Pergamon

Geochimica et Cosmochimica Acta, Vol. 62, No. 19/20, pp. 3229–3237, 1998
Copyright © 1998 Elsevier Science Ltd
Printed in the USA. All rights reserved
0016-7037/98 $19.00 + .00

PII S0016-7037(98)00240-3

Stable isotopes, Sr/Ca, and Mg/Ca in biogenic carbonates from Petaluma Marsh, northern California, USA

B. L. Ingram,*[1] P. De Deckker,[2] A. R. Chivas,[3] M. E. Conrad,[4] and A. R. Byrne [5]

[1]Department of Geology and Geophysics, University of California, Berkeley, California 94720, USA
[2]Department of Geology, The Australian National University, Canberra ACT 0200, Australia
[3]School of Geoscience, University of Wollongong, NSW 2500, Australia
[4]Center for Isotope Geochemistry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
[5]Department of Geography, University of California, Berkeley, California 94720, USA

(*Received January* 2, 1998; *accepted in revised form July* 24, 1998)

Abstract—Stable isotope ($^{18}O/^{16}O$ and $^{13}C/^{12}C$) and minor-element compositions (Sr/Ca and Mg/Ca ratios) of ostracodes and gastropods separated from marsh sediments from San Francisco Bay, Northern California, were used to reconstruct paleoenvironmental changes in Petaluma Marsh over the past 700 yr. The value of $\delta^{18}O$ in the marsh carbonates reflects changes in freshwater inflow, evaporation, and temperature. Mg/Ca and Sr/Ca in ostracode calcite reflect changes in both freshwater inflow and temperature, although primarily reflect temperature changes in the salinity range of about 10–35‰. Ostracode $\delta^{18}O$ values show a gradual increase by 5‰ between 500 yr BP and the present, probably reflecting rising sea level and increased evaporation in the marsh. Superimposed on this trend are higher frequency Mg/Ca and $\delta^{18}O$ variations (3–4‰), probably reflecting changes in freshwater inflow and evaporation. A period of low Mg/Ca occurred between about 100–300 cal yr BP, suggesting wetter and cooler conditions during the Little Ice Age. Higher Mg/Ca ratios occurred 600–700 cal yr BP, indicating drier and warmer conditions during the end of the Medieval Warm Period. Both ostracode and gastropod $\delta^{13}C$ values decrease up-core, reflecting decomposition of marsh vegetation, which changes from C_4 ($\delta^{13}C \sim -12‰$) to CAM ($\delta^{13}C = -26‰$)-type vegetation over time. *Copyright © 1998 Elsevier Science Ltd*

1. INTRODUCTION

Wetland sediments accumulating within the San Francisco Bay estuary and surrounding marshes contain a detailed record of paleoclimatic and ecological changes. Sea-level rise over the past 10,000 yr is the primary variable determining wetlands development in San Francisco Bay (Atwater et al., 1977), but variations in river inflow cause shorter timescale variations in estuarine salinity (Peterson et al., 1989) and associated changes in wetland communities. An understanding of natural variability in the wetlands environment over long timescales (hundreds to thousands of years) is important for understanding how humans have altered natural inflow, salinity, and estuarine ecosystems (Nichols et al., 1986).

Holocene sea level has been reconstructed with radiocarbon dating of inter-tidal organic matter from cores recovered from south San Francisco Bay (Atwater et al., 1977, 1979). Atwater's sea level curve indicates that the sea entered the Golden Gate 10,000–11,000 years ago and for the next 2,000 years rose about 2 cm/yr. Atwater concluded that this rate of sea level rise probably exceeded local sedimentation rates and that marsh formation would, therefore, have been minimal. Since 6,000 years ago the average rate of sea level rise has been only 1–2 mm /yr, causing salt marshes to expand. Most of this expansion apparently occurred within the last several thousand years because the accumulation of peat below San Francisco Bay marshes is rarely more that 2–3 m thick.

Previous studies in San Francisco Bay estuary have shown that oxygen, carbon, hydrogen, and strontium isotopic compositions of estuarine waters vary systematically with salinity, due to the mixing of isotopically distinct river water and seawater (Spiker, 1980; Ingram and Sloan, 1992; Ingram and DePaolo, 1993; Ingram et al., 1996a,b,c). The isotopic composition of ambient water, as recorded in the tests of estuarine foraminifers and shells of mollusks, has been used to reconstruct changes in freshwater inflow to the estuary (Ingram et al., 1996b,c).

This study focuses on stable-isotope compositions of oxygen and carbon, coupled with Sr/Ca and Mg/Ca ratios, of biogenic carbonates from intertidal marsh sediments. These variables are used to assess changes in freshwater inflow, evaporation, and sea level over the past 700 yr in Petaluma Marsh (in the northern reach of San Francisco Bay; Fig. 1).

Salinity varies in San Francisco Bay primarily as a function of freshwater inflow (Conomos, 1979). Over longer timescales, salinity variations in marsh waters are caused by changes in both fluctuating freshwater inflow and changing sea level. These changes are reflected in the chemistry and isotopic composition of estuarine waters. Rising sea level during the Holocene should have increased the volume of the bay and the relative proportion of seawater, increasing its salinity and $\delta^{18}O$ value. Salinity and oxygen isotopic compositions of the marsh waters are also increased by evaporation. To a lesser relative extent, hydrogen isotopes also show this pattern of enrichment during evaporation (Fig. 2).

The chemistry (Sr/Ca, Mg/Ca) of marsh waters reflects the composition of water entering the marsh, as well as mineral precipitation (carbonate, gypsum) associated with evaporation within the marsh. If the Mg/Ca and Sr/Ca ratios of freshwater and seawater entering the marsh are distinct and mix conser-

---

* Author to whom correspondence should be addressed (ingram@socrates.berkeley.edu).

