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Geochemistry of ostracode calcite: Part 2. The effects of water chemistry and seasonal temperature variation on *Candona rawsoni*

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Abstract—Reconstruction of lake paleochemistry from the isotope and trace-element composition of fossil ostracodes requires an understanding of geochemical variations induced by the seasonality of shell formation. Monthly field collections of live *Candona rawsoni* from two hyposaline lakes in the eastern Dakotas reveal large variations in $\delta^{18}O$ values (2–5‰) and Mg/Ca and Sr/Ca ratios (up to 35%) among individual adults within the same assemblage. Because the measured variations in water chemistry were small, the amplitude of ostracode $\delta^{18}O$ and Mg/Ca variations must result from seasonal temperature variation. Ostracode Sr/Ca ratios, which should be temperature independent, shows strong positive covariance with shell Mg/Ca. These results imply that Sr uptake in ostracode calcite increases with the Mg content of the shell. The partitioning coefficient for Mg, on the other hand, appears to decreases at high values of Mg/Ca in the host water.

The geochemical variability in the field collections indicates that *C. rawsoni* populations are composed of multiple overlapping generations that attain maturity at different times. Many juveniles apparently undergo several molts in mid-summer and persist as penultimate instars (A-1) into the following spring. Geochemical analysis of late-instar juvenile *C. rawsoni* from lacustrine sedimentary records is likely to provide information on mid-summer conditions. Large numbers of fossil ostracodes should be analyzed from each stratigraphic interval to eliminate seasonal noise from the paleochemistry records of temperate-region lakes. *Copyright © 1997 Elsevier Science Ltd*

1. INTRODUCTION

Lacustrine ostracodes are common microscopic crustaceans having bivalved shells composed of low magnesium calcite that are commonly preserved as fossils in lake sediments. The fossil shells have been used as source material for geochemical analysis of stable-isotope and trace-element composition in paleolimnological reconstruction of lake hydrochemistry and climate (Lister, 1988; Engstrom and Nelson, 1991; Chivas et al., 1993; Curtis and Hodell, 1993). Laboratory experiments have shown that shell chemistry is controlled by the chemistry and temperature of the water from which the shells are formed (Chivas et al., 1983; Engstrom and Nelson, 1991; Xia et al., 1997b). However, to properly interpret the geochemical records preserved in ostracode shells, the life history of the species under investigation must be understood. The seasonality of molting and shell formation is particularly critical, as most lakes undergo intraannual temperature changes that far exceed the interannual to century-scale variations induced by late-Quaternary climate shifts; intraannual changes in lake chemistry are also significant in many shallow topographically closed-basin lakes. Unfortunately, relatively little is known about the seasonality of most ostracode species, whether shells are formed during a restricted season or throughout the year, and the variability that seasonality might induce in the geochemistry of fossil assemblages.

In this study we explore the seasonal variability in ostracode geochemistry ($\delta^{18}O$, $\delta^{13}C$, Mg/Ca, and Sr/Ca) for *Candona rawsoni,* a common euryhaline species with high potential for paleoenvironmental reconstructions in the North American Great Plains. This work is based on monthly collections of live ostracodes obtained during the 1991 growing season from Coldwater Lake, North Dakota USA and Roslyn Lake, South Dakota, USA. Trace elements and stable isotopes were analyzed from the same ostracode shells to examine potential covariance caused by seasonal changes in temperature and water chemistry. The $\delta^{18}O$ and δD of surface water from a suite of regional lakes were also determined, and their seasonal changes are considered in interpreting variability of isotopes in the ostracodes.

Candona rawsoni is a benthic organism with relatively broad environmental tolerance. It can withstand salinities up to 48‰ (Delorme, 1969a), although this upper threshold is only attained in lakes where SO_4^{2-} is the dominant anion (Forester, 1986). A dataset of sixty-six lakes from the Dakotas and Saskatchewan suggests a much lower salinity optimum (preferred range) of 1–10‰ (Engstrom and Nelson, 1991). Adult *C. rawsoni* are 1.1–1.4 mm long, and well-calcified shells weigh 60–100 μg (30–50 μg/single valve). Delorme (1969b) reports that hatching occurs in the spring. Ostracodes (including *C. rawsoni*) commonly have nine instars (including adult) and molt their bivalved shells eight times before maturity rather than growing them continuously like mollusks, so that the chemistry of a single shell represents environmental conditions only of the few days or hours during which it calcified. Most lakes in the northern Great Plains are small, shallow, and well-mixed, so that the water-column temperatures closely track average air temperatures

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experienced over several days to a week. Consequently, if *C. rawsoni* molts over a wide range of temperatures, the mean isotope and trace-element signatures of the population as a whole may give an integrated seasonal signal for both temperature and water chemistry. Thus, this seasonal weighting of signals recorded by *C. rawsoni* populations need to be critically assessed.

2. STUDY AREA

The lakes we investigated are located in the eastern part of the northern Great Plains (Fig. 1). Geologically the region is underlain by Cretaceous and Tertiary sedimentary units and is thickly blanketed by calcareous drift (Clayton, 1962). The study area is controlled by two major climatic gradients: an east-west trending precipitation-evaporation gradient and a north-south trending temperature gradient (Smith, 1991). The main source of precipitation for the study area is the Gulf of Mexico, and the annual water balance (precipitation-evaporation) is everywhere negative (−10 to −60 cm; Winter, 1989). The natural vegetation is prairie (native grasslands), although most of the landscape is now used for agriculture and grazing. There are thousands of lakes in the northern Great Plains spanning a salinity gradient from freshwater to hypersaline and varying from ephemeral playas to deep permanently stratified (meromictic) lakes. Their salinity and water chemistry depends on aquifer mineralogy and climatic setting. The dominant ions are Ca^{2-} and HCO_3^- in the fresher lakes, and the general trend is toward higher proportions of Na^+ and SO_4^{2-} in highly saline lakes (Hammer, 1978; Gorham et al., 1983; Fritz, 1990).

