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## Stable isotope and salinity systematics in estuarine waters and carbonates: San Francisco Bay

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**Abstract**—Salinities,  $\delta D$  and  $\delta^{18}O$  values of water samples collected bimonthly from two stations in San Francisco Bay estuary during 1991–1993, and along a salinity transect in March of 1992, indicate a linear mixing relation between the isotopic compositions of the waters and their salinities. The salinities and stable isotope compositions of samples from two locations in San Francisco Bay vary in response to changes in freshwater inflow. The data from these locations indicate simple mixtures of Pacific Ocean water (salinity  $\approx 33$ ,  $\delta^{18}O \approx 0$  to  $-1\text{‰}$ ,  $\delta D \approx 0$  to  $-10\text{‰}$ ) and Sacramento–San Joaquin River water (salinity  $\approx 0$ ,  $\delta^{18}O = -10$  to  $-12\text{‰}$ ,  $\delta D = -75$  to  $-85\text{‰}$ ).

Preliminary water balance estimates, using isotopic differences between local and upland runoff, suggest that local runoff (including waste water) comprises less than 20% of total freshwater entering the bay.

The average  $\delta^{18}O$  values of mussel shells (*Mytilus edulis*) collected live from eight locations in San Francisco Bay primarily reflect the  $\delta^{18}O$  of the water in which they grew. Shells subsampled along growth bands show that seasonal shifts in salinity and  $\delta^{18}O$  are recorded in the shells. Therefore, the use of stable isotope measurements should be useful in reconstructing pre-instrumental bay salinity and associated freshwater inflow (both annual average values and seasonal variations) to the San Francisco Bay, as well as potentially other estuarine systems.

### 1. INTRODUCTION

Estuaries occur along the coastal zone where drainage from continental watersheds enters the sea. San Francisco Bay is the second largest estuary on the west coast of North America, draining 40% the area of California. The streamflow entering San Francisco Bay is the primary control on the salinity of San Francisco Bay waters (Peterson et al., 1989) and is perhaps the most important variable controlling the ecosystems (Peterson et al., 1995). Knowledge of the long-term variability of streamflow and salinity in San Francisco Bay is therefore important in understanding and managing the estuarine ecosystems. Due to the relatively short period of time during which measurements of streamflow and salinity have been recorded for the San Francisco Bay (about eighty years), the development of proxy indicators for streamflow are important for documenting long-term natural conditions in the bay. These data are also necessary to separate the natural, climate-induced variability of freshwater inflow and salinity from recent man-made changes, caused by water development, diversion, and the filling of wetlands (Cayan and Peterson, 1989, 1993; Peterson et al., 1995). Here, we describe stable isotopic measurements of modern estuarine waters and biogenic carbonates from San Francisco Bay, their relation to salinity and freshwater flow into the Bay, and their potential use as paleoenvironmental indicators.

The estuarine waters in San Francisco Bay are a mixture of high salinity ocean water (33 psu) and low salinity (0 psu) river water (Conomos, 1979). A horizontal salinity zonation is developed in the estuary from the Golden Gate, where sea-

water enters (Fig. 1), to the Delta, where river waters enter (Conomos et al., 1979; Cloern and Nichols, 1985). The contours of equal salinity move toward the ocean with increasing freshwater inflow, and back upstream as river discharge decreases. Most of the freshwater entering the bay (about 90%) comes by way of the Sacramento–San Joaquin drainage, a land area of approximately 40% of California (162,000 km<sup>2</sup>, Fig. 2; Conomos, 1979). The other 10% of the water is comprised of small stream runoff, small rivers (such as the Petaluma and Napa), and waste water (Conomos, 1979). The drainage basin for San Francisco Bay is fed from the north by the Sacramento River and its tributaries (Feather, Yuba, Bear, and American; 80%), from the south by the San Joaquin River and its tributaries (Merced, Tuolumne, and Stanislaus; 15%), and from the east by the Mokelumne and Calaveras rivers (5%) (Fig. 2; Conomos, 1979). The inflow of freshwater to the Bay is seasonal, with maximum inflow during winter to late spring due to rainfall and meltwater runoff from the Sierra Nevada and Cascade Ranges (Conomos et al., 1979). In response to these changes in river discharge, the salinity at any one location varies seasonally, with minimum salinity conditions occurring during the winter and spring and maximum salinity conditions during the summer and fall. Salinity in the bay is also modified by evaporation, which increases in summer due to increased insolation, air temperatures, and wind speeds (Conomos et al., 1979).

The hydrogen and oxygen isotopic compositions of river water entering the bay is an average of the  $\delta D$  and  $\delta^{18}O$  values of precipitation and groundwater in the river's watershed. The  $\delta D$  and  $\delta^{18}O$  values of precipitation in Cali-

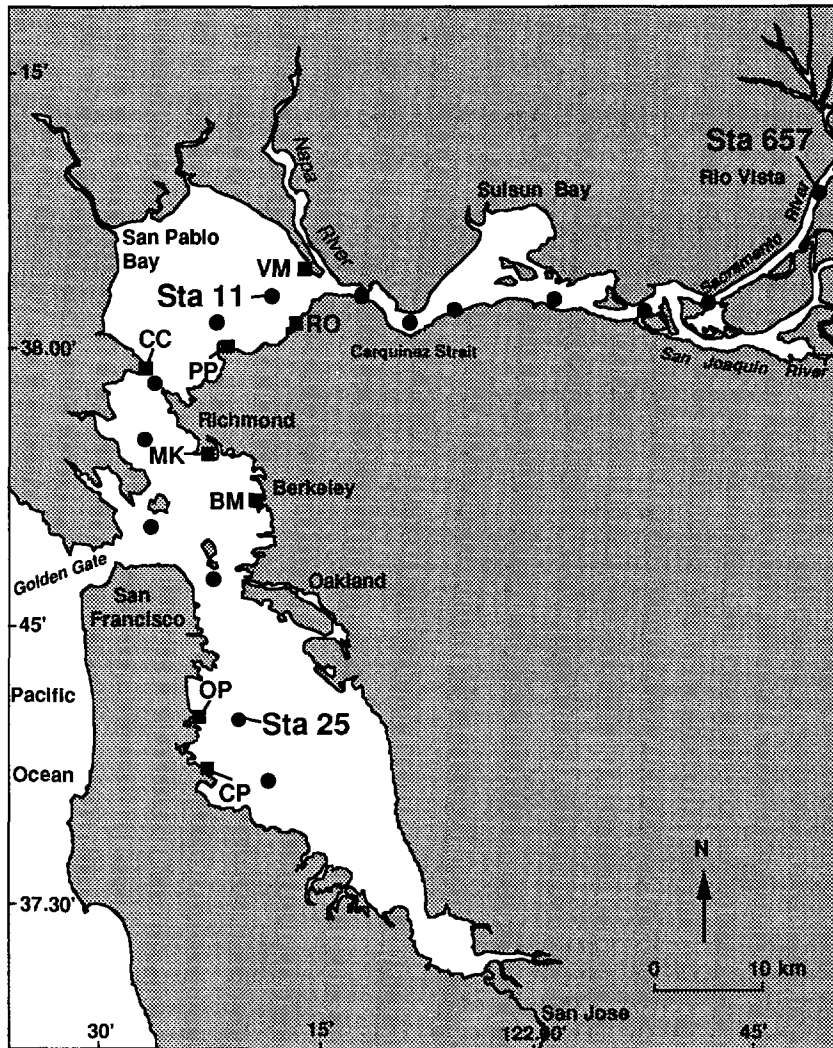


FIG. 1. Map of San Francisco Bay estuary showing water and shell sample locations. Shell sampling abbreviations are given in Table 3.

ifornia decrease towards the east as storm clouds formed over the Pacific Ocean become progressively depleted in the heavier isotopes through a Rayleigh fractionation process (Ingraham and Taylor, 1991). In the Sierra Nevada mountains, increasing altitude also causes decreasing temperature and increased precipitation, resulting in rapid depletion of D and  $^{18}\text{O}$  in both snow and rain. The net effect is that the hydrogen and oxygen isotope ratios of precipitation decreases from  $\delta\text{D} \approx -40\text{‰}$  and  $\delta^{18}\text{O} \approx -5.5\text{‰}$  on the Pacific Coast of California to  $\delta\text{D} \approx -120\text{‰}$  and  $\delta^{18}\text{O} \approx -16.0\text{‰}$  in the eastern Sierra Nevada (Ingraham and Taylor, 1991). River water entering San Francisco Bay is a mixture of surface runoff (from precipitation and snow-melt) and groundwater integrated over the entire drainage basin and would therefore be expected to have  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values representing averages of all these sources.