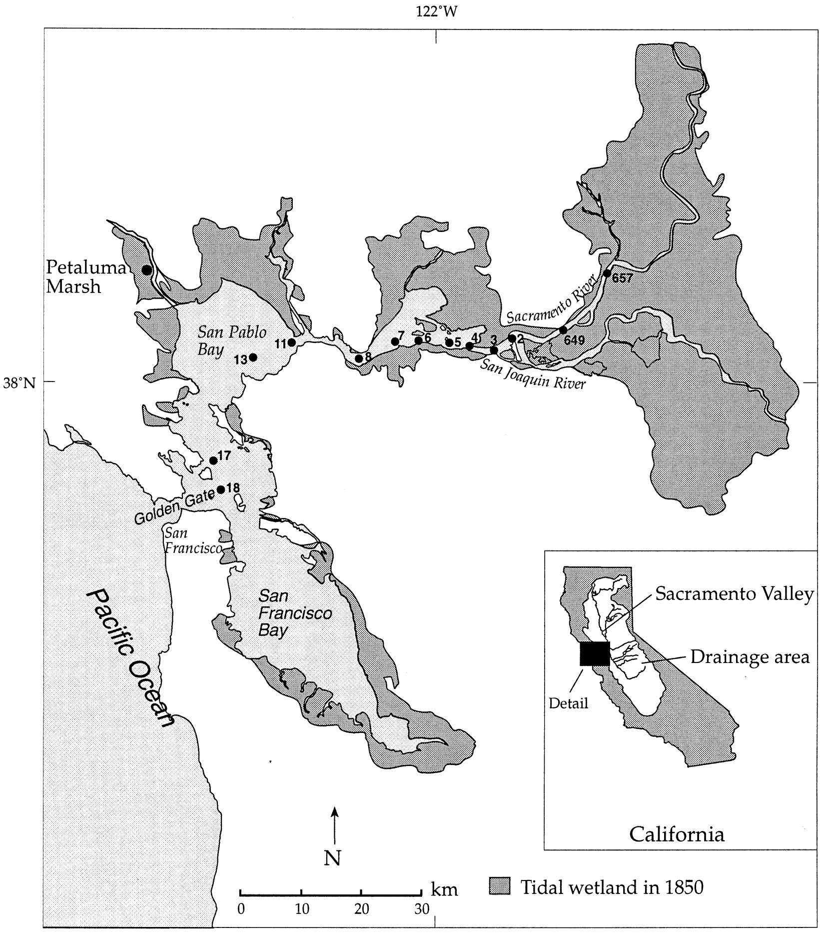

Fig. 1. Location of coring site in Petaluma Marsh, San Pablo Bay (northern reach of San Francisco Bay Estuary), and water collection sites.

vatively, it may be possible to use them as paleosalinity indicators when combined with oxygen isotopic measurements. Thus, the Sr/Ca and Mg/Ca ratios of waters from San Francisco Bay entering Petaluma Marsh were measured as part of this study.

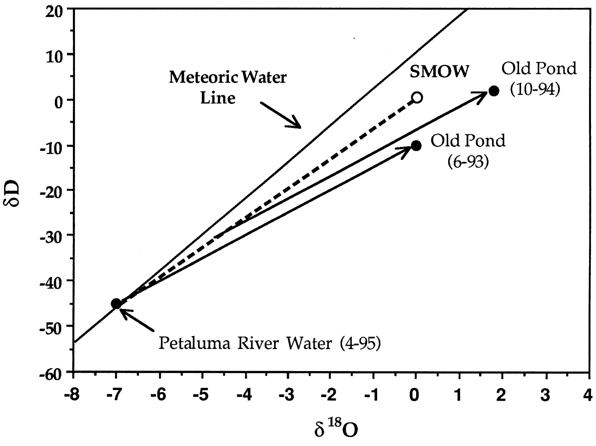

Fig. 2. δD vs. $\delta^{18}O$ for Petaluma Marsh pond waters and Petaluma River water, plotted with meteoric water line and SMOW. Collection dates are shown in parenthesis.

Ostracodes are bivalved microcrustaceans with calcitic carapaces, that live in both marine and nonmarine aquatic environments. They moult their carapaces up to nine times before reaching adulthood. The ostracode species *Cyprideis beaconensis* is used for this study. It is a species typically found in modified (diluted or evaporated) seawater in the nearshore environment (Sandberg, 1964). Field measurements and laboratory cultures have previously been made to establish the distribution coefficients for both Sr and Mg in *Cyprideis* calcite valves (Chivas et al., 1993; De Deckker et al., 1988a,b). The Mg/Ca ratio of ostracode calcite is controlled by both the Mg/Ca ratio of ambient water and water temperature. The Mg/Ca ratio increases by 0.0015 per 1°C increase in water temperature (Chivas et al., 1993). Because Mg is preferentially incorporated in ostracode shells during the early stages of shell growth, we selected fully calcified adult valves for analysis, rather than the smaller juvenile valves. The partitioning of Sr is apparently temperature-independent for calcite ostracode shells, although De Deckker et al. (1998) recently have shown a slight temperature effect on the uptake of Sr. The Sr/Ca ratio in the ostracode shell is thus primarily related to the Sr/Ca in the water, by a distribution coefficient of 0.475 if grown in seawater.

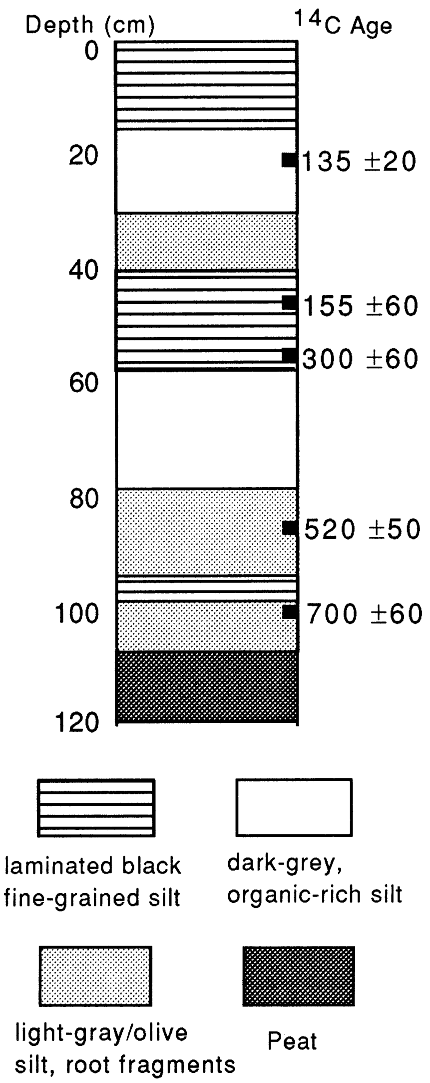

Fig. 3. Stratigraphic column of Petaluma Marsh core. Calibrated radiocarbon dates are shown on the right-hand column.

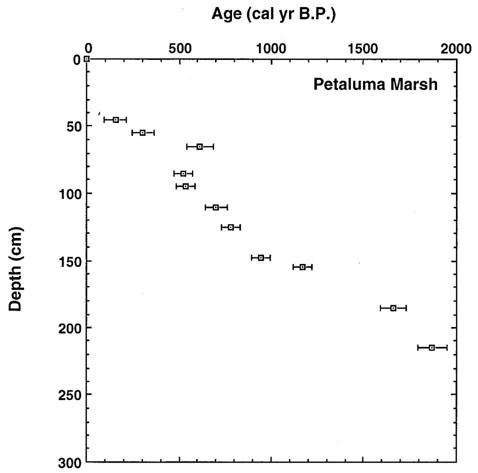

Fig. 4. Calibrated radiocarbon ages of Petaluma Marsh core plotted against depth.