The water samples for $\delta^{18}O$ and δD analysis were taken from twenty-eight lakes scattered throughout the study area and ranging in salinity from 0.5 to 28‰. Three of them (Coldwater, Roslyn, and Pickerel lakes) were sampled more frequently to assess seasonal isotope changes in the lake water, and Coldwater and Roslyn were also sampled seasonally for ostracodes to determine the variability in shell chemistry. Coldwater Lake, located in McIntosh County, North Dakota, USA (46°01′N, 99°05′W), has a surface area of 0.5 km^2 and an average depth of 4.6 m (Fig. 1). Roslyn Lake is located in Day County, South Dakota, USA (45°32′N, 97°17′W) and has a 1 km^2 surface area and 2 m average depth. Both Coldwater and Roslyn are topographically closed-basin lakes with salinity of 3‰. The water chemistry in Roslyn Lake is dominated by Na_2SO_4 and that in Coldwater Lake by $MgSO_4$.

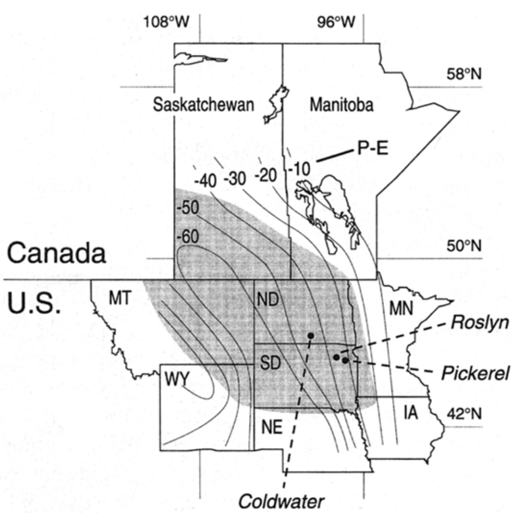

Fig. 1. Map of the northern Great Plains (shaded area) with the location of three studied lakes. Isolines are of equal precipitation minus evaporation, measured in cm yr^{-1}.

3. SAMPLES AND ANALYTICAL METHODS

3.1. Field Collection

Water samples were collected from the lakes (1 m above the bottom) in 1991 with an all-plastic Kemmerer sampler and stored under refrigeration in 60 mL Nalgene bottles for chemical analysis and 30 mL borosilicate bottles for isotope analysis. The samples were not filtered or acidified. Ostracodes were collected monthly by Ekman dredge from Coldwater Lake and Roslyn Lake from May to September in 1991. Successive collections within each lake were made at roughly the same location and depth. The mud-water interface was aspirated from the dredge samples with a suction device and wet sieved to remove fine-grained sediment; the ostracodes and coarse detritus were retained in lake water and stored on ice to induce torpor in the live ostracodes.

3.2. Ostracodes Selection and Cleaning

Live *Candona rawsoni* were aspirated from the field collections under 10× magnification of a dissecting microscope and stored in 100% ethanol for isotope and trace-element analysis. Ostracodes were identified according to Delorme (1970), and juveniles were separated from the adults. The shells were separated from soft tissues with dissecting needle, cleaned in 5% H_2O_2 at 80°C for 10 min, rinsed in triply-distilled water, and air dried on polycarbonate membrane filter in a laminar flow hood.

3.3. Isotope Analysis

The hydrogen isotope composition of lake water was determined from 2 to 5 μl samples that were reduced with 120 mg Zn (<1 mm and cleaned by 30% HNO_3) in Pyrex reaction vessels at 450 ± 10°C for one hour (modified from Kendall and Coplen, 1985). The evolved H_2 was measured by a Finnigan MAT delta E mass spectrometer. The oxygen isotope composition of lake water was measured on 5 mL samples equilibrated overnight with instrument-grade CO_2 (99.99%) at 25°C (Epstein and Mayeda, 1953). V-SMOW and SLAP were used as analytical standard samples. The precision was 1‰ for δD and 0.05‰ for $\delta^{18}O$.

For oxygen and carbon isotope composition of ostracodes, individual adults (one bivalved shell, ~80 μg) or a pooled sample of fifteen late-instar juveniles were reacted at 80°C for 30 min with 104% H_3PO_4, and the evolved CO_2 was measured by the delta E mass spectrometer. NBS-19 was used as analytical standard, and the precision was 0.2‰ for $\delta^{18}O$ and 0.1‰ for $\delta^{13}C$.

3.4. Preparation of Phosphoric Acid

One of the keys to sequential isotope/trace element analysis of the same ostracode sample is the cleanliness of the apparatus in contact with the acid and its reaction products and the purity of the orthophosphoric acid. We mixed ultra-pure P_2O_5 (99.998%) and triply-distilled water to obtain H_3PO_4 with a specific density of 1.92 g/cm^2 (104%), the optimum concentration to be used in the analysis. A pinch of chromic oxide (CrO_3) was added to oxidize impurities, and the solution was heated at 80°C under vacuum for two weeks.

3.5. Trace-Element Analysis

Lake water samples were analyzed for a complete suite of major ions by DC plasma atomic emission spectrometry (DCP-AES), ion chromatography (Cl^- and SO_4^{2-}), and coulometric titration (inorganic carbon). The trace-element analysis of ostracodes was conducted on the acid residue from the isotopic analysis. The solution of acid-reaction products from the isotope analysis was diluted once or twice (depending on quantity of the sample) with 0.5 M distilled HCl using externally-vibrated stirring. The diluted solution was measured on a Perkin Elmer/Sciex Elan 5000 inductively-coupled plasma mass spectrometer (ICP-MS) for unattended Ca, Mg, Sr, and Ba analysis. The mean precision of the analysis was about 2%. Because the acid-reaction residue was diluted to a known mass, not only could the ratios of Mg/Ca and Sr/Ca be determined, but also the absolute quantities of Ca, Mg, and Sr could be derived, and hence the calculated weight of $CaCO_3$, termed the nominal shell weight.