The salinity and stable isotopic compositions of coastal waters along the northern California margin are modified by freshwater from the continents and coastal upwelling (Peter-

son et al., 1989), with average isotopic compositions of  $-10\text{‰}$  to  $0\text{‰}$  for  $\delta\text{D}$  and  $-1\text{‰}$  to  $0\text{‰}$  for  $\delta^{18}\text{O}$ . Because the variations in the stable isotope compositions of coastal waters are relatively small compared with the difference between their isotopic compositions and those of Sacramento River water, we assume the coastal endmember remains constant.

Previous studies have established the relation between salinity, strontium content, and strontium isotopic compositions in San Francisco Bay waters (Ingram and Sloan, 1992; Ingram, 1992; Ingram and DePaolo, 1993). In this study, we similarly demonstrate the relationship between salinity gradients in the bay and stable isotopic composition, and show that these compositional variations are recorded in the carbonate shells of mollusks living in the estuary. We also evaluate the use of stable isotope measurements of growth bands in fossil mussel shells, for determining seasonal freshwater inflow and salinity variations in San Francisco Bay. Seasonal salinity variations are controlled by both natural climatic variations as well as by human-caused changes in the watershed,



FIG. 2. Map of California, showing drainage area for San Francisco Bay, the Sacramento River basin to the north and the San Joaquin River basin to the east and south.

including upstream water storage (reservoirs), diking and filling of wetlands, and water diversion.

## 2. ESTUARINE WATER AND SHELL SAMPLES

To assess the relations between salinity and the  $\delta D$  and  $\delta^{18}O$  values of water within the San Francisco Bay estuary and to determine the effect of seasonal variations of freshwater inflow into the Bay, waters sampled at approximately two month intervals over a three year period (1991–1993) were analyzed. Samples were measured from three sites, one in the Sacramento River and the other two within the San Francisco Bay. The Sacramento River waters were collected from the Delta just upstream of the confluence of the Sacramento and San Joaquin rivers (USGS station 657 at Rio Vista; Fig. 1). The San Francisco Bay sites (USGS stations 11 and 25; Fig. 1) were chosen because of their proximity with core localities in south-central San Francisco Bay and San Pablo Bay. To test whether the relations observed at stations 11 and 25 applied throughout the Bay, a suite of water samples was collected from twenty sites in the estuary on March 12, 1992 (Fig. 1).

In order to verify the relation between  $\delta^{18}O$  in the ambient water and  $\delta^{18}O$  in the biogenic carbonate, five to eight live specimens of *Mytilus* were collected at each of eight locations in San Francisco Bay during June and July of 1994. The average  $\delta^{18}O$  values for the whole shells, representing 0.5 to 1.5 years of growth, were compared with  $\delta^{18}O$  values of waters collected with the mussels and with monthly salinity and temperature records obtained by the USGS at nearby monitoring locations. In addition, shells from two sites were subsampled along growth bands in order to determine the extent to which seasonal salinity and isotopic variations were recorded in the shells.

## 3. LABORATORY METHODS

All stable isotope analyses for this study were done at the Center for Isotope Geochemistry (CIG) at Lawrence Berkeley National Laboratory. The  $\delta^{18}O$  values of water samples were measured using a variation of the method outlined by Sockki et al. (1992) and are given relative to VSMOW. Water samples (2 mL) were equilibrated at

25°C ( $\pm 0.2^\circ C$ ) for at least 12 h with approximately 800 mbars of  $CO_2$  in 7 cm<sup>3</sup> Vacutainers (a registered trademark of Becton Dickinson and Company of Rutherford, NJ). The  $CO_2$  was then extracted from the Vacutainers, purified, and analyzed with a Fisons Instruments Prism Series II isotope ratio mass spectrometer. Raw values from the mass spectrometer were corrected for the fractionation of oxygen isotopes between the  $CO_2$  and  $H_2O$  using an  $\alpha_{CO_2-H_2O}$  value of 1.0412. Duplicate analyses were within  $\pm 0.1\%$ . The  $\delta D$  values of the waters were analyzed using the method described by Venneman and O'Neil (1993) and are given relative to VSMOW. 3  $\mu L$  water samples were injected into evacuated Pyrex tubes containing approximately 50 mg of Zn metal. The water was reduced to  $H_2$  gas by baking the tubes for 30 min at 500°C. The  $\delta D$  values of the hydrogen were analyzed on the Prism. Duplicate analyses were generally within  $\pm 2\%$ .

The mussels were cleaned to remove all tissue and organic material and dried prior to subsampling. The shells were sampled across their full length to determine the average oxygen and carbon isotopic compositions for the entire growth period. Growth bands in the shells were subsampled with a hand-held engraving drill with a 0.5 mm bit.  $CO_2$  for isotopic analyses was produced by reacting 1–2 mg of the shell samples with phosphoric acid (following the methods of McCrea, 1950) using an Isocarb automated carbonate device on line with the Prism. The raw isotopic data from the mass spectrometer was corrected relative to the average values of 6–9 analyses of a carbonate standard, CM-1 ( $\delta^{13}C = 2.05\%$ ,  $\delta^{18}O = -1.94\%$ ), per sample run of 24–36 unknowns. Oxygen and carbon isotopic data for carbonate samples are reported relative to the PDB Belemnite standard. The precision for these analyses is  $\pm 0.05\%$  for carbon and  $\pm 0.1\%$  for oxygen.

## 4. RESULTS AND DISCUSSION

### 4.1. River and Estuarine Waters

The salinities and  $\delta^{18}O$  values of the estuarine waters sampled on March 12, 1992 are given in Table 1. The most saline sample with the highest  $\delta^{18}O$  value taken from 18 m water depth near the Golden Gate. It has a salinity of 29.5 and  $\delta^{18}O$  of  $-1.2\%$ . The samples with the lowest salinities and  $\delta^{18}O$  values were collected from stations 657 at Rio Vista, the Sacramento River just upstream of its confluence with the San Joaquin River in the delta. The rest of the samples from the estuary define a linear mixing relation between these river water and seawater endmembers (Fig. 3), with a correlation coefficient of 0.985. The relation between  $\delta^{18}O$  of the water and salinity ( $S$ ), given as  $\delta^{18}O_{\text{water}} = 0.34S - 11.6$ , indicates a 3 unit change in salinity for each 1‰ change in  $\delta^{18}O$ . Thus,  $\delta^{18}O$  can detect changes in salinity with a precision of  $\pm 0.3$  psu.

The salinities and  $\delta^{18}O$  values of the water samples collected during the period from 1991 to 1993 (Table 2) are plotted vs. collection date (Fig. 4). The Sacramento River waters from station 657 (near Rio Vista; Fig. 1) have very consistent  $\delta^{18}O$  values during 1991 and 1992, averaging  $-10.7\%$ . During 1993, however, the average  $\delta^{18}O$  values of the river water dropped to  $-12.0\%$ . Both 1991 and 1992 were very dry years, coming at the end of a six-year drought, whereas 1993 was an unusually wet year. Some variation in  $\delta^{18}O$  would be predicted due to changing proportions of precipitation vs. groundwater between the wet and dry years. The 1.3‰ decrease in  $\delta^{18}O$  during 1993 may reflect an increased proportion of surface water (precipitation and snowmelt) to groundwater in the river during a wet year as compared with the two drought years, because groundwater is typically

**Table 1.** Salinity and stable isotope data for water samples collected from stations 11 and 25 in the San Francisco Bay and station 657 at the mouth of the Sacramento River. Oxygen and hydrogen isotope ratios are per mil relative to VSMOW.