2. SEDIMENT AND WATER SAMPLES

Sediment cores used for this study were taken within a small pond in Petaluma Marsh, adjacent to the peat coring location for pollen analysis by A. R. Byrne (Fig. 1). The coring was accomplished with a modified 5 cm diameter Livingston Corer equipped with plastic (butyrate) liners.

Three adjacent cores were taken to a depth of 1.5 m, allowing overlap between them. The uppermost core spans a depth of 0–68 cm, the middle core from 32 to 100 cm, and the lowermost core from 73 to 150 cm. The cores were x-radiographed in order to provide a record of core stratigraphy prior to sampling. The marsh pond sediments are comprised of alternating organic- and clay-rich intervals (Fig. 3). The clay-rich intervals are dark gray to black in color and generally laminated. The organic-rich layers are lighter gray to olive green in color and contain abundant root fragments. Ostracodes, gastropods, discoidal gypsum crystals, charophyte oogonia (uncalcified), seeds of marsh vegetation, and insect remains are present thoughout the cores. In addition, discrete gastropod-rich layers (0.5–1.0 cm thick) were present, centered at 24, 42, 49, 54, 67, 70, 73, and 76 cm. Below the pond sediments, the transition to peat sediments (100% organic marsh material) occurred at 107 cm. No calcite was present in the peat sediments, presumably due to dissolution caused by a decrease in pH in the pore fluids associated with increased organic matter with depth. In addition, oxidation of pyrite that would have precipitated in association with organic matter may have produced acidic (H_2SO_4) porewaters.

Cores were sampled at intervals of 1 cm for the near-surface sediments (0–30 cm) and 2 cm from 30 cm to 1.5 m. Sediment

Table 1. Station number, salinity, and trace elemental composition (Sr, Mg, and Ca) for San Francisco Bay waters

Sample number	Station	Salinity	Sr (mg/L)	Ca (mg/L)	Mg (mg/L)	Sr/Ca	Mg/Ca
96-SFB-1	18	31.9	6300	395	1251	0.0159	3.17
96-SFB-2	17	30.3	6310	478	1573	0.0132	3.29
96-SFB-3	13	27.3	5100	321	1064	0.0159	3.31
96-SFB-4	11	22.2	4520	308	962	0.0147	3.12
96-SFB-5	7 to 8	18.2	3530	285	922	0.0124	3.24
96-SFB-6	5 to 6	14.8	3040	224	681	0.0136	3.04
96-SFB-7	5	10.8	2240	142	455	0.0158	3.20
96-SFB-8	4	9.1	1710	109	285	0.0157	2.61
96-SFB-9	2 to 649	6.8	1110	81.4	219	0.0136	2.69
96-SFB-10	651	2.8	430	49.4	89.8	0.0087	1.82

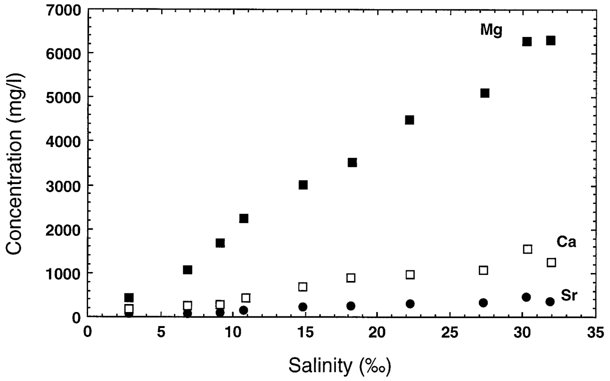

Fig. 5. Strontium, magnesium, and calcium (mg/L) salinity of San Francisco Bay waters.

samples were soaked in deionized water for 12 h and wet sieved with a 63 μm screen. Ostracodes (adult *Cyprideis beaconensis*) were picked from each sieved sample with a wet brush under a binocular microscope. Eight to ten well-preserved valves of the adult ostracode *Cyprideis beaconensis* were separated for stable isotopic (oxygen and carbon) and minor elemental (Sr/Ca and Mg/Ca) analyses. The ostracode samples weighed between 100 and 200 μg.

Estuarine waters were collected on November 13, 1996 at ten locations in San Francisco Bay for minor elemental analyses, during a monthly U.S. Geological Survey cruise (Fig. 1). Waters were collected in 1 L, acid-washed bottles, filtered with a 0.45 μm sieve, and acidified with 1 mL nitric acid. Water salinity was later measured in the laboratory. Water samples were also taken at Petaluma Marsh pond on two occasions during the time of coring.

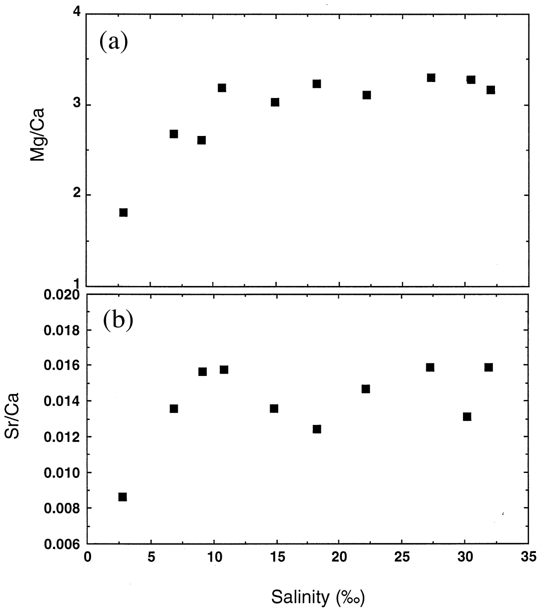

Fig. 6. (a) Mg/Ca of waters plotted against salinity of San Francisco Bay waters, (b) Sr/Ca of waters plotted against salinity of San Francisco Bay waters.