4. RESULTS

The water samples collected monthly from Coldwater Lake, Roslyn Lake, and Pickerel Lake in 1991 showed marked seasonal variation in Mg/Ca, Sr/Ca, $\delta^{18}O$, and δD (Table 1). The $\delta^{18}O$ of Pickerel Lake varied from −4.29 to −3.69‰, and δD varied from −38.2 to −33.3‰. $\delta^{18}O$ and δD in Coldwater Lake were higher than in Pickerel Lake and ranged from −2.39 to −0.61‰ and from −30.5 to −23.6‰, respectively. The $\delta^{18}O$ and δD in Roslyn Lake were close to those in the Coldwater Lake and ranged from −2.88 to −1.37‰ and −41.1 to −18.7‰, respectively.

The water Mg/Ca in Coldwater Lake ranged from 32 to 38 (molar ratio), whereas in Roslyn lake values were an order of magnitude lower and ranged from 2.5 to 3.1. The water Sr/Ca in Coldwater Lake and Roslyn Lake were 1.57–1.62 × 10^{-3} and 3.88–4.11 × 10^{-3} (molar ratio), respectively. Mg/Ca and Sr/Ca ratios of water in both lakes exhibited up to 10% variations during the collection period.

Water temperatures, measured each time ostracodes were collected, varied from 7.0 to 24.8°C in Coldwater Lake and 7.8 to 25.0°C in Roslyn Lake.

The $\delta^{18}O$, $\delta^{13}C$, Mg/Ca, and Sr/Ca values in both adult and juvenile ostracodes from Coldwater Lake and Roslyn Lake are listed in Tables 2 and 3. The adult ostracodes showed a 2–5‰ variation in $\delta^{18}O$ in a single monthly collection, and the juvenile ostracodes showed about 1.0–1.5‰ variation in both lakes. $\delta^{13}C$ of adult ostracodes in monthly collection from both lakes had 1–3‰ variation, whereas juveniles only showed 0.5‰ variation and were isotopically heavier. Both Mg/Ca and Sr/Ca ratios in the adult ostracodes from Coldwater Lake showed variations of 15–35% in a single monthly collection. In Roslyn Lake, Mg/Ca varied by 10–20%, while Sr/Ca varied by 3–4% in adults.

5. DISCUSSION

5.1. Seasonal Variations in Lake-Water Chemistry

Lakes in the northern Great Plains are strongly affected by evaporation and are distant from major sources of moisture. The $\delta^{18}O$ of the lakes in this area ranges from −4.6‰ to −0.4‰, and δD from −55‰ to −20‰ based on our suite of twenty-eight lakes (Fig. 2). All data are located on some evaporation trend below the meteoric water line derived from the relationship between δD and $\delta^{18}O$ in precipitation (Craig, 1961). Fresh water lakes with surface outlets, such as Pickerel Lake (0.4‰ salinity), are closer to the meteoric water line and show less seasonal variation, whereas topographically closed-basin saline lakes, such as Coldwater and Roslyn, are farther removed from the meteoric water line and exhibit more intraannual variability. The isotopic signatures from the three lakes demonstrate two different behaviors of seasonal change, as shown by the time progression of collections (June–September, 1991) in Fig. 2. According to meteorological records, high rainfall in June was followed by relatively low and equal rainfall in July, August, and September. Thus the trends toward lighter isotopic values in the early summer reverse (become heavier) after July because of the seasonal evaporation effect. Pickerel Lake, a flow-through system, shows a steeper seasonal slope of $\delta D/\delta^{18}O$ ratio that is close to that of the meteoric water line,

Table 1. Chemistry of lake water from monthly collections

Lakes	Sampling Date yy/mm/dd	Mg ppm	Sr ppm	K ppm	Na ppm	Ca ppm	Ba ppm	Cl ppm	SO_4 ppm	TIC ppm	Mg/Ca molar	Sr/Ca molar $x10^{-3}$	HCO_3/Ca meq	Cond* µS/cm	Temp (°C)	pH
Roslyn	91/05/01	206	0.98	50.5	584	110	0.040	435.50	1375	87.00	3.09	4.09	5.14	3600	7.8	8.95
Day Co.	91/06/14	207	1.12	54.0	565	126	0.094	423.10	1348	99.70	2.72	4.10	5.22	4200	25.0	8.52
South Dakota	91/07/14	196	1.10	51.0	532	129	0.079	393.10	1275	98.77	2.51	3.90	5.03	3950	24.5	8.57
	91/08/22	207	1.11	57.4	577	130	0.044	424.90	1346	94.25	2.63	3.91	4.67	4800	21.8	8.94
	91/09/22	209	1.17	55.0	568	138	0.095	420.10	1375	103.96	2.50	3.88	4.97	3800	10.0	8.60
Coldwater	91/05/02	437	0.08	129	310	22.7	0.008	95.24	1898	125.10	31.74	1.57	36.07	3500	7.0	8.82
Mcintosh Co.	91/06/13	423	0.08	128	299	21.6	0.003	93.90	1815	120.35	32.29	1.61	36.07	3800	24.8	8.82
North Dakota	91/07/15	426	0.06	128	301	18.3	0.001	95.15	1808	112.30	38.38	1.45	39.54	3700	23.4	8.90
	91/08/20	445	0.07	137	338	20.9	0.021	99.80	1908	105.95	35.10	1.47	32.76	3900	21.6	8.88
	91/09/21	466	0.08	140	327	21.5	0.005	102.80	1975	124.78	35.73	1.62	37.61	3750	13.0	8.93
Pickerel	91/05/02	39.2	0.19	6.6	8.9	33.8	0.060	4.53	78.5	50.90	1.91	2.61	9.96	460	8.6	8.48
Day Co.	91/06/14	36.7	0.18	6.1	8.2	31.9	0.052	4.50	74.6	44.39	1.90	2.58	9.11	535	24.4	8.62
South Dakota	91/07/14	38.4	0.20	6.6	9.2	34.2	0.063	4.76	72.6	44.00	1.85	2.61	8.47	580	22.5	8.50
	91/08/23	39.3	0.18	6.7	8.1	28.6	0.058	4.62	76.3	39.60	2.27	2.85	8.96	700	22.4	8.85
	91/09/22	38.4	0.19	6.6	8.8	31.6	0.060	4.53	69.0	42.80	2.00	2.75	8.94	480	12.8	8.50

