1.37	48	140	5.70	0.00496	0.436	883	216	7.98	0.89	13.8
96/04/22	132	30.34	1.20	43	129	6.15	0.00416	0.379	897	153	8.05	1.02	14.7
96/05/21	113	30.21	1.15	42	126	5.40	0.00466	0.441	814	225	7.57	0.49	18.3
96/06/20	109	30.57	1.17	37	110	5.30	0.00489	0.461	861	180	7.50	0.45	21.5
96/08/01	90	30.29	1.09	44	n.d.	4.45	0.00555	0.555	712	177	7.89	0.73	24.6
96/09/02	128	29.32	1.17	43	n.d.	6.00	0.00418	0.377	857	142	7.69	0.71	18.8

n.d.: not determined. Alk.: alkalinity. Cond.: conductivity. CSI: calcite saturation index.

of Merck Suprapur HNO_3 (65%) and with 100 μl of Merck Suprapur LiNO_3 (1000 ppm Li^+) in polystyrene tubes. The resulting solutions were analysed for Ca ($\lambda = 313.5$ nm), Sr ($\lambda = 460.73$ nm) and Mg ($\lambda = 279.5$ nm), using a plasma emission spectrometer (D.C.P.). No contamination caused by flasks, water, or the acid and lithium solutions was recognised in the blanks. A correction factor had to be calculated for the interference of Ca on Sr. For each specimen analysed, at least three measurements were made in one run for each element. Analytical precision, based on multiple analyses ($n = 7$) of a solution of 8 valves of *Cyprideis torosa* was $\pm 1.8\%$ RSD (relative standard deviation) for Mg, and $\pm 0.7\%$ RSD for Ca and Sr. Repetitive runs ($n \geq 5$) using standards of different concentrations gave a standard error of $\sim 5\%$ for Mg, and $\sim 2\%$ for Sr and Ca.

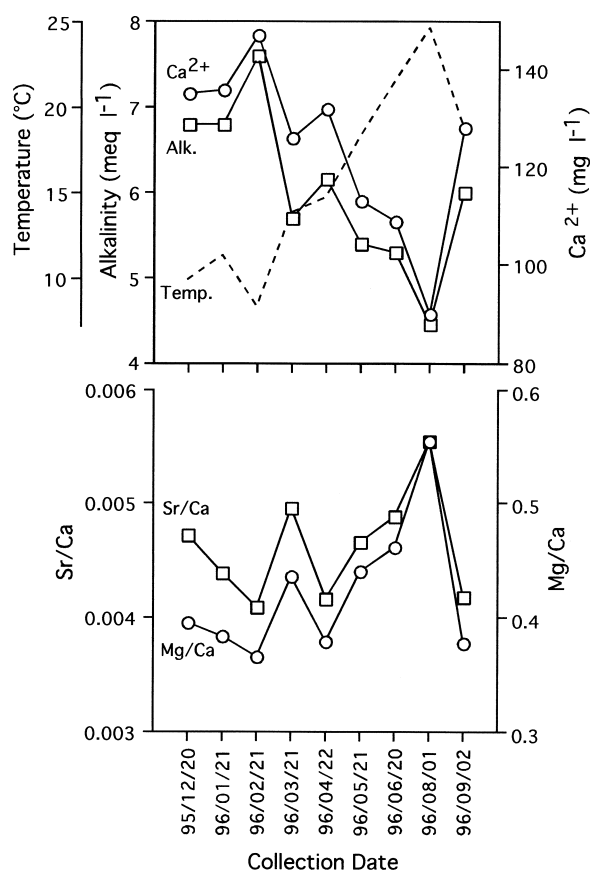


Figure 1. The changes in temperature, alkalinity, Ca^{2+} content, Sr/Ca and Mg/Ca ratios of Maïques pool water during the collection period.

Results

The water chemistry in the investigated pool is dominated by calcium and bicarbonate. The measured pH values ranged from 7.5 to 8.05, and conductivity from 650 to 967 $\mu\text{S cm}^{-1}$. The water samples collected monthly showed marked seasonal variation in alkalinity, Ca^{2+} content, Sr/Ca and Mg/Ca ratios (Table 1). Alkalinity and calcium content were negatively correlated with water temperature (Figure 1), oxygen content and calcite saturation index (CSI). The Sr/Ca ratios showed changes parallel to Mg/Ca ratios (Figure 1). Water Sr/Ca ratio ranged from 0.00409 to 0.00555, and water Mg/Ca ratio ranged from 0.365 to 0.555. Variations in water Sr/Ca and Mg/Ca ratios were respectively $\sim 10\%$ RSD (relative standard deviation) and $\sim 14\%$ RSD during the collection period. Bottom water temperature, measured at the collection time varied from 8.3 $^{\circ}\text{C}$ (in February) to 24.6 $^{\circ}\text{C}$ (in August).

