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The use of oxygen isotope variation in shells of estuarine mollusks as a quantitative record of seasonal and annual Colorado River discharge

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Abstract—We describe a new method for the calculation of river flow that uses the oxygen isotope composition of bivalve mollusk shells that grew in the river-water/seawater mixing zone of the Colorado River estuary. Sclerochronological techniques are used to identify tidally-induced, fortnight-scale bundles of daily growth increments within shell cross-sections. These fortnightly markers are used to establish a chronology for samples taken for $\delta^{18}\text{O}$ analysis. A composite seasonal $\delta^{18}\text{O}$ profile derived from five shells that grew in the absence of river-water flow is used as a baseline against which profiles of river-influenced shells are compared. Because this comparison is between matched fortnights within a year, the temperature of shell growth is likely to be very similar. The difference in $\delta^{18}\text{O}$ between the river-influenced shell and the “no-flow” composite shell therefore represents the change in the $\delta^{18}\text{O}$ of the water due to the presence of river water in the mixing zone. The river water end-member is also determined within a fortnightly context so that the change in the $\delta^{18}\text{O}$ of mixing-zone water can be used to calculate the relative proportions of seawater and fresh-water. The fresh-water end-member is calculated from the $\delta^{18}\text{O}$ of bivalves alive prior to the emplacement of dams and water diversions on the Colorado River. The marine end-member is based on direct measurements of the $\delta^{18}\text{O}$ of northern Gulf of California water during times of no Colorado River flow. The system has been calibrated to absolute flow amounts using recent releases of known volume and rate. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

Quantitative estimates of prehistoric river flow can provide valuable information on the natural range of variability in river discharge and the response of the hydrologic cycle to climate change. In most parts of the world, direct measurements of river discharge have been made for less than 200 yr, so proxy indicators need to be employed to provide a long-term record of drought or floods. Quantitative estimates of river discharge based on tree-rings have been successfully used to provide ~500 yr records of river flow (e.g., Stockton and Jacoby, 1978; Meko et al., 1995). Stable isotopes of strontium, oxygen, and carbon from estuarine mollusk shells have been employed to extend the record back several millennia (see the pioneering work of Ingram and Sloan, 1992; Gagan et al., 1994; Ingram et al., 1996), but calibration of isotopic variation with discharge variation has been very difficult. Other proxy indicators (typically based on proportions of particular estuarine species) have provided only semiquantitative estimates of salinity, and thus, indirectly, river discharge.

In this paper, we describe a method based on comparing seasonal isotopic variation in shells grown in the absence of any river water influence with shells grown in the presence of a known amount of river water. When coupled with information on the $\delta^{18}\text{O}$ mixing relationship of seawater and river water, the offset between river-influenced and “no-flow” shell

$\delta^{18}\text{O}$ profiles can be used to calculate Colorado River discharge at its delta before upstream dam and diversions, and before the oldest direct measurements.

2. CONTEXT OF THIS STUDY

The Colorado River is one of the major sources of water for six states in the southwestern United States and two in northwestern Mexico. Its annual discharge has been completely allocated within the U.S. and Mexico and for the last 40 yr Colorado River water has discharged into the Gulf of California only during unusually wet years. The Colorado River compact of 1922 allocated the water supplied by the Colorado River among California, Arizona, Colorado, Utah, Nevada, and New Mexico. The amount of water distributed by this pact (16.2 million acre-feet or $2.0 \times 10^{10} \text{ m}^3$) was based on approximately 15 yr of historical flow records covering an interval that turned out to be a time of unusually high flow in the century-long historical record of discharge (USGS, 1954; Hely 1969; Stockton and Jacoby, 1978). Thus, there is great interest in developing longer records of river flow to see if the twentieth century was typical or anomalous relative to the last one or two millennia. Tree ring studies have been used to reconstruct the last 450 yr of precipitation and river flow in the upper Colorado River basin (Stockton and Jacoby, 1978; Meko et al., 1995). These studies have suggested that the allocated flow is probably 20% greater than the average flow of the last four centuries.

Our study takes a different approach to the question of estimating long-term flow by looking at the geochemical record of flow reaching the mouth of the Colorado River (summing both the upper and lower Colorado River basins). Using shell

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chemistry has the advantage of applicability over a much longer time interval because individual shells can be directly dated using ^{14}C or radiocarbon calibrated amino acid racemization. A disadvantage of this approach in comparison to the tree ring records is the inability to construct a continuous annual time series greater than a few years in length. The species used in this study, *Chione fluctifraga* and *Chione cortezi*, can live up to 18 yr (Schöne et al., 2003) but after three or four years shell growth slows dramatically making detailed sampling of complete years difficult. Because our fossil specimens are dated to ± 50 yr using a ^{14}C calibrated amino-acid racemization chronology developed using *Chione* from the Gulf of California (Kowalewski et al., 1998), we can only sample one or two years from a shell within 50-yr intervals. Our ultimate goal in this research is to reconstruct the amount of water delivered to the Gulf of California over the last 2000 yr. The ancient record will be presented in another paper; this paper describes in detail our method for reconstructing ancient river flow.

3. MATERIAL AND METHODS

3.1. Mollusk Sclerochronology and the Annual Record

Mollusks add new carbonate material to their shells throughout their life spans. They can be thought of as chart recorders that store chemical information in shells as they grow. However, these chart recorders do not run continuously or at constant speed. Typically, bivalves grow rapidly early in life with a considerable deceleration in growth rate with increasing age. In addition, bivalve shells frequently show growth bands in cross section with a hierarchy of periodicities (Barker 1964; Jones et al., 1978; Jones and Quitmyer, 1996). The most prominent and least frequent bands are usually thought to be annual markers, often caused by a slowing and cessation of shell deposition due to environmental stress (i.e., temperature extremes or turbid conditions). These annual bands can be very useful in guiding the sampling of the shells to recover clear seasonal cycles of environmental change from the shell. In addition to annual bands, the genus of bivalve used here, *Chione*, also shows clear daily growth bands whose widths are modulated by the fortnightly tidal cycle (Schöne et al., 2002). This internal shell sclerochronology allows us to place our samples in the context of a fortnightly calendar within the annual bands.