* Conductivity

Table 2. Trace-element ratios and stable-isotope values of ostracodes from Coldwater Lake field collections

Instar	Collection Date yy/mm/dd	Sample	Mg/Ca ($x10^{-2}$) molar	Sr/Ca ($x10^{-3}$) molar	$\delta^{18}O$ (VPDB) ‰	$\delta^{13}C$ (VPDB) ‰
adults	91/05/02	1	1.98	0.65	-1.21	-2.33
		2	2.00	0.45	1.53	-1.69
		4	3.06	0.33	-2.24	-1.49
		5	1.93	0.43	-0.79	-0.99
	91/06/13	1	2.17	0.27	1.29	-1.48
		2	3.06	0.43	-3.97	1.18
		3	2.82	0.33	-4.46	-1.45
	91/07/15	1	2.46	0.54	-1.97	-1.09
		2	1.83	0.41	-1.00	-0.85
		3	2.83	0.59	-3.81	1.06
		4	2.84	0.45	0.00	-3.52
		5	2.44	0.51	-1.72	-0.34
		6	4.16	1.06	-4.87	0.70
		7	3.50	0.68	-2.80	0.91
	91/08/20	1	5.40	0.36	-3.72	2.21
		2	4.50	0.77	-4.76	0.97
		3	2.27	0.33	-2.29	-1.15
		4	2.26	0.40	1.08	0.35
		5	2.75	0.41	-4.74	0.49
		6	3.91	0.99	-3.84	0.70
		7	2.12	0.46	-2.30	1.22
		8	4.27	0.79	-3.61	0.67
	91/09/21	1	2.98	0.75	-1.74	1.57
		2	1.76	0.41	1.60	-1.16
		3	2.43	0.57	-0.65	-1.58
		5	2.41	0.73	-1.33	0.79
		6	2.90	0.66	0.07	-0.55
		7	2.89	0.88	-2.07	-0.22
juveniles	91/05/02	1	3.26	0.90	-2.82	1.67
		2	1.74	0.57	-2.00	1.81
		3	3.23	1.10	-2.52	1.32
	91/06/13	1	3.32	0.94	-1.74	1.20
		2	3.72	1.08	-2.88	1.73
		3	3.54	0.98	-2.32	1.40
	91/07/15	1	3.14	1.22	-2.77	1.52
		2	2.97	0.97	-3.40	1.24
		3	3.99	0.98	-3.68	1.25
	91/08/20	1	3.04	0.88	-2.45	1.33
		2	3.45	0.87	-2.81	1.77
		3	2.99	1.12	-2.88	1.49
	91/09/21	1	3.62	1.11	-2.64	1.50
		2	3.51	1.30	-2.50	1.10
		3	3.01	0.95	-3.68	1.43

indicating that the isotope composition of the lake water is seasonally controlled by that of the precipitation. In contrast to Pickerel Lake, Roslyn, and Coldwater lakes, which are smaller and have no outlet, have lower slopes that indicate a greater evaporation of the lake water.

The Mg/Ca and Sr/Ca ratios in water from both lakes varied up to 9% during the collection period (Fig. 3), largely due to seasonal precipitation of carbonate from the water column. In Coldwater Lake, Mg/Ca increased in July and August, because high Mg/Ca ratios in the water resulted in aragonite precipitation and Ca removal (Table 1). Sr/Ca in Coldwater Lake decreased during the same time period because of the preferential uptake of Sr in aragonite ($K_d[Sr] > 1$). In Roslyn Lake, however, Mg/Ca and Sr/Ca ratios show parallel trends with high values in spring and lower and nearly stable values in summer and autumn. The positive covariance likely reflects calcite-dominated carbonate precipitation from which both Sr and Mg are excluded. Lower ratios in mid-summer may result from groundwater inputs of Ca driven by high rainfall events in early summer (Table 1).

5.2. Geochemical Variation of Live Ostracodes

Figures 4 and 5 illustrate the variability of $\delta^{18}O$, $\delta^{13}C$, Mg/Ca, and Sr/Ca values in ostracodes from monthly collections in both lakes. The variation among juveniles in all isotopes and trace elements appears smaller than the variation among adults, primarily because adults were analyzed as individuals, whereas juveniles were bulked together in groups of fifteen (to provide sufficient carbonate for isotopic analysis).

The $\delta^{18}O$ of the water in both lakes varied about 1–2‰

Table 3 Trace-element ratios and stable-isotope values of ostracodes from Roslyn Lake field collections