The mean ostracod Sr/Ca ratio calculated for each monthly collection varied from 0.00090 to 0.00121 for juveniles, and from 0.00089 to 0.00119 for adults (Table 2). The mean Mg/Ca ratio calculated for each monthly collection varied from 0.00460 to 0.00775 for juveniles, and from 0.00550 to 0.00812 for adults. In a single monthly collection, the juvenile and adult ostracods showed 2–10% RSD variation in Sr/Ca, and 1.2–15% RSD variation in Mg/Ca (Table 2 and Figure 2). For

Table 2. Trace-element ratios of *H. intermedia* from Maïques pool collections

Sampling date	# animals	Mean(Sr/Ca) $\pm 1\sigma$ Molar ratios	Mean(Mg/Ca) $\pm 1\sigma$
Juveniles			
95/12/21	10	0.00091 \pm 0.00004	0.00460 \pm 0.00033
96/01/22	4	0.00090 \pm 0.00009	0.00480 \pm 0.00042
96/02/22	10	0.00096 \pm 0.00006	0.00499 \pm 0.00075
96/03/22	10	0.00100 \pm 0.00003	0.00517 \pm 0.00018
96/04/23	10	0.00098 \pm 0.00008	0.00596 \pm 0.00058
96/05/22	1	0.00101	0.00668
96/06/21	8	0.00102 \pm 0.00009	0.00743 \pm 0.00065
96/08/02	6	0.00121 \pm 0.00004	0.00775 \pm 0.00091
96/09/03	6	0.00114 \pm 0.00009	0.00695 \pm 0.00054
	65	0.00100 \pm 0.00011	0.00586 \pm 0.00125
Adults			
95/12/21	10	0.00089 \pm 0.00007	0.00550 \pm 0.00041
96/01/22	4	0.00093 \pm 0.00002	0.00574 \pm 0.00009
96/02/22	11	0.00097 \pm 0.00004	0.00581 \pm 0.00040
96/03/22	11	0.00094 \pm 0.00004	0.00585 \pm 0.00038
96/04/23	12	0.00101 \pm 0.00008	0.00658 \pm 0.00070
96/05/22	5	0.00103 \pm 0.00002	0.00713 \pm 0.00041
96/06/21	13	0.00106 \pm 0.00007	0.00704 \pm 0.00048
96/08/02	10	0.00118 \pm 0.00006	0.00812 \pm 0.00084
96/09/03	8	0.00119 \pm 0.00009	0.00755 \pm 0.00098
	84	0.00102 \pm 0.00012	0.00660 \pm 0.00104