Table 2. $\delta^{13}C$ and $\delta^{18}O$ values (‰ relative to the PDB standard) and depth in core (cm) for ostracode samples from Petaluma marsh

Depth (cm)	$\delta^{13}C$	$\delta^{18}O$	Depth (cm)	$\delta^{13}C$	$\delta^{18}OC$
Core 1					
1	−10.00	0.10	56	-3.37	0.32
2	−6.58	−0.02	57	−4.99	−1.50
3	−6.66	−0.10	61	−4.82	−1.80
4	−7.20	0.10	62	−4.79	−2.57
5	−8.32	−1.36	63	−5.36	−2.28
6	−6.76	−0.25	64	−3.27	−3.35
7	−6.52	−0.58	65	−4.10	−0.72
9	−7.42	−0.58	66	−4.53	−0.11
10	−7.74	−1.04	67	−6.84	0.36
11	−5.96	0.56	68	−8.45	−1.69
12	−6.48	0.05	Core 2		
13	−8.25	0.40	32	−6.72	−3.60
14	−7.41	−0.39	34	−5.00	0.32
15	−7.02	−0.32	36	−3.37	−1.35
16	−7.05	−0.62	38	−5.83	−0.32
17	−6.98	−0.73	40	−7.81	1.00
18	−7.93	−0.88	42	−7.24	2.22
19	−6.10	−0.13	46	−3.65	−2.03
20	−6.66	−0.34	48	−4.58	−3.32
21	−7.54	−0.54	60	−4.29	−2.26
22	−7.11	−0.26	64	−4.66	0.06
23	−8.52	−1.77	66	−5.61	−0.45
24	−8.37	−1.26	68	−6.11	−2.39
25	−6.19	0.04	70	−4.53	−1.84
26	−6.36	−0.25	72	−5.19	−0.97
27	−6.27	−1.24	74	−4.09	−3.01
28	−4.90	−1.96	76	−6.99	−2.44
29	−4.60	−2.30	78	−4.25	−3.47
30	−6.66	−1.18	80	−2.92	−4.38
31	−5.46	−0.73	82	−4.96	−1.62
32	−7.56	−1.47	86	−5.37	−1.67
33	−7.46	0.26	88	−5.84	−0.56
34	−4.98	−1.98	90	−5.92	−2.00
35	−6.77	−1.65	92	−6.13	−0.73
36	−5.88	−1.01	94	−5.53	−2.54
37	−5.05	−2.34	96	−7.32	−0.24
38	−6.38	−1.49	98	−5.53	−1.01
39	−5.78	−1.21	100	−8.50	−1.40
40	−7.70	−1.52			
42	−6.23	−3.09	Core 3		
43	−7.43	−0.84	73	−5.01	−2.55
44	−7.13	−1.84	75	−4.14	−2.33
45	−6.00	−2.33	87	−3.20	−2.30
46	−6.96	−2.71	101	−5.74	−1.59
49	−3.51	−1.98	103	−6.35	−2.88
52	−3.86	−1.45	105	−7.63	−1.75
54	−6.23	−2.84	107	−6.75	−1.46

The chronology of Petaluma Marsh sediments was determined using ^{14}C analyses of seeds by accelerator mass spectrometry and the first appearance of alien *Eucalyptus* pollen, which first appeared in 1870 A.D. ± 10 yr (Fig. 4). The resulting chronology indicates a constant sedimentation rate over the past 800 yr of 1.4 mm/yr, allowing a time resolution for a 1 cm thick sample of about 10 yr.

3. LABORATORY METHODS

Stable isotope and trace element analyses of the ostracode samples were made at the Research School of Earth Sciences, The Australian National University (ANU), in Canberra, Australia. The isotope analyses were made on a Finnigan MAT 251 gas source mass spectrometer.

Table 3. δ^{13}C and δ^{18}O values (‰ relative to the PDB standard) and depth in core (cm) for gastropod samples from Petaluma marsh

Depth (cm)	δ^{13}C (‰)	Average δ^{13}C	δ^{18}O (‰)	Average δ^{18}O	Depth (cm)	δ^{13}C (‰)	Average δ^{13}C	δ^{18}O (‰)	Average δ^{18}O
Core 1									
1	−5.567	−5.465	−0.244	−0.299	28	−7.065	−6.929	0.247	0.433
	−5.363		−0.354			−6.793		0.619	
2	−5.843	−5.905	0.565	0.552	29	−5.784	−5.629	−2.073	−1.714
	−5.967		0.539			−9.473		−1.354	
3	−5.840	−5.751	0.637	0.667	30	−6.509	−6.509	−2.541	−2.541
	−5.662		0.696		31	−6.469	−6.679	−1.047	−1.025
4	-6.243	−6.051	1.373	1.274		−6.889		−1.003	
	−5.858		1.175		33	−4.222	−4.816	−0.381	−0.564
5	−6.339	-6.065	1.090	1.005		−5.409		−0.747	
	−5.790		0.919		34	−3.810	−3.907	−1.916	−1.869
6	−5.851	−5.978	0.618	0.670		−4.004		−1.821	
	−6.104		0.722		35	−5.237	−5.200	0.674	0.789
7	−5.291	−5.439	−0.097	−0.157		−5.163		0.904	
	−5.587		−0.217		36	−5.243	−5.257	−0.415	−0.442
8	−4.615	−4.632	0.285	0.342		−5.271		−0.468	
	−4.648		0.399		37	−3.226	−3.374	−0.712	−0.667
9	−4.564	−4.735	0.237	0.341		−3.521		−0.621	
	−4.906		0.444		41	−4.804	−4.812	−0.757	−0.594
10	−5.518	−5.578	0.044	0.001		−4.820		−0.430	
	−5.638		−0.002		48	−3.383	−3.464	−1.795	−2.389
11	−5.265	−5.294	0.040	0.035		−3.545		−2.983	
	-5.322		0.030		49	−3.423	−3.352	−2.232	−2.195
12	−5.392	−5.408	−0.371	−0.454		−3.280		−2.158	
	−5.423		−0.537		56	−2.350	−2.788	−1.581	−1.842
13	−5.091	−5.082	−0.403	−0.356		−3.226		−2.102	
	−5.073		−0.309		57	−4.215	−3.727	−2.459	−2.223
14	−5.159	−5.270	−0.735	−0.661		−3.239		−1.986	
	−5.381		−0.587		Core 2				
15	−4.102	−3.989	−0.631	−0.702					
	−3.876		−0.773		32	−4.769	−4.715	−1.251	−1.046
16	−3.492	−3.699	−1.992	−1.087		−4.661		−0.840	
	−3.905		−0.182		34	−0.137	−0.375	−2.140	−1.846
17	−3.582	−3.855	−0.605	−0.693		−0.612		−1.551	
	−4.127		−0.781		36	−5.414	−5.617	−1.654	−1.743
18	−3.545	−3.697	−1.013	−0.817		−5.819		−1.832	
	−3.848		−0.620		38	−4.837	−5.058	−1.029	−1.559
19	−3.873	−3.699	−0.751	−0.790		−5.279		−2.088	
	−3.524		−0.828		40	−4.845	−5.026	−1.808	−2.088
20	−3.871	−4.121	−0.787	−1.122		−5.207		−2.367	
	−4.370		−1.457		42	−4.926	−4.755	−1.186	−0.944
21	−3.463	−3.576	−1.957	−1.769		−4.584		−0.701	
	−3.689		−1.580		62	−3.287	−3.283	−1.902	−2.016
22	−5.070	−5.268	−0.040	−0.036		−3.279		−2.129	
	−5.466		−0.031		66	−3.620	−3.709	−0.919	−0.916
23	−4.796	−4.708	0.594	0.426		−3.798		−0.913	
	−4.619		0.257		68	−3.930	−4.137	−1.081	−0.428
24	−4.763	−4.634	−0.852	−0.526		−4.344		0.225	
	−4.505		−0.199		70	−4.199	−4.280	−1.202	−1.363
						−4.360		−1.524	