Instar	Collection Date yy/mm/dd	Sample	Mg/Ca ($x10^{-2}$) molar	Sr/Ca ($x10^{-3}$) molar	$\delta^{18}O$ (VPDB) ‰	$\delta^{13}C$ (VPDB) ‰
adults	91/05/01	1	0.65	1.24	-0.51	-1.91
		2	0.55	1.24	-1.91	1.44
		3	0.58	1.22	-0.69	-1.11
		4	0.69	1.29	-2.23	-2.99
		5	0.86	1.32	-1.73	-1.98
		6	0.58	1.26	-1.85	-0.45
		7	0.64	1.23	-1.19	-0.22
	91/06/14	1	1.01	1.15	-2.38	-2.22
		2	1.19	1.29	na	na
		3	1.35	1.21	-4.76	-2.42
		4	1.30	1.20	-2.23	-1.12
		5	0.93	1.24	-1.93	-2.88
		6	1.08	1.22	-2.85	-3.62
		7	0.68	1.31	-6.57	-0.19
	91/07/14	1	1.29	1.23	-2.58	-3.12
		2	1.03	1.26	-1.18	-2.35
		3	1.16	1.75	-2.28	-1.09
		4	0.86	1.15	-2.04	-2.11
	91/08/22	1	1.51	1.26	-2.95	-2.44
		2	1.69	1.16	-2.61	-0.72
		3	1.53	1.14	-5.08	-4.14
		4	1.70	1.20	-2.71	-1.35
		5	1.38	1.27	na	na
		6	1.71	1.21	-3.15	-2.49
		7	1.31	1.27	-6.40	-1.56
		8	1.45	1.22	-5.81	-1.23
	91/09/22	1	1.11	1.13	-1.26	-2.54
		2	1.14	1.17	-4.55	-1.32
		3	1.83	1.24	-2.68	-2.99
		4	1.22	1.16	-1.42	-1.87
		5	1.49	1.23	-4.36	-4.26
		6	1.29	1.27	-2.28	-1.07
		7	1.43	1.32	-1.51	-2.85
		8	1.05	1.11	-1.45	-2.07
juveniles	91/05/01	1	1.16	1.29	-2.26	0.04
		2	1.05	1.21	-3.53	0.22
		3	1.05	1.19	-2.51	-0.38
	91/06/14	1	1.20	1.20	-2.61	0.31
		2	1.27	1.27	-4.05	-0.22
	91/07/14	1	1.17	1.20	-3.32	-0.59
		2	1.27	1.18	-2.78	0.01
		3	1.24	1.15	-3.19	-0.33
	91/08/22	1	1.20	1.23	-1.57	0.17
		2	1.33	1.18	-3.60	0.10
		3	1.28	1.23	-2.88	-0.40
	91/09/22	1	1.32	1.32	-3.03	0.09
		2	1.20	1.19	-3.07	-0.33
		3	1.30	1.23	-3.90	-0.38

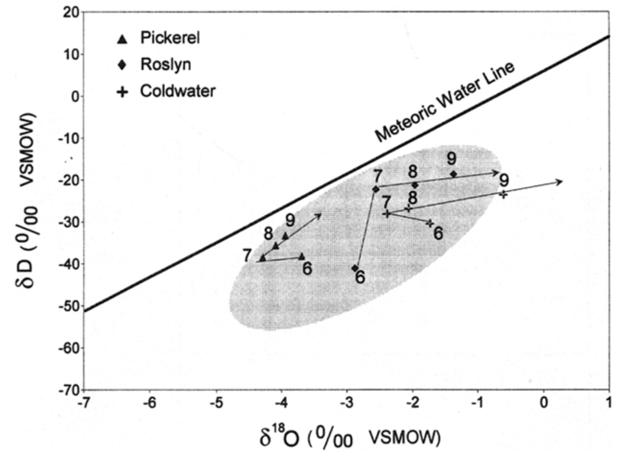

Fig. 2. The changes in isotopic composition of lake water during the 1991 collection period. Shaded area indicates the isotope composition of lake water from twenty-eight lakes in the northern Great Plains.

seasonally, while Mg/Ca varied by 8–9% and Sr/Ca by 3–5%. A 9% variation in water Mg/Ca should cause nearly the same variation in shell composition, but the variation actually measured in adult shells (15–35%) is much greater. During the same collection period temperatures changed by about 20°C, a range equivalent to 4–5‰ variation in $\delta^{18}O$ and 50% variation in Mg/Ca of *C. rawsoni* (Engstrom and Nelson, 1991). Thus, the large variation in shell Mg/Ca must be caused mainly by temperature variation, an interpretation supported by the negative correlation between Mg/Ca and $\delta^{18}O$ in ostracodes in both lakes (Fig. 6). Mg/Ca in ostracodes is positively related to both Mg/Ca and temperature in the lake water, whereas $\delta^{18}O$ in ostracodes is positively related to $\delta^{18}O$ of the water but negatively correlated to temperature. Thus the negative covariance between Mg/Ca and $\delta^{18}O$ indicates that seasonal temperature changes imparted much of the variability in the chemistry of these ostracode populations.

It thus appears that *C. rawsoni* populations are composed of multiple overlapping generations that attain maturity at different seasons. A single monthly collection of adults (or any particular instar) might include individuals that molted and calcified new shells over a range of temperatures. For example, the juveniles collected in late September from Coldwater Lake and those collected in May from Roslyn Lake are higher in Mg/Ca and lower in $\delta^{18}O$ than the adults from those same collections; this suggests that late-instar juveniles might calcify new shells primarily in the warm mid-summer and persist into the following spring if they fail to molt to adults in late-summer. Because of this high intraannual variability in living populations, numerous fossil shells are needed from each stratigraphic interval in paleoclimatic studies to remove seasonal noise (~15°C) from the long-term paleohydrologic trends.

The carbon isotope values of juvenile ostracodes is significantly higher than those of adult ostracodes in both lakes. The explanation for this difference may be twofold: (1) juvenile ostracodes molt and calcify new shells only during a specific season or at a certain temperature range, such as mid-summer, and higher productivity in the lake at that time results in higher $\delta^{13}C$ of the dissolved inorganic carbon, or (2) juvenile ostracodes live in different microhabitats, such as at the surface of the mud, compared to the penultimate instars (A-1), which might live within the soft sediment where porewater $\delta^{13}C$ may be influenced by the decay of organic material.