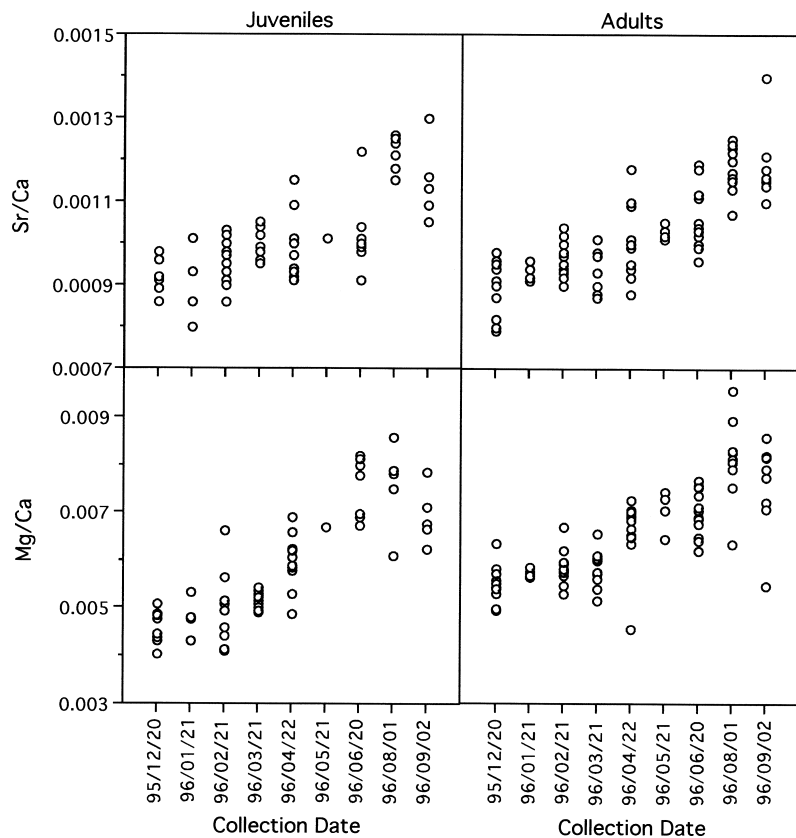


Figure 2. Plot of molar Sr/Ca and Mg/Ca ratios in individual *H. intermedia* for each monthly collection.

the whole study period, variation in Sr/Ca was $\sim 12\%$ RSD, both for juveniles and adults, and variation in Mg/Ca was 15.8% RSD and 21.3% RSD, respectively for adults and juveniles.

Discussion

The marked changes in water chemistry of the studied pool followed the seasonal evolution of water temperature that tracked air temperature. The decrease in alkalinity and calcium content with the increase of water temperature results from carbonate precipitation probably due to the photosynthetic activity of charophytes and algae. From February to August, the relative decrease in Ca^{2+} content was $\sim 40\%$, but only $\sim 15\%$ and $\sim 20\%$ respectively in Mg^{2+} and Sr^{2+} contents. This fact and the positive covariance between water Sr/Ca and Mg/Ca ratios reflect precipitation of low Mg-calcite, which is the expected carbonate phase precipitated in low water Mg/Ca ratios (Müller et al., 1972), from which Sr and Mg are excluded.

The relationship between trace-element contents in ostracod shells and the water properties controlling uptake of trace metals are expressed by a partition coefficient $D(M)$: $D(M) = (M/Ca)_{\text{ostracod shell}} / (M/Ca)_{\text{water}}$, where M is Sr or Mg, and (M/Ca) are molar ratios. The partition coefficient $D(\text{Sr})$ is a constant for all ostracod species within the same genus (Chivas et al., 1985), although De Deckker et al. (1999) have suggested that, at low temperature (i.e., $< 10^\circ\text{C}$), $D(\text{Sr})$ seems to show a weak thermodependence. The partition coefficient $D(\text{Mg})$ for an ostracod genus depends on water temperature (Chivas et al., 1986b; Engstrom & Nelson, 1991) and water Mg/Ca ratio (Xia et al., 1997a; Wansard et al., 1998). Thus the Mg content in ostracod shells is related both to water Mg/Ca ratio and temperature at the time of shell calcification.

The mean Mg/Ca values obtained for each monthly collection of *H. intermedia* calcified in the Maïques pool are highly correlated with the mean ostracod Sr/Ca values (Figure 3). Sr partitioning being considered as temperature independent, the observed variations in the mean Mg/Ca ratios for the Maïques *H. intermedia*

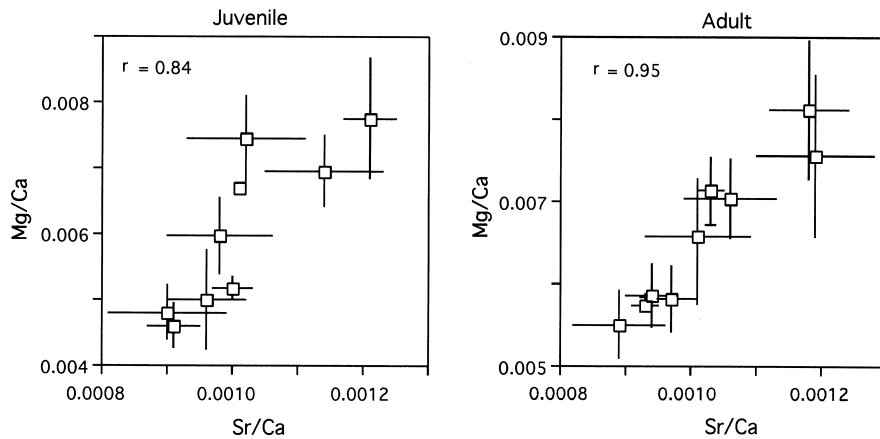


Figure 3. Plot of molar Sr/Ca against molar Mg/Ca ratios for juvenile and adult *H. intermedia*.

specimens do not depend, or only in a weakly manner, on water temperature changes. This result was also found by Wansard et al. (1999) that showed the absence of any temperature effect on $D(\text{Mg})$ in the shells of *H. intermedia* cultured in controlled laboratory conditions.