Sampling Date	Station 25			Station 11			Station 657		
	Salinity	$\delta^{18}\text{O}$	$\delta\text{D}$	Salinity	$\delta^{18}\text{O}$	$\delta\text{D}$	Salinity	$\delta^{18}\text{O}$	$\delta\text{D}$
Feb. 6, 1991				20.91	-4.5	-31			
Mar. 11, 1991	28.93	-1.9	-14	16.82	-5.2	-40			
Apr. 11, 1991	26.03	-2.6	-18	15.16	-5.5	-38			
June 5, 1991	29.75	-1.3	-12	17.71	-4.6	-32	0.10	-10.7	-79
Aug. 1 1991	31.46	-0.9	-9	21.10	-3.6	-29	0.10	-10.6	-76
Oct. 1, 1991	32.27	-1.3	-12	20.22	-3.9		0.10	-10.9	-76
Dec. 10, 1991	31.43	-0.9	-9	21.53	-4.2	-31	0.74	-10.8	-77
Mar. 4, 1992	25.13	-3.0	-21	15.70	-6.0	-41	0.13	-10.4	-76
Apr. 7, 1992	25.68	-2.7	-23	12.94	-6.5	-45	0.13	-11.0	-78
May 27, 1992	29.37	-1.5	-8	22.42	-3.7	-28	1.43	-10.8	-78
July 28, 1992	31.07	-1.1	-7	23.77	-2.8	-22	0.44	-10.5	-77
Oct. 14, 1992	32.11	-0.7	-8	24.84	-2.9	-23	0.84	-10.7	-77
Dec. 2, 1992	31.26	-1.1	-10	24.09	-3.1	-24	0.21	-10.8	-81
Feb. 24, 1993	22.29	-3.7	-32	0.65	-8.7	-66	0.08	-10.6	-75
Apr. 1, 1993	18.80	-4.8	-36	2.65	-10.6	-75	0.08	-12.1	-84
June 16, 1993	25.04	-3.1	-26	6.80	-9.4	-65	0.07	-11.9	-85
Aug. 10, 1993	28.83	-1.8	-17	14.22	-6.5	-48	0.06	-12.0	-83
Sept. 10, 1993	29.34	-1.5	-12	15.44	-6.4				

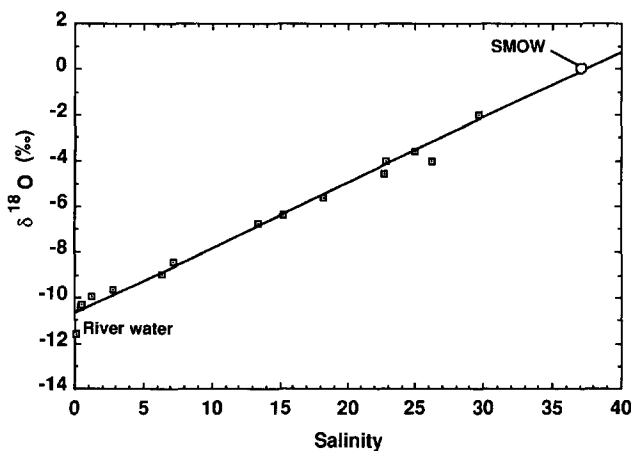
heavier than surface water (Ingraham and Taylor, 1991). Beyond this yearly variation, no seasonal variation in the  $\delta^{18}\text{O}$  values of the Sacramento River waters, such as a decrease in the  $\delta^{18}\text{O}$  value during winter or spring, was observed. At this time, we do not know if the lack of seasonal variation represents the natural situation, or if it is caused by the mixing of waters stored in upstream reservoirs, which may serve to average out seasonal  $\delta^{18}\text{O}$  variations.

Both the salinity and  $\delta^{18}\text{O}$  values of the estuarine waters from stations 11 and 25 show large seasonal fluctuations in response to changes in freshwater flow into the Bay (Fig. 4). The  $\delta\text{D}$  values of the waters also varied in a similar manner. All three were lowest during the winter and early spring of each year and increased during the late spring and fall. Further, the magnitude of this seasonal variability was roughly

twice as large during 1993 (wet year) than during 1991–1992 (dry years; Fig. 4; Table 2). The average salinities and stable isotope compositions of the waters at the two sample sites were much different during 1991–1992 than during 1993 (Fig. 4; Table 2). Like salinity,  $\delta^{18}\text{O}$  and  $\delta\text{D}$  are very sensitive to changes in freshwater flow into the Bay.

**TABLE 2.** Oxygen isotopic composition and salinity of estuarine waters collected on March 12, 1992.

Sample	$\delta^{18}\text{O}$ (‰)	Salinity
SFB-657	-11.60	0.1
SFB-2B	-10.30	0.5
SFB-2T	-10.42	0.4
SFB-4B	-9.64	2.8
SFB-4T	-9.93	1.2
SFB-6T	-8.96	6.3
SFB-6B	-8.38	7.2
SFB-8T	-6.72	13.4
SFB-10B	-5.63	18.2
SFB-10T	-6.40	15.2
SFB-12	-	18.0
SFB-13T	-4.00	22.8
SFB-15T	-4.60	22.7
SFB-15B	-	26.0
SFB-18T	-2.01	29.7
SFB-18B	-	30.0
SFB-21T	-4.00	26.2
SFB-27T	-3.60	25.0

**FIG. 3.**  $\delta^{18}\text{O}$  (‰) vs. salinity for San Francisco Bay waters collected on March 12, 1992.

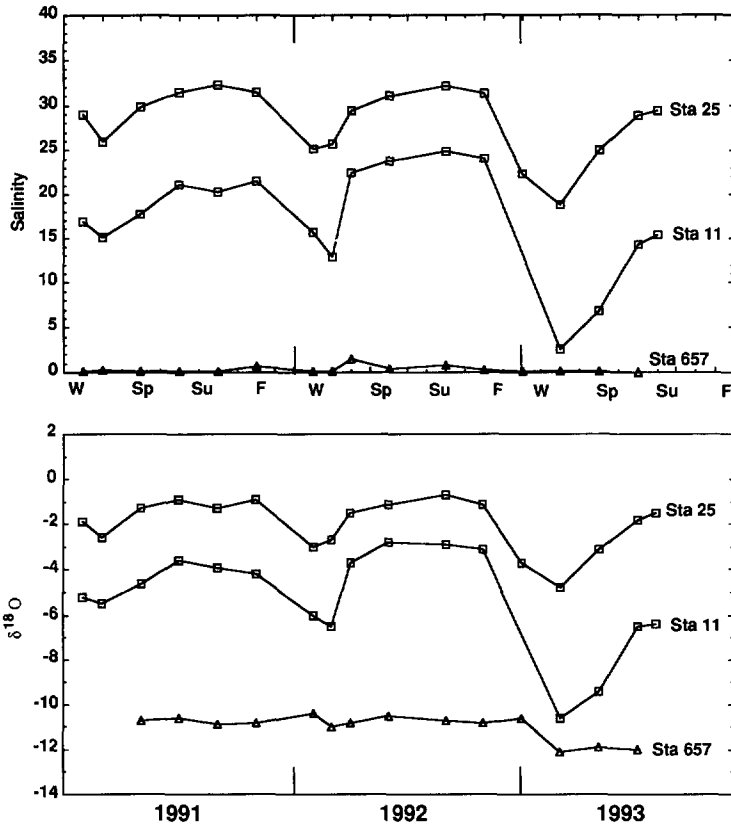


FIG. 4.  $\delta^{18}\text{O}$  (‰) and salinity variations in San Francisco Bay vs. time at three locations in the bay (stations 657, 11, and 25).