Cool temperatures lead to cessation of *Chione* shell growth during the winter months, from approximately mid-December to mid-March (Goodwin et al., 2001), thus part of the annual environmental record is lost. On average, stable isotope data for twenty fortnights are recorded in the shell. To estimate river discharge during the remaining six fortnights, we use the US Geological Survey's river flow record for the Colorado (US Geological Survey, 1954). Thirty years of data exist before the construction of the first dam. The average amount of flow during the six fortnights from mid-December to mid-March is $12\% \pm 3\%$ of the total annual flow. Allowing for ± 1 fortnight uncertainty in the dating of the fortnights in the sclerochronology leads to an additional error of $\pm 3\%$. Thus, the unrepresented six fortnights account for $12\% \pm 6\%$ of the total annual river flow. Therefore adding 12% to our calculated discharge yields an annual discharge.

3.2. Sampling

Live mollusks were collected from tide pools, usually low in the intertidal zone. Live animals were collected at Sacatosa, Isla Montague, Isla Pelicano, and El Golfo de Santa Clara (Fig. 1). Water samples were usually collected from the tide pools along with the live-collected animals. Subfossil shells were collected from cheniers along the western side of Isla Montague and in the Sacatosa area. Cheniers are wave-formed shell islands created during times of low sediment input to the gulf. During times of low sediment input, fines are transported to deeper waters and shells are winnowed and gathered into long linear islands paralleling the shore line. Multiple generations of cheniers mark

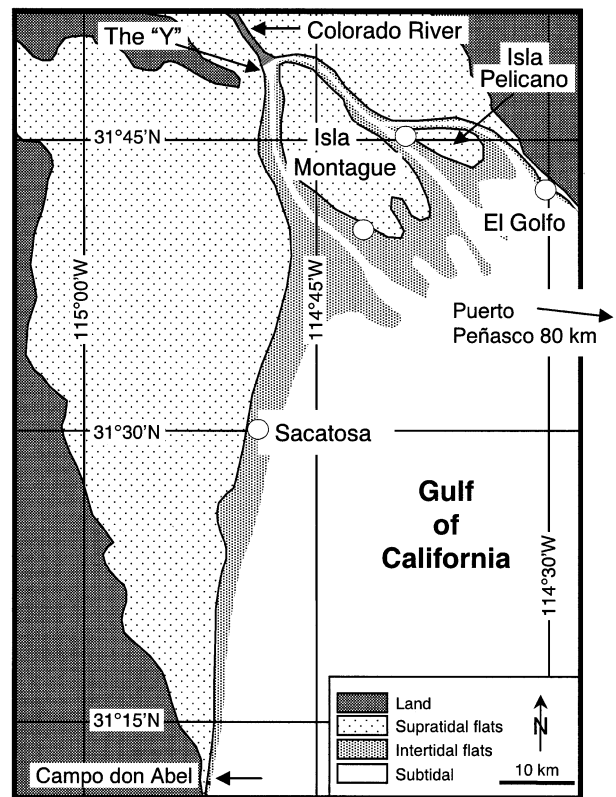


Fig. 1. Study area. Shells were collected from Isla Montague, Sacatosa, Isla Pelicano, and El Golfo de Santa Clara (primary collection localities indicated by circles). Water samples were collected from many locations between Puerto Peñasco and Campo Don Abel.

different intervals of low sediment input (Thompson, 1968; Kowalewski et al., 1994). The shells in a particular chenier are older than the age of chenier formation, although there is an extremely wide range of ages represented in each shell accumulation. *Mulinia coloradoensis* makes up the vast majority of the shells in the cheniers (up to 95% — Kowalewski et al., 1998), but this species is now nearly extinct in the gulf (Rodriguez et al., 2001). We focused our collecting efforts on *Chione* species (*C. fluctifraga*, *C. cortezi*), because they are currently living in the study area and provide the opportunity for stable isotope calibration studies relative to the modern environment. Collecting trips occurred at infrequent intervals over the last 8 yr. The Baja California (western) side was usually visited in November and Isla Montague was usually visited in February. Open gulf water samples were collected on each of these trips.

3.3. Methods

Salinity of seawater samples was measured with an optical salinometer with a 1 ppt precision. Stable isotope composition of water was measured on a Finnigan MAT Delta-S gas ratio mass spectrometer using two automated sample preparation devices. Oxygen isotope composition was measured using CO_2 equilibration at 15°C for a minimum of eight hours. Samples were not distilled before equilibration. Hydrogen isotope composition was measured by reducing the water on chromium at 750°C and direct transfer of H_2 into the mass spectrometer. Samples were normalized to V-SMOW and V-SLAP based on secondary standards. Repeated standards had a standard deviation of 0.06‰ for $\delta^{18}\text{O}$ and 0.8‰ for δD .

Shells were sectioned along the axis of maximum growth, mounted as thick sections (~ 1 mm) on glass slides, and polished. Growth bands in cross-sectioned shells were subsampled using either a stabilized dental drill and 0.5 or 0.3 mm diameter dental burs or a computer-

controlled micro-mill capable of recovering shell material with a 20 micron spatial resolution (Dettman and Lohmann, 1995). Carbonate samples were processed in four different labs, University of Arizona, University of Michigan, University of California at Santa Cruz, or University of California at Davis. All were reacted with dehydrated phosphoric acid under vacuum. The measured $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values were normalized to NBS-19 based on internal lab standards. Precision of repeated standards is $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 0.06\text{‰}$ for $\delta^{13}\text{C}$ (1σ).

The $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of waters were measured in the isotope geochemistry lab of the Department of Geosciences, University of Arizona, following the methods described in Patchett and Ruiz (1987) and Gross et al. (2001).

4. RESULTS

4.1. Modern Colorado River Delta Environment

Before its damming and diversion, the Colorado River emptied into the Gulf of California. The northern end of the gulf is surrounded by the Sonoran Desert and is a very hot and arid region; monthly average temperature ranges from 16 to 34°C. The northern gulf is known for its very large tidal range, often in excess of 5 m. Local rainfall amounts are < 60 mm annually (Hastings, 1964), local runoff is negligible, and the diversion of the Colorado River has led to very little fresh-water input in the last half century. Evaporation therefore dominates the present-day salinity and stable isotope character of seawater in the northern end of the Gulf of California. In this hot desert environment the large tidal amplitude contributes to the evaporative signature by running a relatively thin layer of water across intertidal zones that can be tens of kilometers in width. Salinities are high, ranging from 35 to 42 (practical salinity units) (Fig. 2). Waters trapped in tidal pools or those draining ponded areas in the intertidal zone can reach salinities as high as 240. When the Colorado River is not flowing into the Gulf of California, the isotopic composition of seawater is always positive, typically ranging from 0.3‰ to 0.8‰ SMOW. The mean $\delta^{18}\text{O}$ for water collected offshore in the northern end of the gulf is $0.60\text{‰} \pm 0.16$ (1σ) SMOW. Our measurements of the $\delta^{18}\text{O}$ of water from tide pools ranged from normal seawater values up to 7.6‰ SMOW. The $\delta\text{D}-\delta^{18}\text{O}$ relationship shows that both open Gulf of California seawater and tide pool waters are on evaporative trends with slopes of 5 and 4 respectively (Fig. 3a).