Temporal changes in average monthly ostracod ratios followed the general trend in water Sr/Ca and Mg/Ca (Figure 4). In details however, there was a weak correspondence between average monthly Sr/Ca and Mg/Ca ratios in ostracods and the same ratios in water. This discrepancy is not surprising because the chemical water was determined at the time of ostracod collection that did not correspond exactly to the time of ostracod calcification.

Results from the study of Mezquita (1998) showed that the population density of adult *H. intermedia* increased from January 1996 to August 1996 in the studied Maïques pool. For A-1 specimens, a similar population dynamic was observed, although their population density was minimum in May and June. Such minima may result from several phenomena: higher A-1 mortality, more A-1 individuals moulting to the adult stage, fewer A-2 individuals moulting to A-1 stage, or a combination of some of these factors. Whatever the case, the very good covariation between juvenile and adult trace-element ratios (Figure 4) seems to indicate that the renewal of the A-1 population followed a trend similar to the adult one. As a consequence, most of the collected adults and juveniles must have recorded in their shells the water conditions prevailing during the time spanning between two consecutive sampling dates. This hypothesis is supported by the high covariance obtained between the average monthly ostracod Sr/Ca and Mg/Ca ratios and

the moving average of the same ratios in the water (Figure 5).

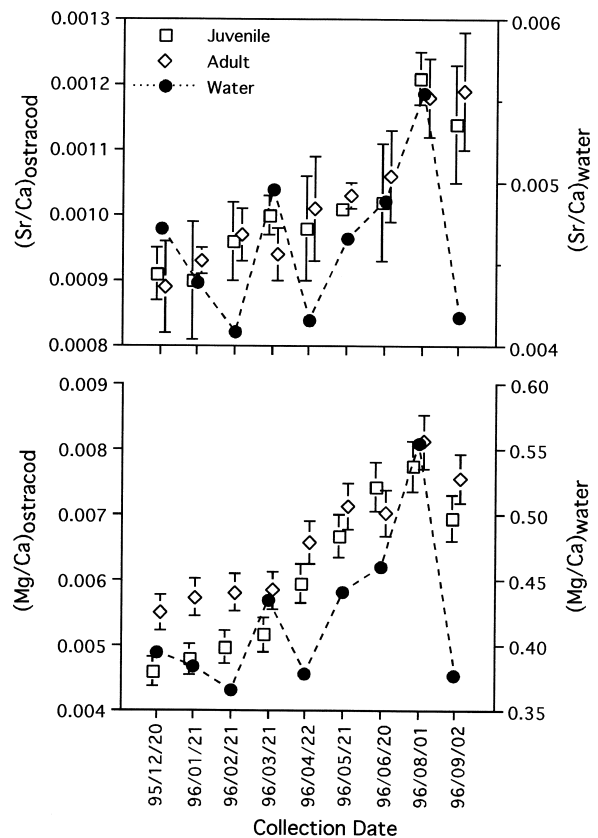


Figure 4. The seasonal changes of mean Sr/Ca and Mg/Ca ratios of live ostracods, compared with the seasonal changes in the corresponding ratios in the Maïques pool water.

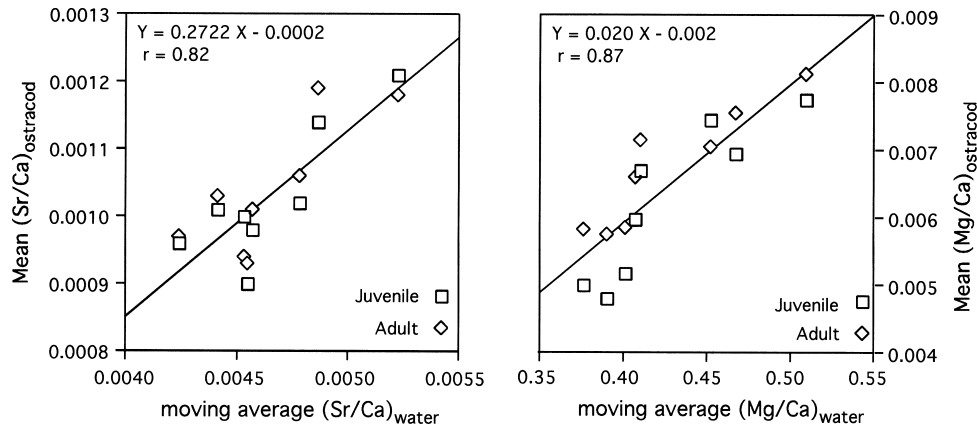


Figure 5. The covariance between the moving average water Sr/Ca (or Mg/Ca) ratios and the mean Sr/Ca (or Mg/Ca) ratios of juvenile and adult *H. intermedia*.