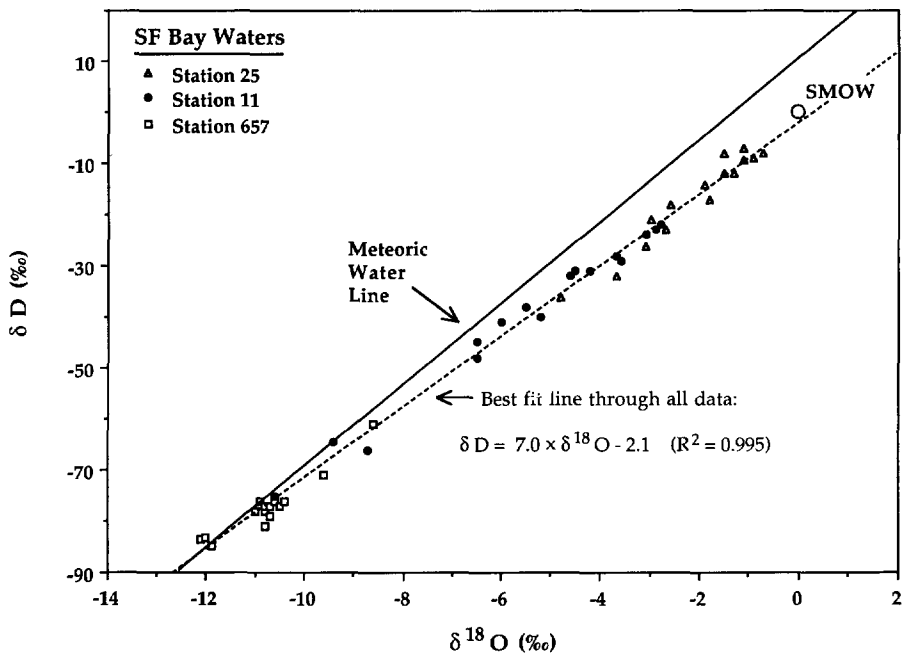


FIG. 5. Hydrogen vs. oxygen isotopic compositions in bay waters.

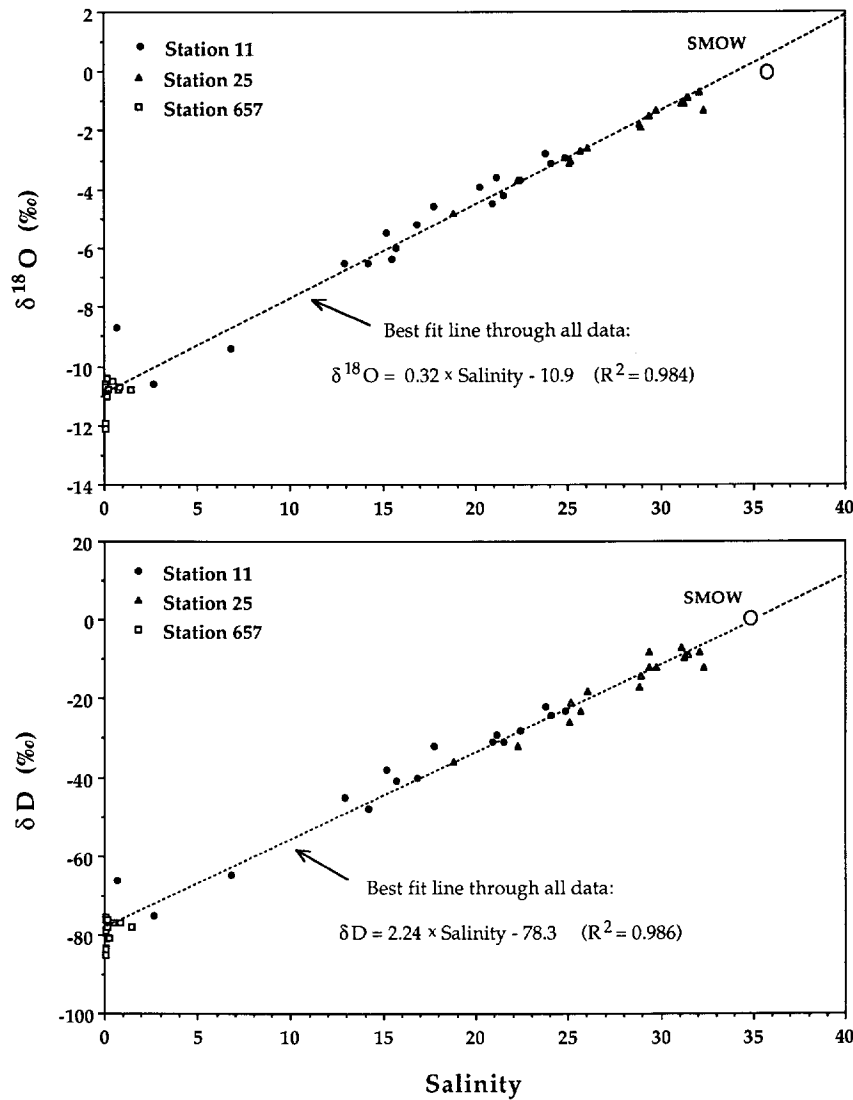


FIG. 6. (a) Oxygen and (b) hydrogen isotopic compositions (‰) plotted against salinity.

It is necessary to evaluate the degree to which factors other than freshwater inflow from the delta, such as evaporation or local runoff, influence the relations between salinity and the isotopic compositions of the waters. This is of importance not only for evaluating the impact of these processes on the estuarine environment, but for the successful application of stable isotopic measurements of fossil samples in determining paleo-streamflows. To some extent, this can be done by examining the relations between the different isotopic ratios. Hydrogen data is plotted against oxygen isotope data for the water samples from stations 11, 25, and 657 (Fig. 5). The data form a well-defined, linear mixing line between the river waters from Station 657, which fall on the global meteoric water line, and SMOW. If there had been significant evaporation (greater than  $\sim 20\%$ ) of either upstream water or surface waters from the estuary, the data would fall below this line.

The hydrogen and oxygen isotope data for the samples are each plotted vs. salinity (Fig. 6). On both of these plots, the data form linear mixing lines between river water and ocean water. Some data fall to the left of the mixing lines, especially for the samples from Station 11, the San Pablo Bay sampling site (Fig. 2). This scatter could be due to a component of local meteoric water and wastewater (salinity  $\approx 0$  psu,  $\delta\text{D} \approx -40\text{‰}$ ,  $\delta^{18}\text{O} \approx -5.5\text{‰}$ ) entering the Bay.

Because the data (Table 2, Fig. 6) show some scatter toward a local meteoritic component, we performed simple mass balance calculations based on the salinity and  $\delta^{18}\text{O}$  values of the samples from Stations 11 and 25 to assess the approximate size of the component of local runoff and wastewater (non-delta flow) into San Francisco Bay. For purposes of this exercise, we assume a single, relatively homogeneous component of water entering the Bay and that other processes, such as evaporation, had a negligible effect on bay salinity and  $\delta^{18}\text{O}$ . We thereby have a simple three-component system