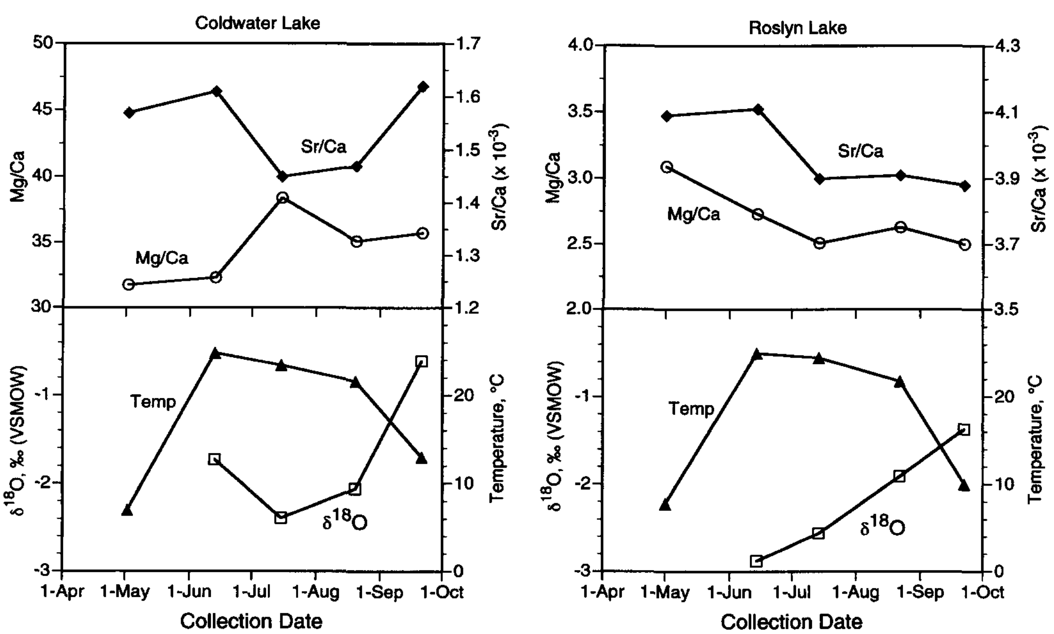

Fig. 3. The changes in temperature, $\delta^{18}O$, Mg/Ca, and Sr/Ca ratios of Coldwater Lake and Roslyn Lake during the 1991 collection period.

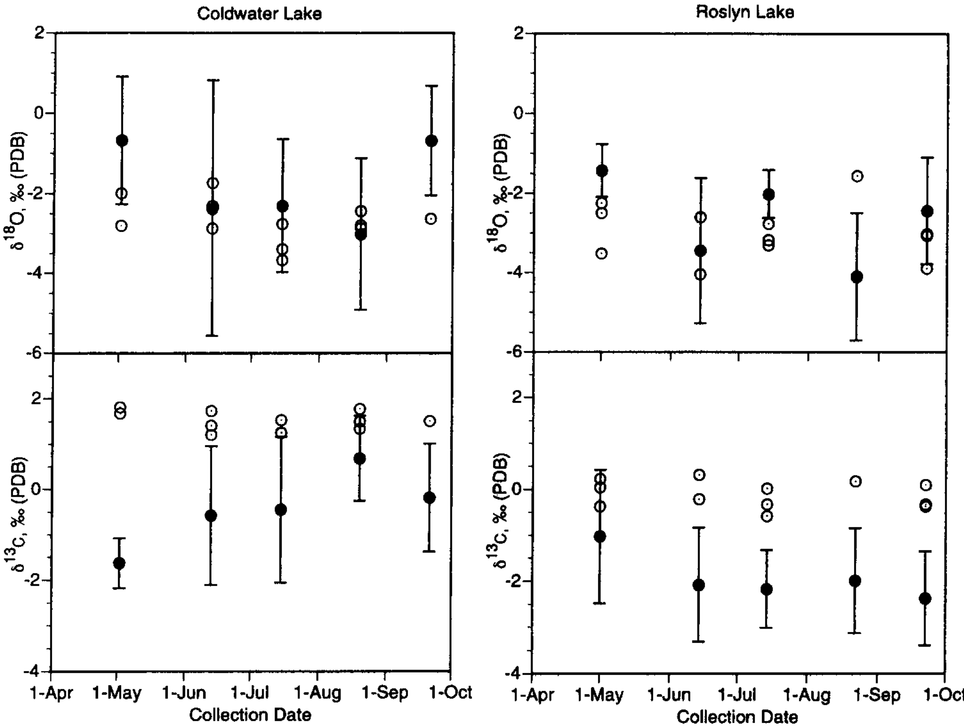

Fig. 4. The seasonal changes of $\delta^{18}O$ and $\delta^{13}C$ in live ostracodes. Filled symbols are the average values with the ranges for adults; unfilled symbols are the values for pooled samples of juveniles.