Water samples with $\delta^{18}\text{O}$ values less than 0‰ SMOW are primarily the result of recent controlled releases of Colorado

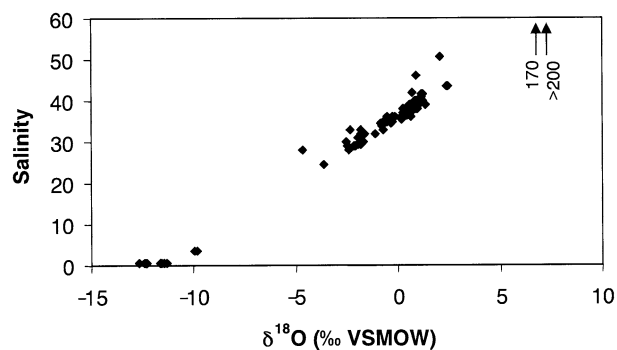


Fig. 2. Salinity vs. $\delta^{18}\text{O}$ for water samples in the northern Gulf of California. Samples with salinity greater than 42 are tide pool samples.

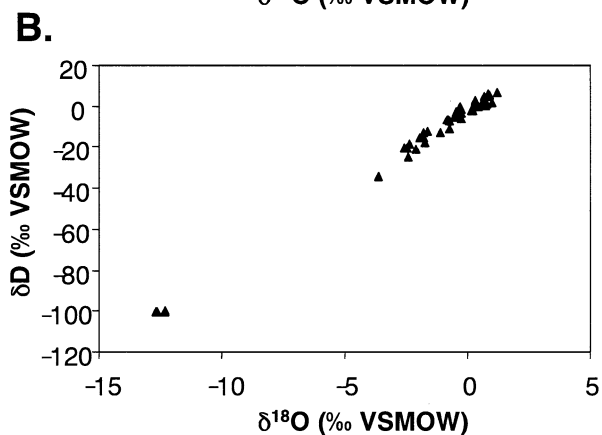
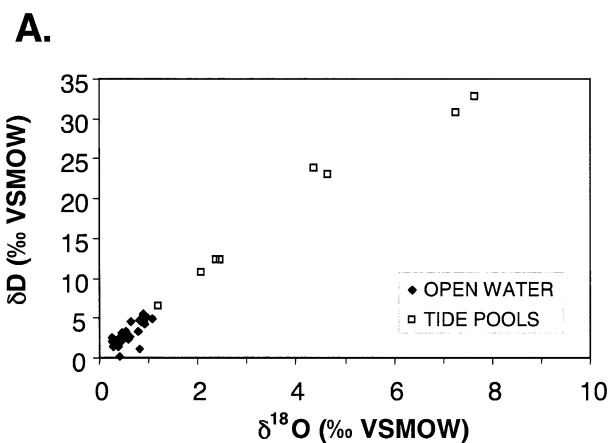


Fig. 3. (a) Water samples collected during times when the Colorado River was not flowing. (b) Waters collected during or shortly after releases of Colorado River water.

River water into the Gulf of California (Fig. 3b). This is seen in the salinity and isotopic composition of water samples during months when significant amounts of Colorado River water entered the northern end of the Gulf of California. The trends in both salinity and $\delta^{18}\text{O}$ or δD show simple linear mixing between gulf water (salinity = 38, $\delta^{18}\text{O}$ = 0.60‰, δD = 2.8‰) and Colorado River water (average $\delta^{18}\text{O}$ = -12.0‰, δD = -95‰).

Two types of temperature records show that the shallow water in the northern end of the Gulf of California is warm to hot throughout the year. Monthly average sea surface temperature from satellite data ranges from 11 to 31°C, integrated over a 14 km grid, for the grid cell immediately south of Isla Montague (NOAA-CIRES, 2000). Water temperatures in the low intertidal zone were recorded every two hours from mid-February 1999 to mid-February 2000 (using a HOBO-Temp® temperature logger). Averaged monthly or fortnightly temperatures cover the same range as the satellite data, but show extreme variability on short time scales, up to 15°C differences between day and night (Fig. 4). High temperatures occur invariably in the late afternoon, no matter what phase of the tidal cycle is active. This indicates that both ambient seawater temperature and direct solar heating play roles in controlling water temperature in the intertidal zone.

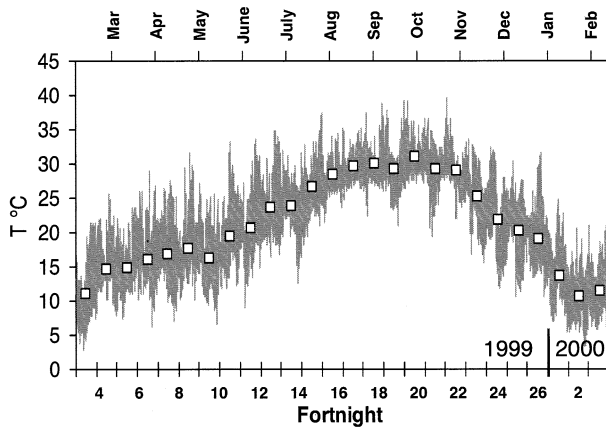


Fig. 4. Digital temperature recorder data from Isla Montague. Solid line is a continuous temperature logger record from the intertidal zone from mid-February 1999 and to mid-February 2000. Squares are average temperature of fortnights.