The carbonate-reaction apparatus for the system is the acid on individual carbonate (or Kiel device), in which carbonate samples are placed in glass reaction vessels and reacted with phosphoric acid (three drops of 107% for 10 min at 70°C) sequentially into each individual vessel. Four carbonate standards (NBS-18 and NBS-19) were run for each set of forty samples. NBS-18 has a δ^{13}C value of −5.0‰, and a δ^{18}O of −23.0‰. NBS-19 has a δ^{13}C value of 1.95‰ and a δ^{18}O of −2.2‰. The internal precision of both δ^{13}C and δ^{18}O measurements is 0.03–0.09%, and the external precision is ≤0.1%.

The Kiel apparatus was modified to allow subsequent chemical analysis of the acid residue for Ca, Mg, and Sr concentrations. Minor element analyses were made on an inductively-coupled argon plasma (ICP) atomic emission spectrometer. The limits of detection of Ca, Mg, and Sr are 36, 24, and 32 pg/g (parts per trillion), respectively. The mean precision of the analyses is 3%.

The gastropod shells were analyzed for stable isotopic compositions of oxygen and carbon with a Fisons Instruments Prism Series II isotope ratio mass spectrometer at the Center for Isotope Geochemistry at Lawrence Berkeley National Laboratory. CO_2 for isotopic analyses was produced by reacting 0.5 mg of the shell samples with phosphoric acid using an Isocarb automated carbonate device online with the Prism. The raw data from the mass spectrometer are corrected relative to the average values of six to nine analyses of a carbonate standard, CM-1 (δ^{13}C = 2.05‰, δ^{18}O = −1.94‰, calibrated vs. NBS-19 to the same values used at ANU), per sample run of twenty-four to thirty-six unknowns. Oxygen and carbon isotopic data for carbonate samples are both reported relative to the PDB standard. The precision for these analyses is ±0.05‰ for carbon and ±0.1‰ for oxygen.

The δ^{18}O values of water samples were measured using a variation of the method outlined by Socki et al. (1992). Raw values from the mass spectrometer were corrected for the fractionation of oxygen isotopes between the CO_2 and H_2O using an a_{CO_2}-H_2O value of 1.0412. For inter-run comparison, the δ^{18}O values for each set of twenty-four samples were normalized relative to the average value for three analyses of the CIG water standard, TW-1 (−11.7‰ relative to VSMOW). The δ^{18}O values of all water samples are reported relative to SMOW. Duplicate analyses were within ±0.1‰.

Strontium, magnesium, and calcium concentrations of San Francisco Bay waters were determined using a Cetac U-5000AT Ultrasonic Nebuliser coupled to a Perkin-Elmer Plasma 400 Emission Spectrometer. The samples were diluted 100-fold prior to analysis to minimize matrix interferences and viscosity influences.

4. RESULTS AND DISCUSSION

Concentrations of Ca, Sr, and Mg, ratios of Mg/Ca, Sr/Ca, and salinities of San Francisco Bay waters are listed in Table 1. Seawater measured just inside the Golden Gate (Sta. 18) has a salinity of 31.9‰, a Mg/Ca ratio of 3.17, and a Sr/Ca ratio of 0.0159. Freshwater entering the estuary at the delta has Mg/Ca ratios between 1 and 1.5, and Sr/Ca ratios of about 0.007. Strontium, magnesium, and calcium concentrations decrease with decreasing salinity (Fig. 5). However, Mg/Ca ratios in modern waters in the estuary do not change with salinity in the 10–35‰ range, but do decrease markedly below about 10‰ (Fig. 6a). Sr/Ca ratios also do not vary consistently over a salinity range of 32–7‰, but the freshest sample (2.8‰) had a significantly lower Sr/Ca ratio (Fig. 6b).

The oxygen isotopic composition (δ^{18}O) of Petaluma River water is ∼−7‰, due to fractionation as storm clouds formed over the Pacific Ocean travel towards the east over California (Ingraham and Taylor, 1991). Saline water entering Pelaluma Marsh from San Francisco Bay has a δ^{18}O value of 0 to −3‰ (lower than seawater), due to mixing in San Pablo Bay of seawater and freshwater entering the bay by way of the Sacramento-San Joaquin rivers (which has a δ^{18}O value of −11‰; Ingram et al., 1996a). During the wet season (winter and spring), runoff increases in both the Petaluma River and the Sacramento-San Joaquin rivers, further decreasing the δ^{18}O of waters entering Petaluma Marsh. Conversely, during the summer, evaporation should cause an increase in δ^{18}O due to preferential evaporation of the lighter isotope (^{16}O). Pond waters collected in Petaluma Marsh during the summer of 1993 and fall of 1994, respectively, had δ^{18}O values of 0.75‰ and 1.80‰.

Mg/Ca, Sr/Ca, and δ^{18}O values are not correlated, suggesting that they are controlled by different factors. The δ^{18}O values of ostracodes from the cores vary between −4.38 and 0.56‰, and the δ^{13}C values vary between −10.00 and −2.92‰ (Table 2). Assuming that δ^{18}O is primarily controlled by freshwater inflow and evaporation, this increase in δ^{18}O represents a salinity increase of about 10‰. For the gastropod samples, the δ^{18}O values vary between −2.54 and 1.27‰, and the δ^{13}C values vary between −6.93 and −0.37‰ (Table 3). The δ^{13}C and δ^{18}O values in both the ostracode and gastropod samples are inversely correlated (Fig. 7a,b).

Mg/Ca ratios vary between 0.0138 and 0.0355, and the Sr/Ca ratios vary between 0.0031 and 0.0042 (Table 4). While Mg/Ca ratios in ostracode calcite are controlled by both Mg/Ca in ambient waters and temperature, the latter normally has a more pronounced effect on the uptake of Mg by ostracodes (De Deckker et al., 1998). The range in Mg/Ca in the ostracode calcite represents a temperature range of about 14°C.