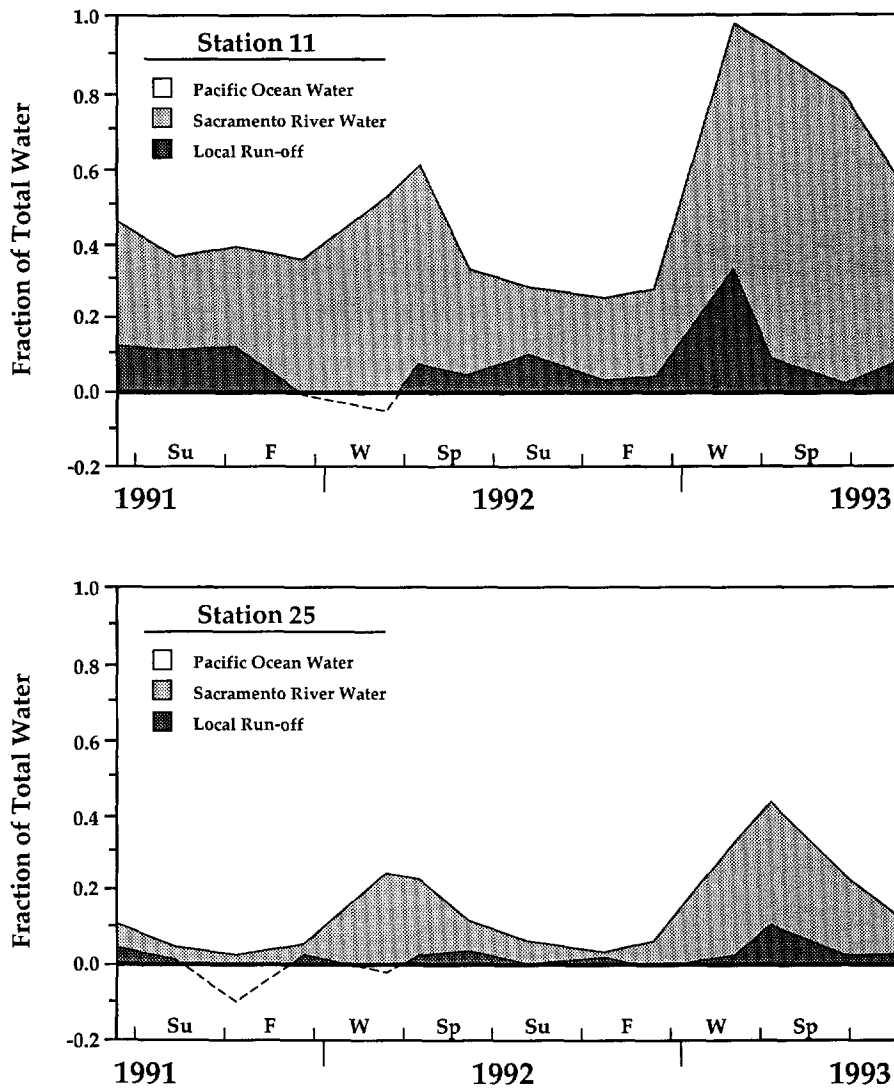


FIG. 7. Water balances calculated from  $\delta^{18}\text{O}$  and salinity measurements of San Francisco Bay waters, showing relative contributions of waters from the Sacramento-San Joaquin basins, ocean waters, and local runoff.

consisting of river water entering the San Francisco Bay through the Sacramento-San Joaquin Delta ( $R$ ), Pacific Ocean water entering the Bay through the Golden Gate ( $P$ ), and local runoff ( $L$ ). This gives the following three equations:

$$S_R \cdot X_R + S_P \cdot X_P + S_L \cdot X_L = S_S; \quad (1)$$

$$\delta^{18}\text{O}_R \cdot X_R + \delta^{18}\text{O}_P \cdot X_P + \delta^{18}\text{O}_L \cdot X_L = \delta^{18}\text{O}_S; \quad (2)$$

$$X_R + X_P + X_L = 1, \quad (3)$$

where  $X_R$ ,  $X_P$ , and  $X_L$  are the fractions of the three components,  $S_R$ ,  $S_P$ ,  $S_L$ , and  $S_S$  are the salinities of the three components and of the sample, and  $\delta^{18}\text{O}_R$ ,  $\delta^{18}\text{O}_P$ ,  $\delta^{18}\text{O}_L$ , and  $\delta^{18}\text{O}_S$  are the oxygen isotope ratios of the three components and of the sample. For these calculations, we used the measured values for  $S_R$ ,  $S_S$ ,  $\delta^{18}\text{O}_R$ , and  $\delta^{18}\text{O}_S$  (Table 2), 33 for  $S_P$ , 0 psu for  $S_L$ ,  $-0.5\text{‰}$  for  $\delta^{18}\text{O}_P$  and  $-5.5\text{‰}$  for  $\delta^{18}\text{O}_L$ .

The calculated results of Eqns. 1, 2, and 3 are plotted against time (Fig. 7). At station 11, the total freshwater com-

ponent ( $X_R + X_L$ ) ranges from 25–40% in the summer and fall to almost 100% during the winter of 1993. The proportion of that coming from local runoff is small (averaging 15% of the total), with the exception of the sample taken Feb. 24, 1993. For this sample, local water was calculated to have made up 34% of the total water. Given that January and February of 1993 were extremely wet months, with local flooding occurring in the northern San Francisco Bay area, this is not unreasonable. Flow out of the Napa and Petaluma Rivers was undoubtedly very high during that period and, as station 11 is very near the mouths of those rivers (Fig. 1), it is likely that there would be high levels of water from these rivers present at station 11 during those months. The calculated amount of freshwater inflow at station 25 was much less than at station 11 due to its south-central bay location and proximity to the Golden Gate (Fig. 1). Calculated freshwater inflow ranged from less than 3% during the summer and fall to 43% in the winter of 1993. The average proportion of local

**Table 3.** Stable isotope compositions *Mytilus edulis* collected live and water samples collected from San Francisco Bay sites (Fig. 2).

Location <sup>1</sup>	$\delta^{18}\text{O}_{\text{water}}^2$	$\delta^{18}\text{O}_{\text{shell}}^3$	$\delta^{13}\text{C}_{\text{shell}}^3$	Location <sup>1</sup>	$\delta^{18}\text{O}_{\text{water}}^2$	$\delta^{18}\text{O}_{\text{shell}}^3$	$\delta^{13}\text{C}_{\text{shell}}^3$
Berkely Marina (BM) June 29, 1994	-1.2	-0.6	-1.0	Vallejo Marina (VM) July 11, 1994	-3.8	-4.0	-3.4
		-1.0	-1.4			-4.1	-3.6
		-1.6	-1.8			-4.2	-3.4
		-1.4	-1.6			-4.4	-4.0
		-1.8	-2.3			-4.4	-5.3
		<u>-0.7</u>	<u>-1.7</u>			<u>-4.1</u>	<u>-4.8</u>
Ave	-1.2	-1.6	Ave	-4.2	-4.1		
Rodeo Marina (RO) June 29, 1994	-2.7	-2.1	-3.5	China Camp (CC) July 11, 1994	-1.5	-1.6	-2.7
		-1.7	-2.5			-1.7	-3.2
		-1.9	-2.9			-2.0	-3.3
		-2.0	-3.5			-1.2	-3.5
		-2.2	-2.0			-2.1	-3.8
		-2.9	-2.6			-2.2	-3.0
<u>-1.9</u>	<u>-2.8</u>	-1.5	-3.8				
Ave	-2.1	-2.8	Ave	<u>-1.2</u>	<u>-3.7</u>		
Pinole Point (PP) June 29, 1994	-1.4	-1.9	-3.1	Oyster Point (OP) July 29, 1994	-1.1	-1.1	-1.5
		-1.2	-1.9			-1.0	-1.6
		-1.4	-2.5			-0.8	-1.6
		-1.5	-2.7			-1.1	-1.4
		<u>-1.5</u>	<u>-3.2</u>			<u>-1.1</u>	<u>-1.5</u>
		Ave	-1.5			-2.7	Ave
Miller-Knox (MK) June 29, 1994	-1.4	-0.7	-1.7	Coyote Point (CP) July 29, 1994	-1.0	-1.3	-2.7
		-1.2	-1.1			-0.4	-3.7
		-0.5	-0.8			-1.1	-2.1
		-0.9	-1.5			-1.5	-2.9
		-0.8	-1.3			-0.4	-2.7
		<u>-0.9</u>	<u>-0.8</u>			<u>-0.7</u>	<u>-2.3</u>
Ave	-0.8	-1.2	Ave	-0.9	-2.7		

<sup>1</sup> Letters in parentheses indicate abbreviation used on Fig. 1; date refers to sampling date.

<sup>2</sup>  $\delta^{18}\text{O}$  values for water samples as reported relative to VSMOW.

<sup>3</sup>  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values for shells reported relative to PDB belemnite.

runoff to total freshwater at this location, however, is actually higher than in the north Bay (at about 20%), perhaps from the much higher inflow of wastewater to the south bay. There is also a peak for local runoff at station 25 during the winter-spring of 1993, but it is offset until the sample taken April 1. Similar calculations using the salinity and hydrogen isotope data result in approximately the same proportions of the three components, but the endmember compositions of ocean water and local runoff are not as well constrained for hydrogen, so the calculations done with the oxygen data are believed to be more reliable. The overall numbers are almost twice as high as the figure for local runoff given by Conomos et al. (1979) of 10%. While our primary goal was to demonstrate that the effect of local runoff is relatively small, this exercise illustrates that stable isotopes may be a potential tracer of the amount (and source) of local runoff and wastewater entering San Francisco Bay.