4.2. Shell $\delta^{18}\text{O}$ in the Presence and Absence of Colorado River Water

The $\delta^{18}\text{O}$ of shell material depends on the temperature and $\delta^{18}\text{O}$ of the water in which the specimen lives. Under today's conditions, where no river water reaches the gulf, the oxygen isotope profile in a shell is primarily the result of the seasonal temperature change in the gulf, possibly combined with a small evaporation-driven cycle in seawater $\delta^{18}\text{O}$. A comparison of five annual profiles in the $\delta^{18}\text{O}$ of live-collected shells from no-flow years shows relatively good agreement, even though the specimens lived in different years and at different locations around the mouth of the river (Fig. 5). Figure 5 and all other shell plots show $\delta^{18}\text{O}$ vs. fortnight number. The sclerochronological methods are discussed in detail in Schöne et al. (2002) and will be described only briefly here. Daily increments are

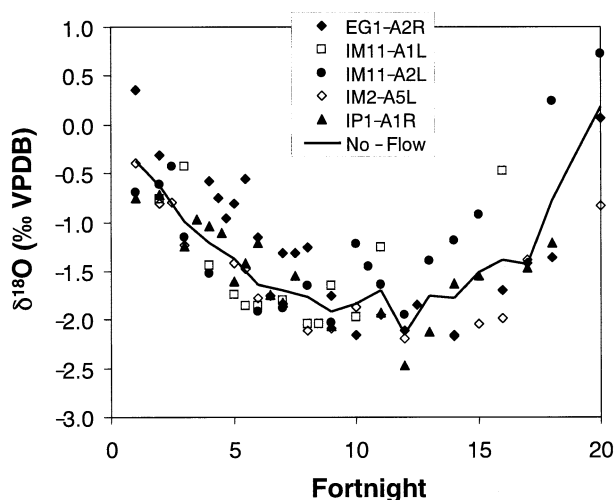


Fig. 5. $\delta^{18}\text{O}$ records for five live-collected shells in years during which no Colorado River flow occurred. Shell numbers beginning with IM are from Isla Montague, IP are from Isla Pelicano, and EG are from El Golfo. The "no-flow record" is the average of these by fortnight.

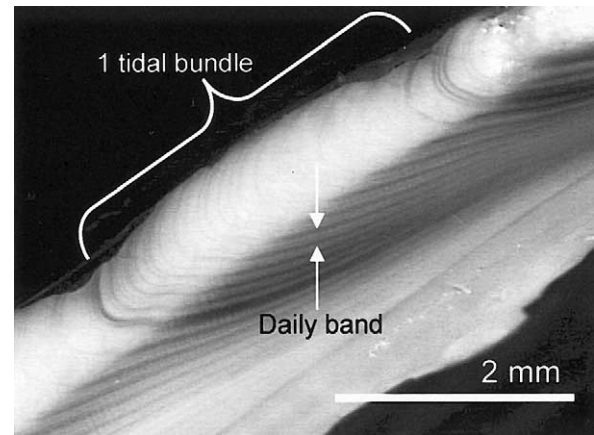


Fig. 6. Photograph of polished cross section of a small *Chione cortezi* (<1 yr old) showing one fortnight of growth. Daily growth increments are grouped into tidally controlled bundles.

relatively easy to count in *Chione* sp. and in most cases are clearly grouped into fortnightly bundles that match the tidal cycles (Fig. 6). The widest daily growth bands approach 0.25 mm. Growth in *Chione* slows and stops in the cooler winter months resulting in an average of 20 fortnights of identifiable shell growth in a year. An exception to this is the first winter of the animal's life, where growth often continues through the winter. All shell $\delta^{18}\text{O}$ data presented here are from the first four full years of life of the animal. The sclerochronological uncertainty is most likely ± 1 fortnight (Schöne et al., 2002).

The total $\delta^{18}\text{O}$ range within the five shells from no-river-flow conditions is approximately $+0.6\text{‰}$ to -2.2‰ PDB (Fig. 5). The differences between the curves are due to temperature and water $\delta^{18}\text{O}$ variation between the years and locations of growth. Localized evaporation of seawater in tide pools plays a role in offsetting the $\delta^{18}\text{O}$ values to more positive values on the time scale of the tidal cycle. This probably explains the jagged nature of some of the curves. There is also uncertainty in the matching of fortnights, which may offset records horizontally. This figure shows that the $\delta^{18}\text{O}$ variance between shells during no-flow years is probably on the order of 0.5‰ PDB. Averaging these records yields a relatively smooth curve that removes evaporative anomalies of any single measurement. This averaged $\delta^{18}\text{O}$ curve (line in Fig. 5) is what we call the "no-flow record." This represents the expected $\delta^{18}\text{O}$ cycle of *Chione* sp. shell carbonate at the mouth of the river when no river water reaches the Gulf of California.

Because the $\delta^{18}\text{O}$ of Colorado River water is much more negative than seawater, its presence in the delta region should lead to $\delta^{18}\text{O}$ values that are more negative than the no-flow record of Figure 5. Many fossil shells show a large offset to more negative $\delta^{18}\text{O}$ values (Fig. 7). Shell IM4-D2 (late 18th century) has a minimum $\delta^{18}\text{O}$ value of -8.75‰ PDB and reveals a sustained pulse of river water lasting at least six fortnights. Shell NI2-D14 (late 11th century) has a much shorter peak in river input and reaches a minimum of -7‰ . Recent releases of known amounts of river water to the gulf have also been recorded in live-collected shells (Fig. 8). These anomalies can be matched to known amounts of water released and, as

discussed below, allow us to calibrate the relationship between isotope offsets and river discharge.

4.3. An Aside on $^{87}\text{Sr}/^{86}\text{Sr}$ Ratios

Some studies quantifying river flow into estuarine systems have used strontium isotope ratio gradients to measure the mix of seawater and fresh-water (e.g., Ingram and Sloan, 1992). The use of $^{87}\text{Sr}/^{86}\text{Sr}$ in the mixing zone has a major advantage over oxygen isotope ratios because there is no temperature effect and no measurable fractionation between the isotope ratio in water and that preserved in shell. However, because there is usually a much higher concentration of strontium in seawater than in fresh-water, high precision $^{87}\text{Sr}/^{86}\text{Sr}$ analysis is needed to calculate variations in salinity as the system approaches the marine end-member (Bryant et al., 1995). In our study area, seawater Sr concentration is 8.4 ppm at El Golfo and Colorado River water is 1.2 ppm at Lake Mead (Gross et al., 2001). The $^{87}\text{Sr}/^{86}\text{Sr}$ of water from the mixing zone of the delta during a significant release of river water to the Gulf of California (Feb. 1999) shows moderate change as salinity varies from 36 to 29, but because of the uncertainties on the $^{87}\text{Sr}/^{86}\text{Sr}$ measurement, we cannot distinguish between salinities of 36 and 33 (Table 1). The Ingram and Sloan (1992) study of waters from San Francisco Bay also failed to measure significant differences in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio across a range of salinities from 24.4 to 29.5,