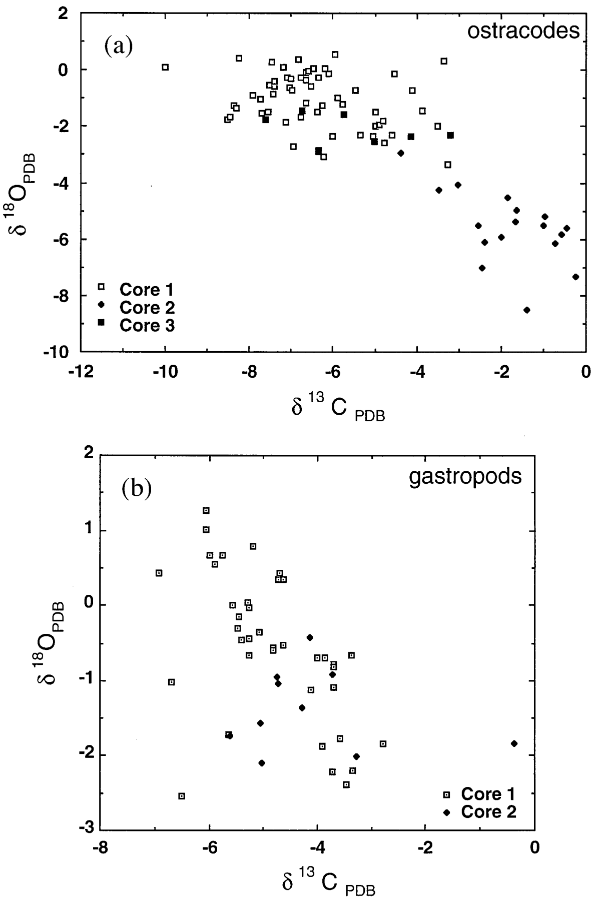

Fig. 7. (a) δ^{18}O vs. δ^{13}C for ostracode samples. (b) δ^{18}O vs. δ^{13}C for gastropod samples.

The δ^{13}C and δ^{18}O of gastropod samples are plotted vs. depth in Fig. 8, and δ^{13}C, δ^{18}O, Mg/Ca, and Sr/Ca values of the ostracode samples are plotted vs. depth in Fig. 9. The δ^{18}O values show a general increase between 80 cm (500 cal yr BP) and the top of the core, from about −3 ‰ (80 cm) to about 0‰ (0 cm). In contrast, the δ^{13}C values decrease from −4‰ (80 cm) to about −8‰ (0 cm). In the interval from 110 to 80 cm (700–500 cal yr BP), the average δ^{18}O value is −1.5‰, and the average δ^{13}C value is −6.5‰. The δ^{18}O values of the gastropod samples vary in a similar manner as do the ostracode δ^{18}O values, but show a more pronounced increase between 20 and 5 cm (125 to about 30 yr BP), and a marked decrease over the past 30 yr (Fig. 8).

The Mg/Ca ratio shows a more complicated pattern than δ^{18}O (Fig. 9). The average Mg/Ca ratio stays essentially constant between 650 and 380 cal yr BP (with an average value of 0.019), followed by a decrease between 380 and 150 cal yr BP The Mg/Ca ratio then increases between 150 cal yr BP and the present.

The general trend of increasing δ^{18}O over the past 500 yr probably reflects a gradual rise of salinity in the marsh. Increased salinity would be caused by either a gradual increase in sea level, increased evaporation in the marsh, or decreased in freshwater inflow. Sea level reconstructions in San Francisco Bay indicate a rise of ∼1–2 mm/yr between 6,000 ^{14}C yr and the present, allowing the salt marshes surrounding the bay to

Table 4. Mg/Ca and Sr/Ca, and depth in core (cm) for ostracode samples from Petaluma Marsh

Depth (cm)	Mg/Ca	Sr/Ca	Depth (cm)	Mg/Ca	Sr/Ca
Core 1					
1	0.0203	0.0032	52	0.0155	0.0035
2	0.0225	0.0036	54	0.0174	0.0037
3	0.0237	0.0039	56	0.0172	0.0037
4	0.0192	0.0034	57	0.0177	0.0035
5	0.0167	0.0032	61	0.0179	0.0036
6	0.0195	0.0035	62	0.0168	0.0034
7	0.0175	0.0034	63	0.0218	0.0043
8	0.0189	0.0038	64	0.0217	0.0043
9	0.0178	0.0032	65	0.0247	0.0037
10	0.0227	0.0033	66	0.0181	0.0035
12	0.0163	0.0040	67	0.0184	0.0036
13	0.0156	0.0029	68	0.0190	0.0039
14	0.0175	0.0032	Core 2		
15	0.0174	0.0030	42	0.0147	0.0031
16	0.0153	0.0035	46	0.0174	0.0037
17	0.0219	0.0035	48	0.0199	0.0039
18	0.0151	0.0036	60	0.0194	0.0040
19	0.0206	0.0033	62	0.0223	0.0034
20	0.0198	0.0035	66	0.0235	0.0037
21	0.0212	0.0034	68	0.0208	0.0033
22	0.0151	0.0035	70	0.0174	0.0034
23	0.0174	0.0038	72	0.0225	0.0035
24	0.0191	0.0036	74	0.0179	0.0042
25	0.0172	0.0037	76	0.0224	0.0037
26	0.0198	0.0040	78	0.0188	0.0037
27	0.0117	0.0041	80	0.0183	0.0040
28	0.0145	0.0037	82	0.0214	0.0038
29	0.0119	0.0035	86	0.0196	0.0035
30	0.0179	0.0040	88	0.0157	0.0035
31	0.0144	0.0034	90	0.0202	0.0037
32	0.0144	0.0036	92	0.0216	0.0036
33	0.0125	0.0032	94	0.0226	0.0039
34	0.0172	0.0037	96	0.0212	0.0034
35	0.0169	0.0036	98	0.0226	0.0034
36	0.0162	0.0038	100	0.0356	0.0038
37	0.0166	0.0039	Core 3		
38	0.0190	0.0037	69	0.0222	0.0039
39	0.0166	0.0038	71	0.0194	0.0036
40	0.0130	0.0034	73	0.0197	0.0035
43	0.0136	0.0034	75	0.0210	0.0035
44	0.0183	0.0037	87	0.0173	0.0038
45	0.0175	0.0040	101	0.0168	0.0037
46	0.0171	0.0040	103	0.0157	0.0035
49	0.0181	0.0037	105	0.0228	0.0034
			107	0.0145	0.0033

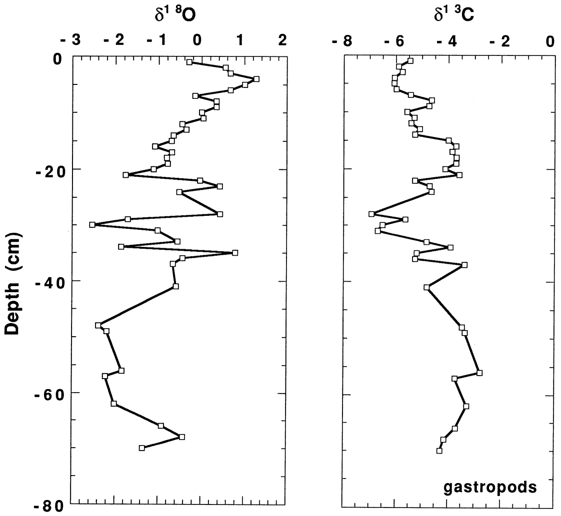

Fig. 8. δ^{18}O and δ^{13}C values (relative to PDB standard) of gastropods plotted against depth in core.