#### 4.2. Modern Shells

The carbon and oxygen isotope data for the whole *Mytilus* (mussel) shells are listed with the  $\delta^{18}\text{O}$  values of the water samples collected with the shells in Table 3. Despite large ranges in the isotope data and the comparison of  $\delta^{18}\text{O}$  values of shells that grew over an extended period of time with a single water sample, there is a very good correlation ( $r^2 = 0.9$ ) between the average  $\delta^{18}\text{O}$  values of the shells and the

$\delta^{18}\text{O}$  values of the waters (Fig. 8). The relation between  $\delta^{18}\text{O}_{\text{shell}}$  and  $\delta^{18}\text{O}_{\text{water}}$  is the following:  $\delta^{18}\text{O}_{\text{water}} = 0.84(\delta^{18}\text{O}_{\text{shell}}) - 0.36$ . The  $\delta^{18}\text{O}$  ratios of marine carbonates measured relative to VPDB (Table 3) are approximately equal to the  $\delta^{18}\text{O}$  ratios of waters measured relative to VSMOW because the VPDB carbonate standard is based on the isotopic composition of the PeeDee belemnite, an organism that grew its shell in equilibrium with ocean water (on which VSMOW is based), cancelling out the fractionation effect between carbonate and water.

The scatter in the oxygen isotope composition of the shells may be due in part to differences in the ages of the mussels collected at each of the sites. For example, a 1.5 year-old mussel shell collected in June would record two winter/spring periods and only one summer/fall period, giving a lower average (whole shell)  $\delta^{18}\text{O}$  value than a one year-old shell that grew during only one winter/spring period. Another factor that probably increased the variability in the  $\delta^{18}\text{O}$  values of the shells is that many of the mussels were collected from different subenvironments. Some came from tide pools, others were wedged in cracks, and some were attached to open surfaces of rocks at different levels relative to sea level. Although we were unable to identify any systematic relations, these variables must have had some effect on the isotopic compositions of the shells.

Due to the large difference between the oxygen isotope compositions of seawater and freshwater, we expect that the  $\delta^{18}\text{O}$



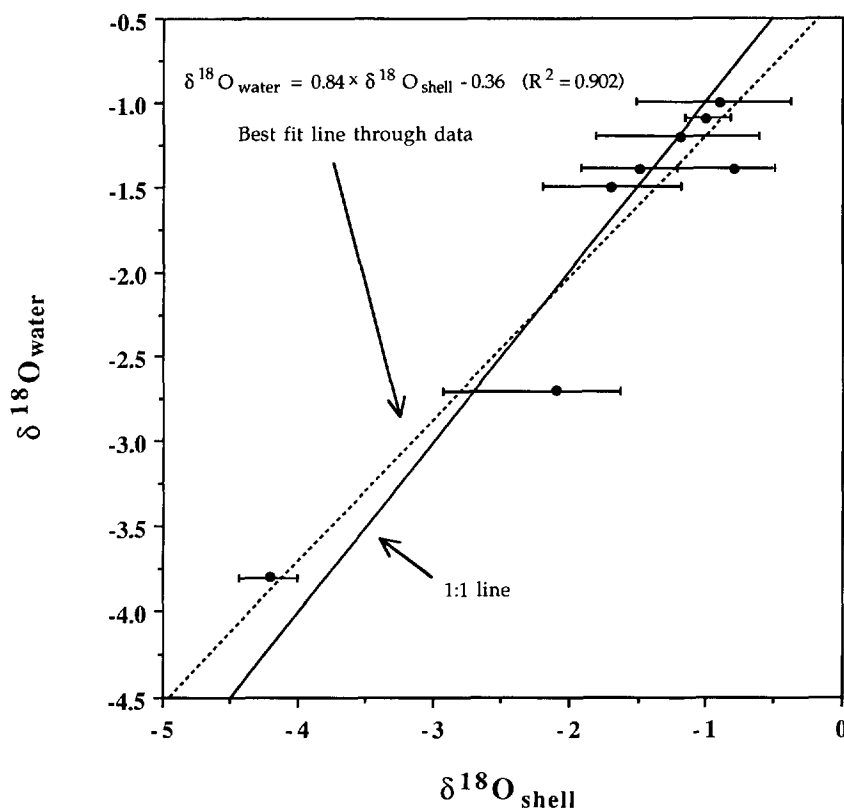


FIG. 8.  $\delta^{18}\text{O}$  values of whole shells vs. that in waters from San Francisco Bay.

variations in mussel shell carbonate primarily reflect those produced by mixing those two water masses. However, because water temperature also causes fractionation in the oxygen isotopes during carbonate precipitation, we must also consider temperature effects in San Francisco Bay. The temperature of estuarine waters is a function of local weather conditions (ambient air temperature) and the proportions and temperatures of seawater and freshwater entering the estuary. The residence time of bay waters is also a factor, because longer residence times in the summer months, due to decreased river inflow, causes an increase in temperature of shallow areas of the bay (particularly the south bay; Conomos, 1979).

While large seasonal temperature variations have been observed throughout most of the bay, year to year variations in the average annual water temperatures are relatively small (Conomos, 1979; Conomos et al., 1979). We compared the average measured  $\delta^{18}\text{O}_{\text{carbonate}}$  at the sites with the predicted  $\delta^{18}\text{O}_{\text{carbonate}}$ , as determined by average annual temperature and salinity at each site. To determine the predicted  $\delta^{18}\text{O}_{\text{carbonate}}$ , we used the following equation:  $\delta^{18}\text{O}_{\text{carbonate}} = \{(T^{\circ}\text{C} - 16.9)/-4.2\} + \delta^{18}\text{O}_{\text{water}}$ . The  $\delta^{18}\text{O}_{\text{water}}$  values were determined using the following relation derived in this study:  $\delta^{18}\text{O}_{\text{water}} = 0.34(\text{Salinity} - 11.6)$ . The measured  $\delta^{18}\text{O}_{\text{carbonate}}$  values are well correlated with predicted  $\delta^{18}\text{O}_{\text{carbonate}}$  values, as shown in Fig. 9.

### 4.3. Seasonal Salinity Changes in Shell Growth Bands

In addition to measuring the average oxygen isotopic compositions of the shells, we also measured the isotopic com-

positions of growth bands within several shells from eight sites, to determine if seasonal salinity and oxygen isotopic changes in the water are recorded by the shells. Three individual shells (with an average length of 3.5 cm) measured from the Vallejo Marina Site, and two shells from Oyster Point (with an average length of 4.5 cm) (Fig. 1), are illustrated (Fig. 10).

The oxygen isotope data for shells from Vallejo Marina and Oyster Point are plotted against the distance (mm) from the outer edge of the shell (Fig. 10). Although we know only the date of collection, the data clearly show one complete seasonal cycle, representing 1–1.5 years of growth. At both locations, the oxygen isotopic variations from the different shells correlate extremely well with each other (Fig. 10), demonstrating that water composition (salinity and temperature) exerts primary control on shell  $\delta^{18}\text{O}$ . The shells from the Vallejo Marina have  $\delta^{18}\text{O}$  values varying from  $-2.6\text{‰}$  to  $-5.9\text{‰}$ , showing a seasonal isotopic variation of about  $4\text{‰}$ . Salinity measured by the USGS (Branch of Water Resources) at Station 11 (close to this site) indicates an average summer salinity of 22.5, and a winter salinity of 11.5 (annual average salinity of 17), consistent with these oxygen isotopic compositions. The oxygen data for the shells from Oyster Point (close to station 25) ranged between  $-0.1\text{‰}$  to  $-2.5\text{‰}$  (average value of  $-1.2\text{‰}$ ). Salinity at this site averaged 30.6 in summer and 25.6 in winter, with an annual average of 28, also consistent with the oxygen isotopic compositions in the shells.