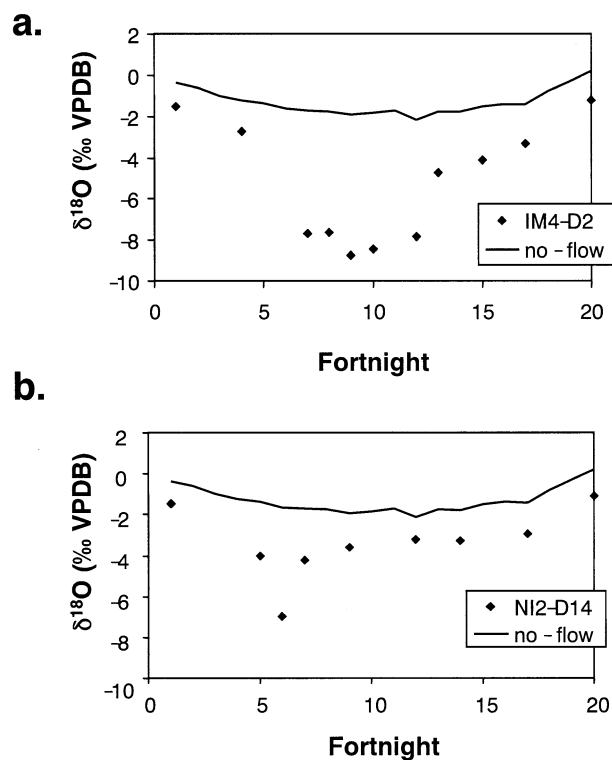


Fig. 7. Shell $\delta^{18}\text{O}$ profiles from 2 shells dated using amino acid racemization (Kowalewski et al., 1998). Dates are tied to ^{14}C ages with uncertainties of approximately ± 50 yr. (a) Year 3 of a shell dated to 1775 AD (IM4-D2) from Isla Montague. Note the strong river water spike in fortnights 7 to 12 and the overall more negative values throughout the profile in comparison to the no-flow profile. (b) Year 2 of a shell dated to 1075 AD (NI2-D14) from Sacatosa.

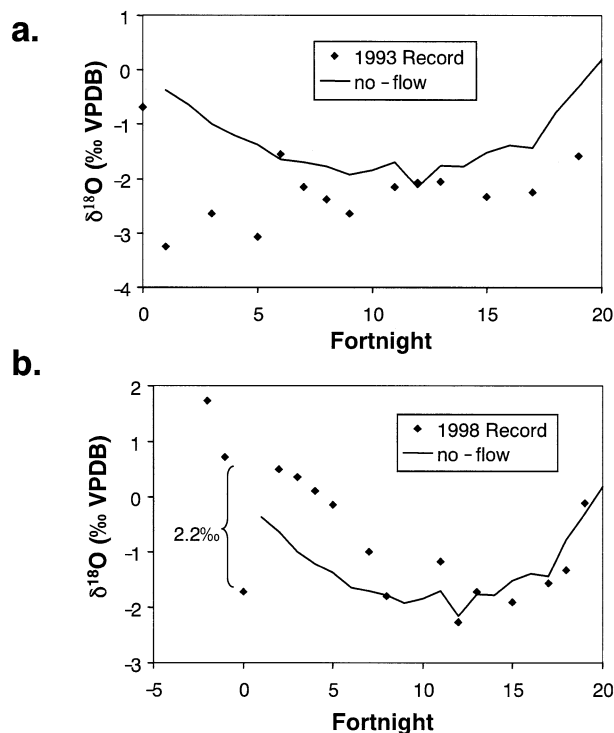


Fig. 8. (a) Shell $\delta^{18}\text{O}$ profile from a shell collected in 1996 at Isla Montague (IM2-EC2). The release of river water in early 1993 is recorded in that year's shell growth. (b) Shell $\delta^{18}\text{O}$ profile from a *Chione* collected in November of 1998 at Sacatosa (ST8-A2R). A river water release in February of 1998 is seen in the -2.2% offset during first winter growth before fortnight 1 (see text).

although clear differences should have been present based on their modeling. This suggests that oxygen isotope ratios may be more effective in quantifying salinity variation when conditions approach normal marine salinity. The major advantage of stable oxygen isotopes over $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in this study is practical. Because river discharge varied greatly within the year, we use oxygen isotope ratios, which are easy and inexpensive to acquire, for extensive intra-annual documentation of this variation.

5. DISCUSSION

5.1. $\delta^{18}\text{O}$ Differences and the Mixing Zone

The comparison of the no-flow $\delta^{18}\text{O}$ profile with the profiles of fossil shells allow us to track seasonal change in the $\delta^{18}\text{O}$ of gulf water in the delta region through time. We minimize the temperature effect on shell carbonate by comparing the $\delta^{18}\text{O}$ values by fortnight. We assume that the average temperature of a particular fortnight is similar for all shells, no matter what year the carbonate was produced (see the discussion of error estimates, below). If this is the case, then the only factor causing a difference in the $\delta^{18}\text{O}$ of the shells is the $\delta^{18}\text{O}$ of the water in which the animal lived. The most important feature controlling the isotopic composition of seawater in the mixing zone is the amount of river water being delivered. Thus the $\delta^{18}\text{O}$ difference in a fortnight-by-fofortnight comparison of fossil shell with the no-flow record gives us the change in the $\delta^{18}\text{O}$ of

Table 1. Sr isotope ratios from waters collected in February 1999.

Location	Salinity	84Sr/86Sr $\pm 2\sigma$	87Sr/86Sr $\pm 2\sigma$	87Sr/86Sr (norm) ¹
El Golfo	36	0.056516 \pm 19	0.709194 \pm 18	0.709174
Isla Montague	33	0.056493 \pm 12	0.709221 \pm 13	0.709201
The Y	29	0.056492 \pm 12	0.709282 \pm 11	0.709262
NBS-987 std		0.056500 \pm 13	0.710255 \pm 5	
Colorado River (Cibola, Mar 96) ²			0.710274 \pm 13	0.710254
Colorado River (L. Mead, Jan 99) ²			0.710437 \pm 16	0.710417

¹ Ratio after NBS-987 is normalized to 0.710235 (Hodell et al., 1991; Farrell et al., 1995).

² Data from Gross et al., 2001.

gulf water due to the addition of Colorado River water at the location of bivalve growth.

Almost all of our fossil samples are more negative in $\delta^{18}\text{O}$ than the no-flow bivalve record. This offset to more negative values is due to growth in less saline water in the delta region. The magnitude of this difference allows us to quantify the amount of fresh-water at the place and year of shell growth with fortnightly resolution. Note that there are a few times when the shell $\delta^{18}\text{O}$ is more positive than the no-flow profile (e.g., Fig. 8b). This is most likely due to shell growth in water that is more positive in $\delta^{18}\text{O}$ than normal seawater due to evaporation, probably in a tide pool environment. These occurrences, attributable to very localized evaporation, are not used in our calculations and we treat them as identical to the no-flow profile.