expand (Atwater, 1977). Sedimentation rates at Petaluma Marsh based on ^{14}C and pollen dating indicate that the rate of marsh accretion is constrained by sea level rise (Fig. 4). The mean accretion rate for the Petaluma high marsh study site (1.3 mm/yr) is essentially identical to the rise in mean annual sea level at San Francisco for the period 1855–1993. Therefore, the salinity increase observed in the core most likely is a result of sea level rise. This is consistent with pollen analyses from Petaluma Marsh, which reveal an increase in the relative abundance of Chenopodiaceae pollen (presumably *Salicornia,* or pickleweed) from the base to the top of the core (Byrne et al., unpubl. data).

Superimposed on the general trend of increasing salinity are higher frequency variations in δ^{18}O, δ^{13}C, Mg/Ca, and Sr/Ca (Fig. 9). These shorter-timescale variations may reflect changes in freshwater inflow, temperature, and evaporation in the marsh.

This record suggests that the duration of wet and dry periods was greater over the past 700 yr than in the twentieth century instrumental record. δ^{18}O and Mg/Ca ratios were low between 150 and 400 cal yr BP, indicating higher than modern freshwater inflow and low temperature, suggesting cool, wet conditions during the Little Ice Age in central California. δ^{18}O and Mg/Ca ratios were highest 400–450 cal yr BP and 550–650 cal yr BP, indicating lower than modern freshwater inflow and higher temperature during the end of the Medieval Warm Period, and again in the following century (Fig. 9).

Some similarities exist between this record of inferred freshwater inflow and other paleoclimatic records in California. Tree ring evidence from the Sierra Nevada indicates that the period from 510 to 420 cal yr BP was warmer and wetter than any part of the twentieth century (Graumlich, 1990). This is in close agreement with our interval of highest inferred inflow to Petaluma Marsh. It is also in agreement with paleo-inflow records from south-central San Francisco Bay, based on stable isotope measurements in mollusk shells, that indicate that the highest inflow over the past 2700 yr was from 450 to 550 cal yr BP (Ingram et al., 1996a). The tree ring record indicates that periods of below average precipitation occurred at 416–406 cal yr BP, 359–376 cal yr BP, 299–314 cal yr BP, 202–215 cal yr BP, and 137–152 cal yr BP (Earle, 1993).

The inverse correlation between δ^{13}C and δ^{18}O values of both the ostracodes and gastropodes samples indicates that the carbon isotopic values are not controlled by changes in freshwater inflow. This is in contrast to δ^{13}C and δ^{18}O values in the estuary, where there is a positive correlation between δ^{13}C and δ^{18}O values in waters and biogenic carbonate shells taken from sediment cores (Ingram et al., 1996b,c). The carbon isotopic composition of dissolved inorganic carbon in Petaluma Marsh may be dominated by respired CO_2 and decomposition of marsh vegetation. The carbon isotopic composition of marsh vegetation has been shown to reflect the relative proportion of C_3, C_4, and CAM plants in the marsh (Byrne et al., 1999).

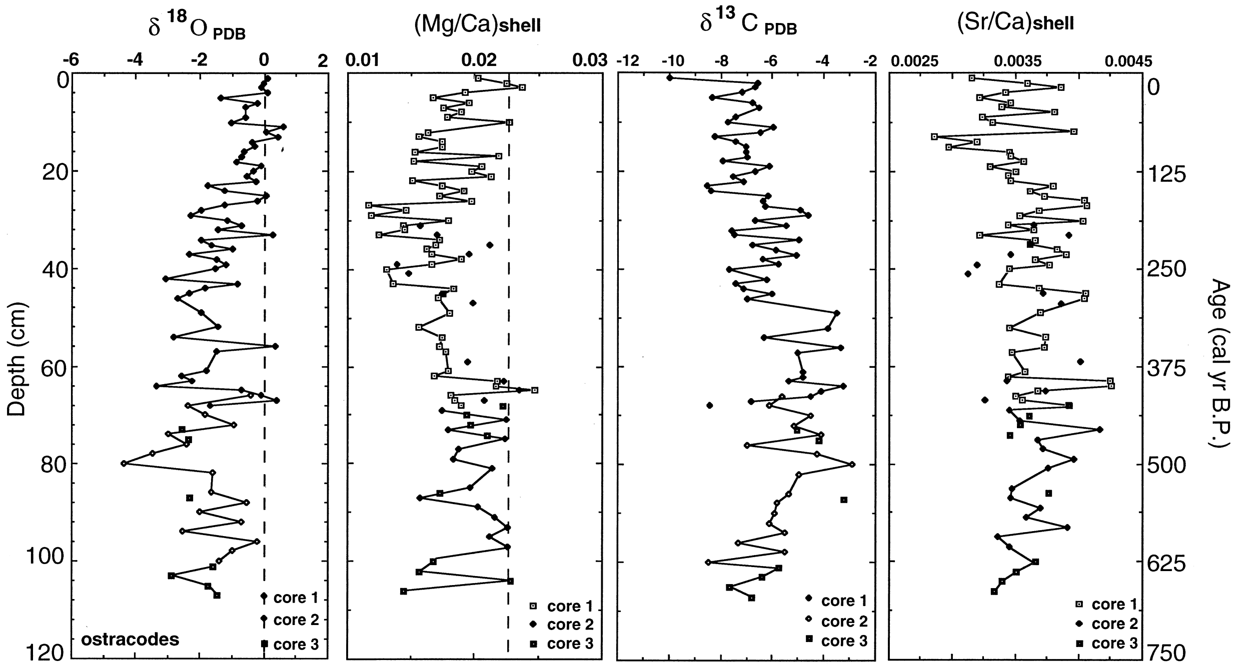

Fig. 9. δ^{18}O, Mg/Ca, δ^{13}C, and Sr/Ca values of ostracodes plotted against depth in core. Calibrated radiocarbon ages (in cal yr BP) are shown on the right hand column.

In Petaluma Marsh, the δ^{13}C values of sedimentary organic carbon decreases upcore, reflecting the relative increase in *Salicornia* (a CAM plant, which a δ^{13}C value of -26‰) over C_4 vegetations (with δ^{13}C values of ~-14‰).