**Table 4.** Stable isotope compositions of growth bands in *Mytilus edulis* shells collected live from the San Francisco Bay (Fig. 2). All isotope ratios are per mil variations relative to VPDB.

	mm <sup>1</sup>	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$		mm <sup>1</sup>	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$		mm <sup>1</sup>	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$
<b>Coyote Point</b>				<b>Oyster Point</b>				<b>Vallejo Marina</b>			
Mussel #2	27	-1.9	-3.2	Mussel #1	40	-0.6	-1.1	Mussel #1	35	-2.6	-2.9
	22	-1.0	-3.7		30	-0.4	-1.2		20	-5.8	-5.2
	19	-0.4	-3.6		20	-2.5	-3.2		10	-4.1	-4.3
	14	-0.3	-4.3		16	-1.4	-1.4	#3	30	-2.8	-2.4
	11	0.1	-4.8		12	-0.9	-1.6		20	-5.6	-4.5
	8	-1.1	-3.7		9	-1.0	-1.6		12	-3.9	-3.5
	2	-0.8	-3.5		6	-0.5	-1.5		4	-3.4	-4.4
Mussel #3	36	-2.2	-2.4	Mussel #2	44	-0.6	-1.7	#4	35	-3.2	-3.1
	31	-2.3	-1.8		39	-0.4	-1.5		20	-5.9	-4.8
	28	-2.0	-1.8		31	-0.1	-1.8		10	-4.3	-3.9
	26	-1.1	-1.6		25	-2.5	-3.3		5	-3.8	-4.9
	22	-0.9	-2.2		21	-2.0	-1.8				
	18	-0.2	-2.2		17	-1.6	-1.5				
	13	0.0	-2.8		13	-1.0	-1.4	<b>Miller Knox</b>			
	8	-1.1	-2.5		8	-0.4	-1.9	Mussel #1	54	-2.1	-1.6
	5	-0.8	-3.4		3	-0.7	-1.7		46	-1.8	-1.7
									37	-1.3	-1.2
									33	-1.0	-1.3
<b>Pinole Point</b>				<b>Berkeley Pier</b>					27	-0.2	-1.4
Mussel #2	57	-1.2	-0.9	Mussel #2	61	-0.8	-0.9		22	-1.5	-2.8
	48	-0.9	-1.2		56	-0.4	-1.0		17	-1.2	-2.2
	37	-1.1	-0.9		48	-0.4	-0.7		11	-1.4	-2.3
	30	-1.4	-1.1		39	-3.9	-3.6		5	-1.0	-2.6
	21	-1.8	-2.0		34	-4.1	-2.5		1	-0.9	-1.8
	14	-1.5	-1.9		28	-2.5	-1.7				
	7	-1.0	-2.1		21	-2.9	-1.9				
	2	-2.3	-3.0		14	-1.8	-1.3	Mussel #2	57	-2.5	-1.5
					9	-1.4	-1.6		53	-2.7	-2.0
Mussel #3	65	-2.9	-2.3		2	-1.1	-1.7		50	-2.7	-1.9
	56	-1.6	-1.8						47	-2.3	-1.2
	49	-1.6	-1.3	Mussel #3	57	-0.8	-0.9		42	-2.6	-1.5
	41	-1.6	-1.3		48	-0.4	-1.0		40	-2.2	-1.4
	36	-2.3	-1.7		39	-0.4	-0.7		36	-2.2	-1.5
	30	-1.4	-1.5		34	-3.9	-3.6		31	-2.0	-1.4
	23	-1.0	-1.5		31	-4.1	-2.5		22	-0.8	-1.5
	15	-1.3	-2.0		25	-2.5	-1.7		19	-0.3	-1.6
	9	-1.4	-2.6		19	-2.9	-1.9		13	-1.2	-1.5
	2	-2.4	-3.5		12	-1.8	-1.3		9	-1.3	-1.6
					6	-1.4	-1.6		1	-0.9	-1.2
					1	-1.1	-1.7				
<b>Rodeo Marina</b>								Mussel #5	54	-0.9	-1.4
Mussel #2	43	-2.1	-1.6						46	-1.1	-1.9
	32	-1.2	-2.1	<b>China Camp</b>					41	-1.3	-1.5
	20	-1.5	-2.1	Mussel #2	32	-1.2	-2.4		35	-1.3	-1.6
	15	-2.2	-2.7		22	-1.1	-2.7		30	-1.1	-1.7
	9	-1.5	-3.0		17	-1.3	-3.2		27	-0.6	-1.5
	6	-1.3	-3.3		10	-1.1	-4.6		24	-1.0	-1.5
	2	-2.2	-3.7		1	-1.4	-3.6		20	-1.8	-1.8
									17	-1.5	-1.5
Mussel #5	38	-2.0	-3.1	Mussel #10	33	-0.7	-2.3		13	-1.3	-2.1
	29	-2.2	-3.1		20	-0.6	-3.1		7	-1.0	-1.9
	22	-2.9	-4.0		13	-0.3	-3.3		2	-0.6	-1.2
	17	-2.4	-3.3		2	-0.9	-3.4				
	10	-1.6	-3.6								
	2	-3.2	-4.1								

<sup>1</sup> Distance in mm of sample point from the edge of the shell.

Seasonal temperature variations in the bay occur due to changing river water temperature, which ranges from 21°C in the summer to 9°C in winter (Conomos et al., 1979), and changing ocean water temperature, which ranges from 12°C in winter to 15°C in summer (Conomos et al., 1979). Measurements between 1969–1977 show that the temperature in the south-central part of the Bay (station 25) ranged between 12°C (winter) and 18°C (summer). In San Pablo Bay (station 11) the temperature range was great due to its proximity to the Delta, varying between 10°C (winter) and 19°C (summer) (Conomos et al., 1979). As an example of the effect of changing temperature on the  $\delta^{18}\text{O}$  of the carbonate shell, we have used monthly temperature and salinity values from Oyster Point to calculate the  $\delta^{18}\text{O}$  of shells growing in that location. We have also calculated the monthly  $\delta^{18}\text{O}$  of the shells using the variable salinity but assuming an average annual temperature at Oyster Point of 15.7°C. The calculated  $\delta^{18}\text{O}$  of the shells for both cases is plotted against time (Fig. 11). This plot illustrates that using the annual average temperature (15.7°C),  $\delta^{18}\text{O}$  values in the shell

would be 0.8‰ lower in the winter, and about 1.0‰ higher in the summer. Thus, the corresponding seasonal salinity contrasts would be increased (Fig. 11). However, the annual average  $\delta^{18}\text{O}$  (and corresponding salinity) is the same in both cases. This implies that measurements of bulk fossil shells should yield a reliable annual average salinity value, assuming a reasonable value for the annual average temperature at a particular location is used in the calculation.

#### 4.4. Carbon Isotopes

Because the carbon isotopic composition ( $\delta^{13}\text{C}$ ) is low in river water (about -10‰) relative to seawater (0‰), we would predict it to vary with salinity in estuarine waters (and carbonate shells) as does  $\delta^{18}\text{O}$ . However, the modern shell data indicates that in the modern environment the carbon isotopic composition in the shells does not vary consistently with salinity or  $\delta^{18}\text{O}$ . The correlation between oxygen and carbon isotopic compositions varies from site to site, ranging from well-correlated (at Berkeley Marina and Pinole Point, central

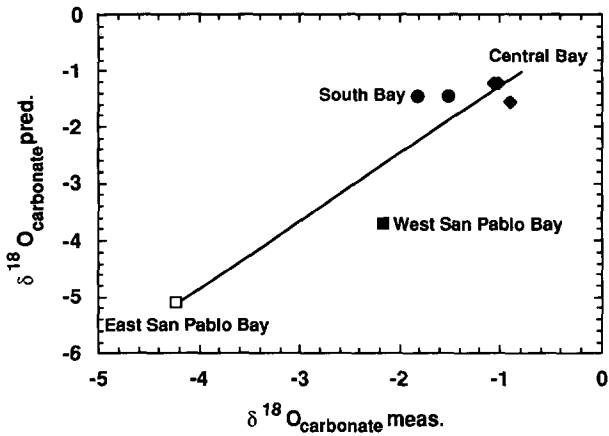


FIG. 9. Measured  $\delta^{18}\text{O}$  of shells (averaged at each locations) plotted against the predicted values based upon average temperature and salinity. Diamonds: Central Bay samples; circles: south bay samples (Oyster and Coyote Point); open squares: west San Pablo Bay samples; filled squares: eastern San Pablo Bay samples.