Because salinity and $\delta^{18}\text{O}$ are conservative properties, the mixing of waters yields a simple proportional sum of the two waters' characteristics. If we know the $\delta^{18}\text{O}$ of end-members (pure river water and pure seawater) and the $\delta^{18}\text{O}$ change in the water due to the addition of river water, we can calculate the percentage of river water at these locations during a particular fortnight. While the seawater end-member may change slightly seasonally, our sampling has not been adequate to document seasonal or spatial variation. We therefore use the mean seawater $\delta^{18}\text{O}$ value (+0.60‰ SMOW) for the seawater end-member of our mixing relationship.

Before dams were emplaced on the Colorado River, the seasonal $\delta^{18}\text{O}$ cycle in the river was very large. The isotopic cycle was mainly driven by a large pulse of snow-melt from the Rocky Mountains delivered to the river in May, June, and July (USGS, 1954; Rodriguez et al., 2001). Today the lower Colorado River has virtually no seasonal cycle because water in the reservoirs has a residence time of more than one year. The reservoirs therefore mix the normal seasonal inputs to the river and may also cause an increase in the $\delta^{18}\text{O}$ value of reservoir water due to evaporation. We collected water samples from the Colorado River in southern Arizona between December 1994 and March 2003 and obtained $\delta^{18}\text{O}$ values of -11.4‰ to -12.8‰ , with an average of -12.0‰ SMOW ($n = 9$).

Because the $\delta^{18}\text{O}$ value of predam river water and its seasonal variation was very different from that measured today, we cannot use modern river chemistry as our fresh-water end-member in predam mixing calculations. Modern conditions will be used for calibration and verification of the mixing model when examining recent releases of known amounts of river water to the Gulf of California. Calculating predam river discharge requires knowledge of the seasonal cycle in the $\delta^{18}\text{O}$ values of predam Colorado River water. We therefore use

fresh-water bivalve shells collected before the dams were built to calculate the seasonal variation in $\delta^{18}\text{O}$ of fresh-water being delivered to the Gulf of California by the river. Oxygen isotope profiles of two *Anodonta dejecta*, collected in the late 1800s from the river near Yuma show a large change in $\delta^{18}\text{O}$ (Fig. 9). Using average river water temperatures and stable isotope fractionation factors calibrated for these fresh-water bivalves (Dettman et al., 1999), we can calculate the $\delta^{18}\text{O}$ of the river water if seasonal shell growth can be modeled. Unfortunately, daily bands are not visible in these shells and there are no tides to generate fortnightly growth markers. Note, however, that uncertainties in temperature lead to only small uncertainties in the calculated $\delta^{18}\text{O}$ of the water because it takes a 4.6°C change in temperature to change shell $\delta^{18}\text{O}$ by 1‰. Thus a mis-assignment of temperature by 4.6°C leads to a 1‰ error in the calculated $\delta^{18}\text{O}$ of the water.

Growth in this subfamily of fresh-water bivalves is not continuous throughout the year; some genera of unionid bivalves hibernate below temperatures of $\sim 12^\circ\text{C}$ (Dettman et al., 1999). They are also very sensitive to suspended sediment and may have stopped growing during the full flood-stage flow triggered by snow melt in the Rocky Mountains. In each year (identified by the $\delta^{18}\text{O}$ cycle) there are two bands in the shell where a thickened prismatic layer shows growth cessation. Our growth model for these bivalves is based on these hiatuses: the winter months are missing due to cold temperatures and are associated with the growth break at the more positive $\delta^{18}\text{O}$ values (approximately -6 to -8‰ PDB); the annual midsummer snow melt event is a turbidity triggered growth check, associated with the most negative $\delta^{18}\text{O}$ values in the shell (Fig. 9). The latter was a major annual flood event, which, during the 30 yr of instrumental records before the first dam was installed, delivered 60% of the annual flow in a period of about three months (Fig. 10; USGS, 1954; Harding et al., 1995). To calculate the $\delta^{18}\text{O}$ of river water we must associate river water temperatures with shell $\delta^{18}\text{O}$ values guided by simple assumptions about growth. Because predam temperatures are not available, we use Colorado River water temperatures from southern Arizona, well away from any dams and after the river has reached thermal equilibrium with ambient conditions (US Geological Survey, 1964). March and April temperatures (14.4°C and 18°C respectively) are associated with shell $\delta^{18}\text{O}$ values leading up to the very negative $\delta^{18}\text{O}$ values in the shell. The increase in flow associated with snow melt occurs in May in the predam records. We associate temperatures for May (22°C) with the most negative $\delta^{18}\text{O}$ values in the shell. Growth during June (25°C) and July (28°C) may not be present in the shell because of the turbidity induced growth check. Temperatures

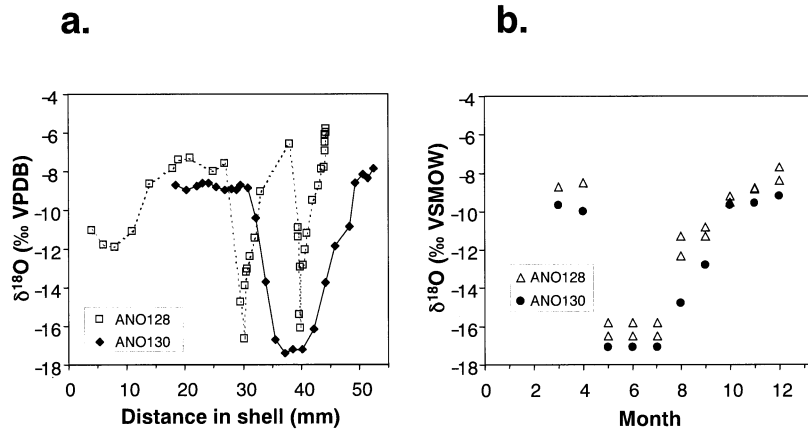


Fig. 9. (a) Oxygen isotope composition of two *Anodonta dejecta* shells collected before dam emplacement (ANO128 collected in 1894 – squares; ANO130 collected in 1902 – diamonds) from the Colorado River. (b) The $\delta^{18}\text{O}$ of predam Colorado River water can be calculated from shell $\delta^{18}\text{O}$ values using the temperature - oxygen isotope fractionation relationship of Dettman et al. (1999) and a model for shell growth to identify months (see text). Mean monthly values are listed in Table 2.