Our results show that *H. intermedia* is able to record the evolution of the water chemistry at a seasonal, and even in this case at a monthly time scale, thanks to the rapid renewal of its population. In that case, ostracod geochemistry may provide a better tool for monitoring the seasonal water chemistry changes than limited water analyses.

Implications for palaeohydrological reconstruction

Travertine and tufa deposits are important archives for reconstructing past hydrology and environmental changes, particularly during the Holocene (Griffiths & Pedley, 1995; Pentecost, 1995; Pedley et al., 1996; Sancho et al., 1997). Ostracods are often well preserved in great numbers in such deposits, and the study of their faunal assemblages provided palaeoecological and palaeohydrological information (Van Frausum & Wouters, 1990; Forester & Smith, 1992; Taylor et al., 1994; Cors et al., 1998).

Trace-element contents in the ostracod shells offer the opportunity to quantify such past changes. In particular, our results show that low variations in water chemistry (~10% RSD over the entire period) are tracked by trace-elements incorporated in ostracod shells. If sufficient individual fossil shells are analysed, both seasonal fluctuations and long-term variability in water chemistry can be significantly quantified, even if such variability is expected to be low as in some Holocene travertine deposits from temperate regions.

The water Sr/Ca and Mg/Ca ratios are expected to covary with salinity in water systems in which the concentration of Ca^{2+} is held constant by precipitation of calcite, and Mg^{2+} and Sr^{2+} are conservative ions (Engstrom & Nelson, 1991). In such conditions the Sr/Ca and Mg/Ca ratios measured in fossil ostracod shells will be a useful indicator of past salinity. However as warned by some authors (Engstrom & Nelson, 1991; Holmes et al., 1995; Holmes, 1996), the positive correlation between trace-element ratios and salinity is far from universal.

The Maïques pool water is oversaturated with respect to calcite, but the Ca^{2+} concentration obviously is not held constant during the studied period. The seasonal decalcification of the water (cf. Figure 1) probably results from the precipitation of calcite biogenically-mediated by characeae and algae.

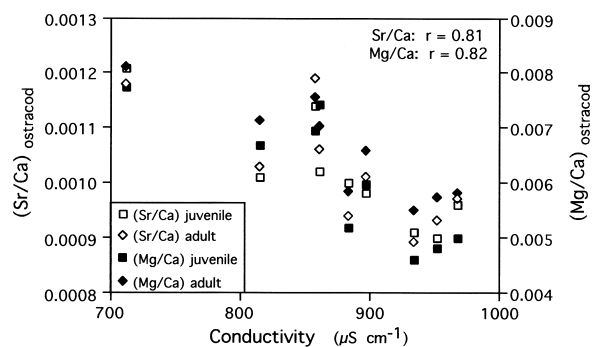


Figure 6. The relationship between Maïques water conductivity and mean Sr/Ca, and Mg/Ca ratios of juvenile and adult *H. intermedia*.

Whatever the case, water and ostracod Sr/Ca and Mg/Ca ratios increase with the decrease in Maïques water salinity (or conductivity) (Figure 6). This may be an important point to keep in mind for reconstructing palaeohydrological change based on trace element contents in ostracods of travertine deposits.

Conclusions

Our study of the shell chemistry of *H. intermedia* collected monthly in the Maïques pool showed:

- (1) the rapid response of the ostracod Sr/Ca and Mg/Ca ratios to the seasonal change in water. The technique could provide a better tool for monitoring the seasonal water chemistry changes than limited water analyses;
- (2) that the trace-elements incorporated in the ostracod shells are sensitive to low variability in water chemistry;
- (3) that the ostracod Sr/Ca and Mg/Ca ratios are negatively correlated with the salinity of the freshwater carbonate studied pool.

This work on spring dwelling ostracods also shows that future palaeoenvironmental works based on the geochemistry of ostracods preserved in tufa and travertine deposits are promising for reconstructing hydrological changes during the Holocene.

Studies aimed at understanding the hydrological context of a fossil tufa sequence, with the knowledge of the precise habitat and the seasonal life cycle of the studied ostracod species, are thus vital for the use of ostracod shell chemistry as a paleoenvironmental indicator.

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