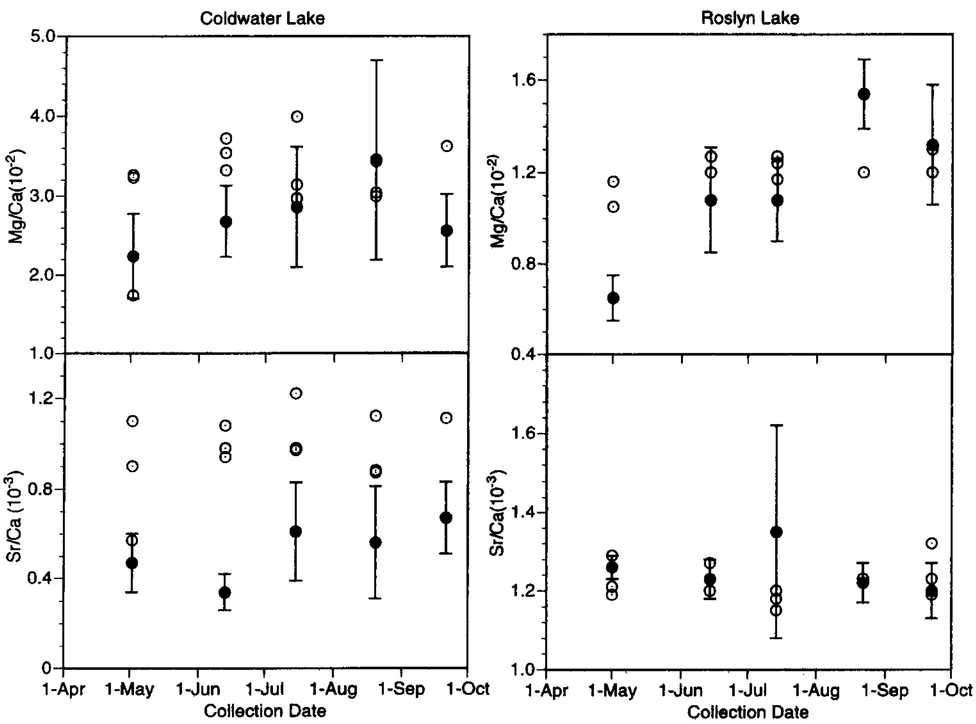

Fig. 5. The seasonal changes of Mg/Ca and Sr/Ca ratios of live ostracodes. Filled symbols are the average values with the ranges for adults; unfilled symbols are the values for pooled samples of juveniles.

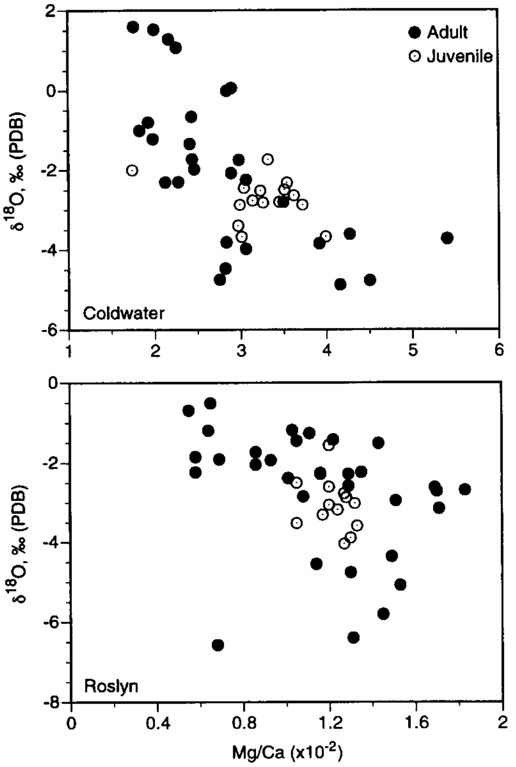

Fig. 6. The covariance between $\delta^{18}O$ and Mg/Ca ratios of live ostracodes from Coldwater Lake and Roslyn Lake. Filled symbols are the values for individual samples of adults; unfilled symbols are the values for pooled samples of juveniles.

5.3. Re-Evaluation of Sr and Mg Partitioning

The Sr/Ca ratio in ostracode calcite should depend only on Sr/Ca of the host water, Sr partitioning in calcite being temperature independent. Up to 2% variation in ostracode Sr/Ca is expected in both Coldwater and Roslyn lakes based on the seasonal variation of Sr/Ca in the lake water. In Roslyn Lake, the range of Sr/Ca in the monthly ostracode collections (3–4%) is similar to that predicted from lake-water Sr/Ca, whereas in Coldwater Lake the variation in ostracode Sr/Ca (15–35%) is much greater than expected and shows strong positive covariance with Mg/Ca (Fig. 7). The covariance is exactly opposite that shown by lake-water chemistry in which Sr/Ca and Mg/Ca are inversely correlated because of aragonite precipitation that results in Sr and Ca depletion in water (Table 1, Fig. 3). These results imply that K_d[Sr] varies directly with Mg concentration in ostracode calcite, as has been suggested for some marine biogenic carbonates by Carpenter and Lohmann (1992).

One possible reason for the correlation is crystallographic: greater Sr uptake as calcite crystal structure becomes more distorted due to greater Mg content. However, it is more likely that K_d[Sr] increases with Mg concentration because of the large physiological energy required to exclude Mg (and Sr) during shell calcification when ostracodes are growing in lake waters of high Mg/Ca. A similar effect has been observed for the inorganic precipitation of calcite or Mg-calcite. Mucci and Morse (1983) and Morse and Bender (1990) observed that Sr incorporation increased in the presence of Mg. Nonequilibrium incorporation of Sr into the calcite lattice caused by slower precipitation in the presence of high Mg has also been suggested by Reddy and Wang (1980).

If the seasonal trends in Mg/Ca in adult Coldwater ostracodes are actually temperature driven as the covariance with $\delta^{18}O$ suggests (Fig. 6), the Sr/Ca variation is an indirect consequence of temperature change. Consistently higher Sr/Ca in juveniles than adults from Coldwater Lake (Figs. 5, 7) may follow from juveniles molting and calcifying their shells at warmer mid-summer temperatures and incorporating more Mg in their shells. Alternatively, K_d[Mg] may be higher (and consequently higher K_d[Sr]) in juveniles owing to the more rapid calcification of their smaller shells (Chivas et al., 1986; Engstrom and Nelson, 1991). The possible indirect dependence of K_d[Sr] on ostracode Mg/Ca suggests that ostracode Sr/Ca should covary with long-term changes in Mg/Ca of the lake (as well as Sr/Ca and temperature of the lake).

It is clear that the distribution coefficients for *C. rawsoni* from laboratory growth-experiments (Engstrom and Nelson, 1991) are inadequate to explain some of the results observed here. Not only does K_d[Sr] vary with water Mg/Ca ratio (Fig. 7), but the predicted values for ostracode Sr/Ca in Roslyn Lake and that for Mg/Ca in Coldwater Lake are much greater than anything observed in the five monthly collections of live ostracodes (Fig. 8).