for August (29°C) through December (when temperatures drop below 12°C, the minimum for growth) are distributed evenly between the flood-triggered hiatus and the winter growth cessation. Because part of the record is lost during the summer maximum flow, we use the same minimum $\delta^{18}\text{O}$ value for May, June and July (Fig. 9). It is possible that the $\delta^{18}\text{O}$ of river water may have been more negative at peak flow. The calculated $\delta^{18}\text{O}$ values for river water during each month are averaged to obtain the seasonal cycle in the $\delta^{18}\text{O}$ of the river water

end-member (Table 2). Stable isotope data from old (predam) groundwaters in the southern Colorado River floodplain corroborate our calculations. Two studies suggest that the $\delta^{18}\text{O}$ of the river during maximum flood-stage, which would be the primary recharge water for distal areas in the floodplain, had very negative $\delta^{18}\text{O}$ values (Robertson, 1991; Guay, in press). These groundwaters lie on $\delta\text{D}-\delta^{18}\text{O}$ trends that intersect meteoric water line at approximately -17‰ SMOW.

5.2. Calculation of River Water Percentage and River Flow

If equivalent fortnights in different shells represent growth at identical temperatures, the $\delta^{18}\text{O}$ difference between a fossil

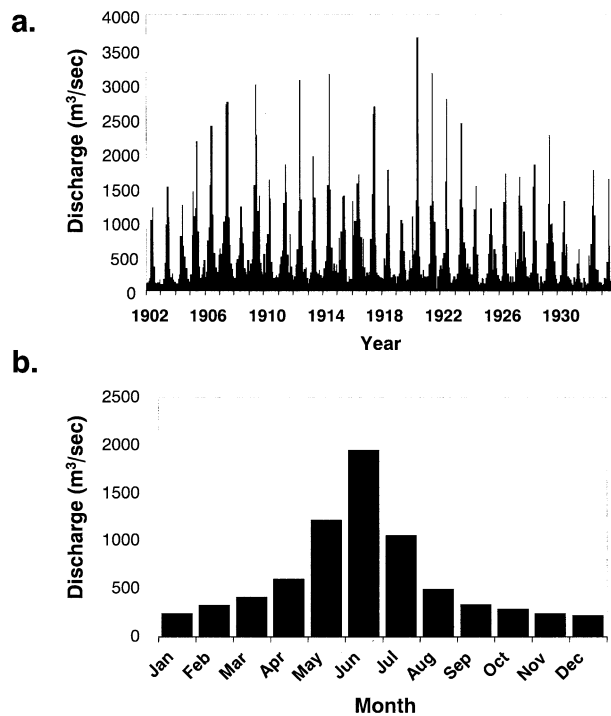


Fig. 10. (a) Monthly discharge records for the lower Colorado River before construction of the dams. (b) Average monthly discharge. Note that 60% of the total annual flow occurs in three summer months.

Table 2. River water $\delta^{18}\text{O}$ values used in mixing relationship.

Fortnight	Month*	$\delta^{18}\text{O}$ river water
1	March	-9.2 SMOW
2	April	-9.25
3	April	-9.25
4	May	-16.47
5	May	-16.47
6	May	-16.47
7	June	-16.47
8	June	-16.47
9	July	-16.47
10	July	-16.47
11	August	-12.8
12	August	-12.8
13	September	-11.63
14	September	-11.63
15	October	-9.47
16	October	-9.47
17	October	-9.47
18	November	-9.07
19	November	-9.07
20	December	-8.43

* Because there are 26 fortnights in the year and only 12 months, monthly data from the figures must be distributed such that two months are associated with 3 fortnights; we use May and October.

shell and the no-flow profile is due to the difference in the $\delta^{18}\text{O}$ of the water. The magnitude of this offset can be used to calculate the percentage of river water present by scaling it to the $\delta^{18}\text{O}$ values of the end-members, pure seawater (+0.60‰ SMOW) and pure river water (Table 2). The ability to identify fortnights in the shell is important, not only with respect to seasonal temperature change, but also placing the offset within the context of the seasonally changing river-water end-member. The calculation of the proportion of river water is based on a two component mixing equation:

$$f_{\text{river water}} = (\delta^{18}\text{O}_{\text{fossil shell}} - \delta^{18}\text{O}_{\text{no-flow shell}}) / (\delta^{18}\text{O}_{\text{river water}} - 0.60\text{‰}) \quad (1)$$

where f is the fraction river water in the mixture, each $\delta^{18}\text{O}$ value is for an equivalent fortnight, and the 0.60‰ is the value of seawater under no-flow conditions. For example, the percentage of river water at the location of shell growth for the late 18th century shell (Fig. 7a) in fortnight 9 is calculated using Eqn. 1 and the following data: $\delta^{18}\text{O}_{\text{fossil shell}} = -8.74$, $\delta^{18}\text{O}_{\text{no-flow shell}} = -1.92$ (from Fig. 5) and $\delta^{18}\text{O}_{\text{river water}} = -16.47$ (from Table 2). The proportion of river water at that location is 0.40 or 40%. Eqn. 1 allows us to calculate the proportion of sea and river water at the shell location throughout the growth season of the shell (late March to December).

To convert these proportions to actual river discharge, we make use of known amounts of river water released in 1998 and 1999. The stable isotope effects of these releases were monitored at Isla Montague, in the mouth of the river, where most of our fossil shells were collected. Waters and shells were collected at both Montague and Sacatosa during and after the releases. Using the fortnightly chronology of shell growth, we can correlate negative shifts in shell $\delta^{18}\text{O}$ with release amounts. We can also compare the $\delta^{18}\text{O}$ of water samples collected during releases with those of similar months under no-flow conditions to determine the effect of a release of known isotopic composition, volume, and duration on seawater in the delta.

First we discuss the response of water at the mouth of the river, Isla Montague. Waters at Isla Montague were collected during two recent releases of river water to the gulf (382 m³/s average during Feb. 1998, and 188 m³/s average discharge in Feb. 1999 [Bureau of Land Reclamation, Yuma office, US Department of the Interior: Carol Grimes, personal comm.; <http://www.usbr.gov/lc/yuma>]). These are plotted with the average $\delta^{18}\text{O}$ of water during no-flow conditions (Fig. 11a), showing the linear mixing of seawater with differing amounts of river water. Converting these $\delta^{18}\text{O}$ values to percent river water (using -12‰ for the isotopic composition of present-day Colorado River water) yields a 0.01 increase in proportion of river water at Isla Montague for a discharge of 20.2 m³/s,

$$\text{Discharge} = \left(\frac{20.2 \text{ m}^3/\text{sec}}{0.01} \right) f \quad (2)$$

where f is the fraction river-water from Eqn. 1.