Bay), to poorly correlated in China Camp and Rodeo Marina (north bay; Fig. 12; Table 4). Previous studies show that dissolved inorganic carbon is not conservative in estuarine en-

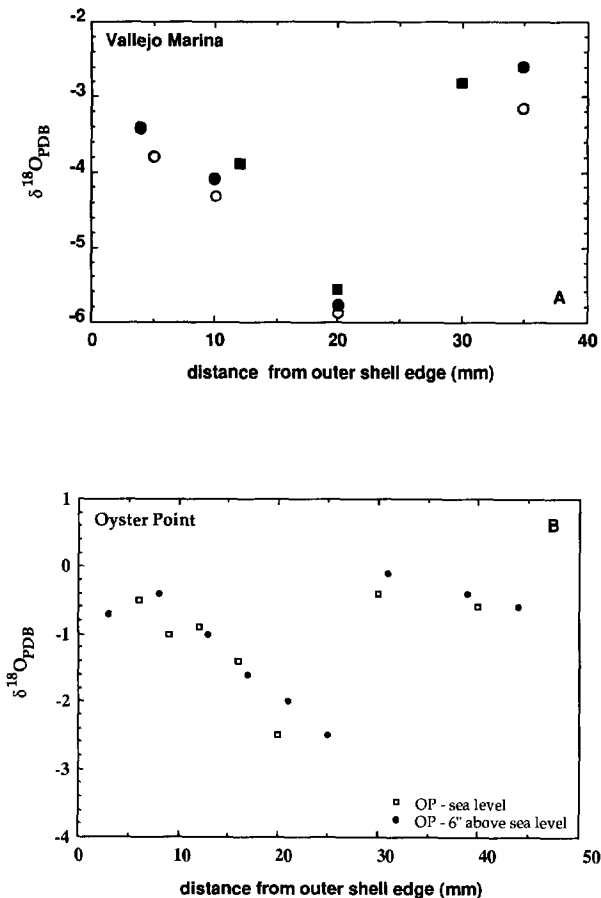


FIG. 10. Oxygen isotopic compositions of shell bands plotted against distance from outer shell edge (mm) of three separate shells from Vallejo Marina (a) and two separate shells from Oyster point (b).

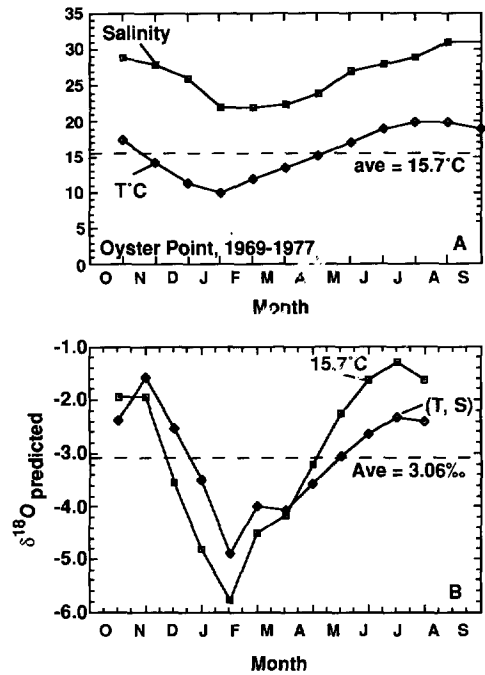


FIG. 11. (a) Seasonal temperature and salinity at Oyster Point (b) predicted  $\delta^{18}\text{O}$  at Oyster Point based upon variable temperature and salinity and based upon calculations using an average temperature value of  $15.7^\circ\text{C}$  and variable salinity.

vironments, due to modification by plankton productivity and benthic respiration (Spiker, 1980). Other processes affecting the  $\delta^{13}\text{C}$  in carbonate shells include feeding mode of the benthic mollusks (for example, filter feeding vs. detrital feeding), the type of organic matter consumed by the organism (i.e., phytoplankton vs. organic detritus), and, in modern environments, the carbon isotopic composition is affected by anthropogenic inputs (such as wastewater). Our study suggests that different regions of the bay are more effected by these processes than others, and suggest that carbon isotopes may be an important tracer of estuarine processes. The input of wastewater and sewage may also be a factor controlling modern  $\delta^{13}\text{C}$  in the bay, although this should not affect fossil samples. It is necessary, therefore, to distinguish between anthropogenic effects on the carbon isotopic composition of bay organic and dissolved inorganic carbon, and natural variability caused by changes in biological activity, input of detrital carbon, and carbon recycling in the estuary. This will be the subject of a future study.

5. CONCLUSIONS

In this study, we demonstrate the systematic variations in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values with changing freshwater and salinity in San Francisco Bay estuarine waters. The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values and estuarine salinity show a linear mixing relationship between seawater from the Pacific Ocean and freshwater from the Sacramento-San Joaquin river system. This mixing line is additionally modified by inflow of freshwater from local runoff. Thus, the salinity and isotopic compositions of the water can be directly related to the amount of freshwater en-

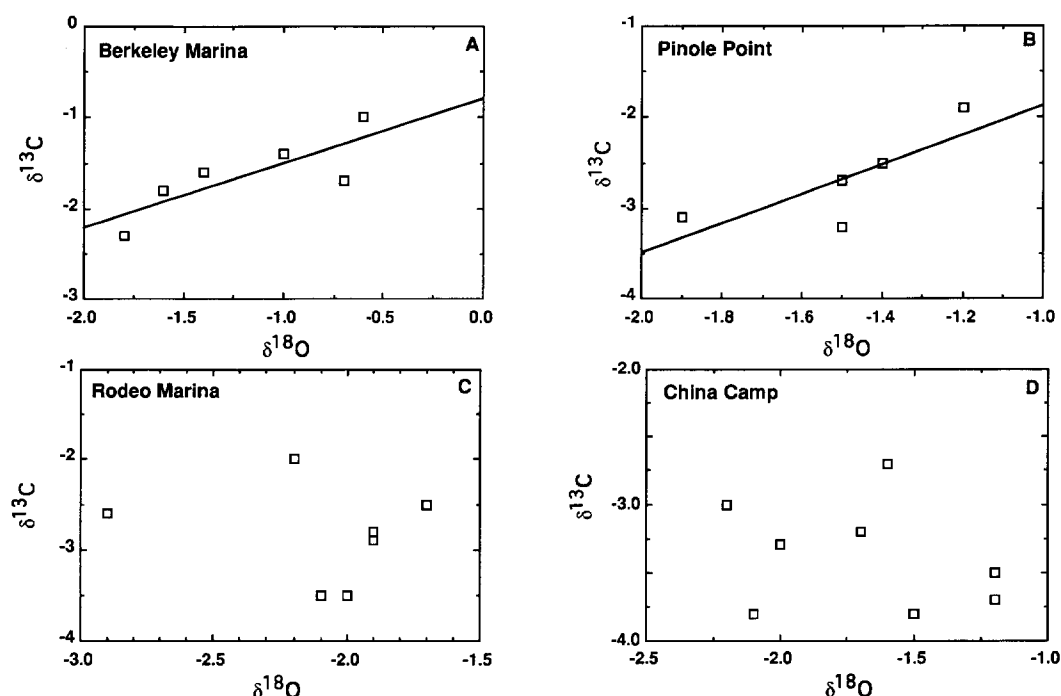


FIG. 12.  $\delta^{18}\text{O}$  plotted against  $\delta^{13}\text{C}$  for modern mussel shell growth bands from San Francisco Bay, plotted separately according to location: (a) Berkeley Marina, central bay; (b) Pinole Point, San Pablo Bay; (c) Rodeo Marina, San Pablo Bay; (d) China Camp, San Pablo Bay (marsh).

tering San Francisco Bay through the delta. Water balance calculations show local runoff and wastewater comprises on average about 15–20% of the freshwater entering San Francisco Bay. This study demonstrates that stable isotopes may be a useful tracer of freshwater water entering the bay.

The oxygen isotopic compositions of mussel shells were shown to accurately record both the average  $\delta^{18}\text{O}$  values of ambient water over the entire growth period, as well as the salinity variations in estuarine waters reflecting seasonal changes in freshwater inflow. This study demonstrates the potential use of oxygen isotopic variations in mussel growth bands for reconstructing both the pre-instrumental annual average salinity (and freshwater inflow) within an estuarine environment, and the natural variability in seasonal salinity/freshwater inflow through time. This technique may also have applicability in documenting anthropogenic effects on estuarine salinity over the past 150 years, including effects of hydraulic mining (Gilbert, 1917), upstream storage, and diversions within the Sacramento–San Joaquin river basins (Nichols et al., 1986; Peterson et al., 1995).

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