5. CONCLUSIONS

In this study, ^{18}O/^{16}O and minor element chemistry (Sr/Ca and Mg/Ca ratios) of ostracodes (*Cyprideis*) from Petaluma Marsh sediments were used to reconstruct changes in sea level and freshwater inflow to the marsh over the past 700 yr. The δ^{18}O values gradually increase over the past 500 yr, reflecting an increase in salinity (either rising sea level or increasing evaporation) in the marsh. Increasing salinity is also indicated by pollen and plant macrofossils from Petaluma Marsh. Superimposed on this trend are higher frequency δ^{18}O variations of 3 to 4‰, reflecting changes in freshwater inflow, temperature, and evaporation in the marsh, with periods of 35–115 yr. δ^{13}C values varied over a wide range (0‰ and -10‰) and are inversely correlated with δ^{18}O. δ^{18}O and Mg/Ca ratios were low ca 150–400 cal yr BP, indicating cool, wet conditions during the Little Ice Age in California. δ^{18}O and Mg/Ca ratios were high from 480 to 650 cal yr BP, indicating low freshwater inflow and higher temperature during the Medieval Warm Period. The carbon isotopic composition of biogenic carbonate from the marsh reflects the decomposition of marsh vegetation and has shown a general decrease between 500 yr and the present, due to a shift in vegetation from C_4 to CAM plants.

Acknowledgements—This work was supported by the Western Regional Center of the National Institute For Global Environmental Change. We thank Josh Collins at the San Francisco Estuary Institute for assistance with coring and interpretation of Petaluma Marsh sediments. Joe Cali at the Australian National University in Canberra provided invaluable help with laboratory analyses. Christina de la Rocha collected and filtered San Francisco Bay water samples. We thank David Peterson, Ellen Thomas, and Paul Baker for thoughtful reviews of the manuscript.

REFERENCES

Atwater B. F., Hedel C. W., and Helley E. J. (1977) Late Quaternary depositional history, Holocene sea-level changes, and vertical crustal movement, southern San Francisco Bay, California. *U.S. Geol. Surv. Prof. Pap. 1014*.

Atwater B. F., Conard S. G., Dowden J. N., Hedel C. W., MacDonald R. L. and Savage W. (1979) History, landforms, and vegetation of the estuary's tidal marshes. In *San Francisco Bay: the Urbanized Estuary* (ed. T. J. Conomos), pp. 347–385. Amer. Assoc. Advance. Sci.

Byrne R., Collins J., and Esser B. (1984). Late-Holocene Saltmarsh Formation at Petaluma, California. *Geol. Soc. Amer. Abstr. Prog*. **26,** A-530

Byrne A. R., Ingram B. L., Conrad M. E., and Starratt S. (1999). *Geology* (in review).

Chivas A. R., De Deckker P., Cali J. A., Chapman A., Kiss E., and Shelley J. M. G. (1993) Coupled stable-isotope and trace-element measurements of lacustrine carbonates as paleoclimatic indicators. In *Climate Change in Continental Isotopic Records* (ed. P. K. Swart et al.); *Amer. Geophys. Monogr*. **78,** 113–121.

Conomos T. J. (1979) Properties and circulation of San Francisco Bay waters. In *San Francisco Bay: The Urbanized Estuary* (ed. T. J. Conomos), pp. 47–84. Amer. Assoc. Advance. Sci.

De Deckker P., Chivas A. R., Shelley J. M. G., and Torgersen T. (1988a), Ostracode shell chemistry: A new palaeoenvironmental indicator applied to a regressive/transgressive record from the Gulf of Carpentaria, Australia. *Palaeogeogr., Palaeoclim., Palaeoecol.* **66,** 231–241.

De Deckker P., Chivas A. R., Shelley J. M. G., and Torgersen T. (1988b) Palaeoenvironment of the Messinian Mediterranean Lago Mare from strontium and magnesium in ostracode shells. *Palaios* **3,** 352–358.

De Deckker P., Chivas A. R., and Shelley J. M. (1998) The uptake of magnesium and strontium in the euryhaline ostracod *Cyprideis* determined from in vitro experiments. *Palaeogeogr. Palaeoclim. Palaeoecol*.

Earle C. J. (1993) Asynchronous droughts in California streamflow as reconstructed from tree rings: *Quat. Res.* **39,** 290–299.

Graumlich L. J. (1990) Interaction between variables controlling subalpine tree growth: Implications for the climatic history of the Sierra Nevada. Proc. Sixth Annu. Pacific Climate (PACLIM) Workshop, pp. 115–118.

Ingram B. L. and DePaolo D. J. (1993) A 4300 year strontium isotope record of estuarine paleosalinity in San Francisco Bay, California. *Earth Planet. Sci. Lett.* **119,** 103–119.

Ingram B. L. and Sloan D. (1992) Strontium isotopic record of estuarine sediments as paleosalinity-paleoclimate record indicator. *Science* **255,** 68–72.

Ingram B. L., Conrad M. E., and Ingle J. C. (1996a) Stable isotope and salinity systematics in estuarine waters and carbonates: San Francisco Bay, *Geochim. Cosmochim. Acta* **60,** 455–467.

Ingram B. L., Ingle J. C., and Conrad M. E. (1996b) A 2,000-yr record of San Joaquin and Sacramento river inflow to San Francisco Bay, California. *Geology* **24,** 331–334.

Ingram B. L., Ingle J. C., and Conrad M. E. (1996c) Stable isotope record of Late Holocene paleosalinity and paleodischarge in San Francisco Bay, California. *Earth Planet. Sci. Lett.* **141,** 237–247.

Ingraham N. L. and Taylor B. E. (1991) Light stable isotope systematics of large-scale hydrologic regimes in California and Nevada. *Water Resourc. Res.* **27,** 77–90.

Nichols F. H., Cloern J. E., Luoma S. N., and Peterson D. H. (1986) The modification of an estuary. *Science* **231,** 525–648.

Peterson D. H. et al. (1989) Climate variability in an estuary: Effects of riverflow on San Francisco Bay. In *Aspects of Climate Variability in the Pacific and the Western Americas* (ed. D. H. Peterson); *AGU Monogr.* **55,** 419–442.

Sandberg P. A. (1964) The ostracode genus *Cyprideis* in the Americas. *Stockholm Contrib. Geol.* **12,** 1–178.

Socki R. A., Karlsson H. R., and Gibson E. K. (1992) Extraction technique for the determination of oxygen-18 in water using pre-evacuated glass vials. *Anal. Chem.* **64,** 829–831.

Spiker E. C. (1980) The behavior of ^{14}C and ^{13}C in estuarine water: Effects of *in situ* CO_2 production and atmospheric exchange. *Radiocarbon* **22,** 647–654.