The low observed Sr/Ca in Roslyn ostracodes follows directly from the Mg-dependence of K_d[Sr]. The Mg/Ca of Roslyn Lake water is much lower than that used in laboratory cultures to determine Sr partitioning (3 vs. 9); that is to say, the published K_d[Sr] (0.406) is too high for low Mg/Ca waters like Roslyn. The lower Mg/Ca of this lake and the narrower range of ostracode Mg/Ca may also explain the lack of covariance between Sr and Mg in Roslyn ostracodes. Assuming that changes in Mg/Ca of water is the primary factor affecting K_d[Sr], a more generalized representation of Sr partitioning, where K_d[Sr] varies with Mg/Ca is shown in Fig. 8a.

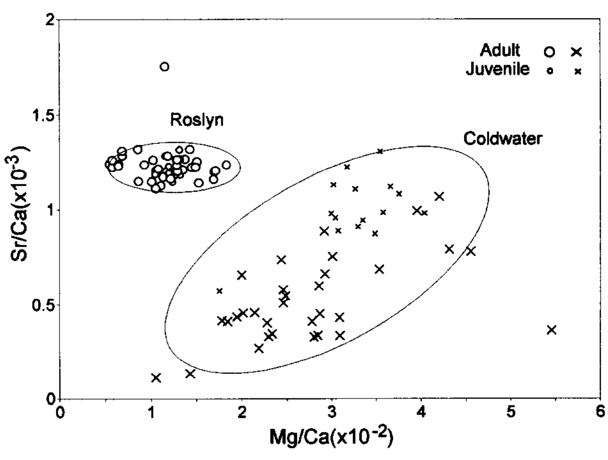

Fig. 7. The covariance between Mg/Ca and Sr/Ca ratios of live ostracodes from Coldwater Lake and Roslyn Lake.

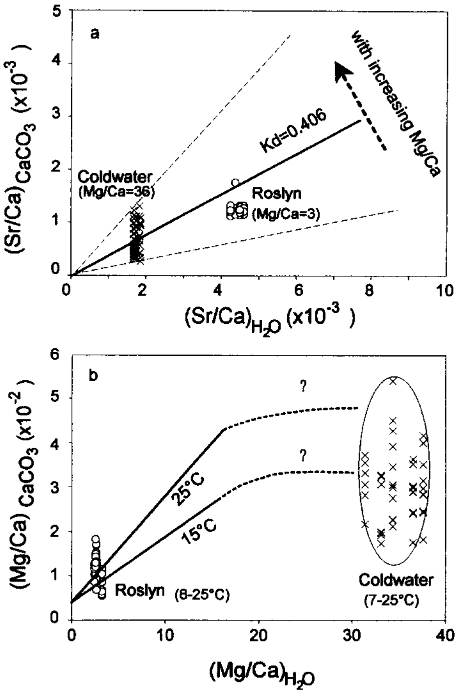

Fig. 8. The relationships between measured Mg/Ca and Sr/Ca ratios from Coldwater Lake and Roslyn Lake waters, and measured Mg/Ca and Sr/Ca ratios for live ostracodes collected from these lakes, and the laboratory-determined K_d's for Mg and Sr (Engstrom and Nelson, 1991). Dashed lines represent hypothesized changes in K_d's with increasing Mg/Ca ratio of lake water.

The low observed Mg/Ca in Coldwater ostracodes may also follow from the limited range of Mg/Ca water used in previous laboratory cultures. The Mg/Ca of Coldwater Lake waters (32–38) is twice that of any of the culture experiments of Engstrom and Nelson (1991), and K_d[Mg] may not be constant in high Mg/Ca waters. There is likely to be an upper limit to the amount of Mg that ostracodes will incorporate into their shells. Ostracodes are able to synthesize low-Mg calcite shells from waters in which calcite would not otherwise precipitate (e.g., Coldwater Lake) by metabolically excluding Mg ions from the growing calcite lattice. The proportion of Mg excluded to that in the host water is likely to increase with increasing Mg concentration, such that K_d[Mg] will decline with increasing Mg/Ca of the lake (Fig. 8b). For inorganic Mg-calcite, the nonthermodynamic partition coefficient D for Mg decreases as a function of mol% $MgCO_3$ in Mg-calcite, i.e., the higher the Mg/Ca ratio in solution, the lower the partition coefficient of Mg into the solid phase (Morse and Bender, 1990).

6. CONCLUSIONS

Populations of live *Candona rawsoni* from our two study lakes show high variability in $\delta^{18}O$, $\delta^{13}C$, Mg/Ca, and Sr/Ca in their calcite shells caused mainly by seasonal changes in water temperature and secondarily by variations in water chemistry. The ranges of Mg/Ca and Sr/Ca measured in Coldwater ostracodes are large and positively correlated, in contrast to the negative covariance observed between lake-water Mg/Ca and Sr/Ca. Measured values of Mg/Ca in Coldwater ostracodes and Sr/Ca in many Roslyn ostracodes are low compared to laboratory determined K_d's. Such results suggest that Mg/Ca and Sr/Ca in ostracodes are strongly influenced by the physiological cost of calcification, which becomes substantial in high Mg/Ca waters. More controlled culture experiments and longitudinal field observations are needed to clarify these vital effects. It is clear, however, that the partitioning of both Mg and Sr into ostracode calcite is strongly affected by the Mg/Ca ratios of the lake water, a fact which complicates the interpretation of paleochemistry signals from sediment cores.

Our study also showed that the molting and shell calcification of A-1 instars to adults may occur at different times of the year, and the resulting intraannual noise may overwhelm long-term paleoclimatic signals. The particular species investigated here, *C. rawsoni,* appears to molt into late-instar juveniles during mid-summer, whereas adults may calcify in late summer or the following spring. If juvenile ostracodes form over a more restricted season than adults, they may be preferred as paleoclimatic indicators. Statistically large numbers of fossil ostracodes (10 ~ 15) are needed from each stratigraphic sampling interval to eliminate the intraannual signal, so that long-term climatic trends can be detected.

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