Dispersion of the Colorado River water coming into the gulf leads to changes in this relationship as distance increases from the mouth of the river. The other location of our collections, Sacatosa, is about 30 km from Isla Montague (Fig. 1) and a separate calibration must be constructed for this new location.

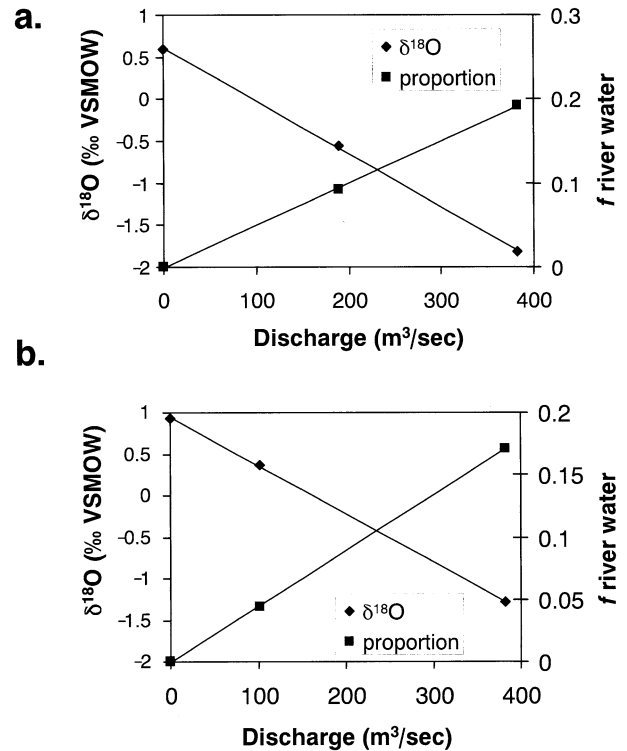


Fig. 11. (a) Oxygen isotope response to river water releases to the Gulf of California measured at Isla Montague based on water collections during releases. Proportion river water in sample derived from the mixing of seawater (0.6‰ SMOW) and river water (-12‰ SMOW). (b) Oxygen isotope response to river water releases measured in water or shell from Sacatosa. Proportion river water based on the mixture of seawater at Sacatosa (0.93‰ SMOW) and river water of -12‰ SMOW.

At Sacatosa only one water collection coincided with a known release (which averaged 97.9 m³/s during November of 1998). The $\delta^{18}\text{O}$ value of this sample was +0.36‰ SMOW. Under no-flow conditions the average $\delta^{18}\text{O}$ of water at Sacatosa is 0.93‰, which is significantly more positive (and saline) than open marine conditions in the northern Gulf of California. This high salinity region is a persistent feature and is attributed to trapping and evaporation of seawater in the extensive tidal flats lying inland of Sacatosa (Carbajal et al., 1997). The calculation of river-water proportion changes slightly because of higher salinity. The difference between the mean $\delta^{18}\text{O}$ value of no-flow seawater at the two locations is 0.33‰ SMOW [Sacatosa +0.93‰ SMOW, Isla Montague +0.60‰ SMOW]. We do not have a no-flow shell isotope record from Sacatosa, nor do we have a detailed annual cycle in seawater $\delta^{18}\text{O}$ values. Therefore we will assume that the 0.33‰ difference in the $\delta^{18}\text{O}$ of seawater is present throughout the year at Sacatosa, which leads to the following modification of Eqn. 1:

$$f_{\text{river water}} = (\delta^{18}\text{O}_{\text{fossil shell}} - (\delta^{18}\text{O}_{\text{no-flow shell}} + 0.33\text{‰})) / (\delta^{18}\text{O}_{\text{river water}} - 0.93\text{‰}) \quad (3)$$

in which the $\delta^{18}\text{O}$ of the no-flow record is increased by 0.33‰.

Sclerochronological analysis of a one-year old specimen collected in November of 1998 shows that it was living during

the large release of February of 1998 (382 m³/s) and it recorded this discharge of river water in the oxygen isotope ratio of the shell. A -2.2‰ offset at fortnight 0 in Figure 8b matches the February release, based on sclerochronology. Like many *Chione* specimens, it continued to grow through the first winter of its life, although the usual pattern for later years is a cessation of growth during winter. This short-term departure to more negative values and a return to more positive values by fortnight 2 reflects a -2.2‰ change in the $\delta^{18}\text{O}$ of the local water from approximately $+0.9$ to -1.3‰ SMOW. This inferred change in the $\delta^{18}\text{O}$ of local water is used in Figure 11b as a third calibration point to relate proportion river water to river discharge. Again using -12‰ SMOW for the $\delta^{18}\text{O}$ of river water, the relationship is:

$$\text{Discharge} = \left(\frac{22.75 \text{ m}^3/\text{sec}}{0.01} \right) f \quad (4)$$

where f is the fraction river water derived from Eqn. 3.

5.3. Two Examples

Two examples will demonstrate this calculation in detail. The first is from a shell collected at the river mouth that grew during a major release of river water in the first half of 1993. Because the magnitude of this release is known, we can use this release to verify the relationships upon which our calculations are based. The second example is from a fossil specimen which lived in the late 11th century.

The shell plotted in Figure 8a was collected from Isla Montague in 1996. Growth bands indicate that its earliest growth was in late summer 1992. Samples for stable isotope analysis were taken from the earliest shell growth into the second full year of growth, thus spanning all of 1993 and into 1994. Sclerochronology was used to place the 1993 samples into fortnights and the stable isotope data were compared with the no-flow profile. The offset between the two curves (Fig. 12a) is assumed to be a result of the addition of the controlled release of river water. In this (postdam) case, the two end-members that are being mixed do not change significantly throughout the year. Therefore the difference between the no-flow and shell $\delta^{18}\text{O}$ curves mimics the records of river water release very well (Fig. 12a). Both are largest in March (Fortnight 1) and decline to small values in the summer. There is a small increase again near the end of the year.

To calculate the amount of water released, Eqn. 1 is first used to calculate the proportion river water for each fortnight of the year. Because this specimen lived under postdam conditions, we assume that the $\delta^{18}\text{O}$ of the river water end-member was -12‰ SMOW. Because we do not have river water measurements for 1993, we use the average $\delta^{18}\text{O}$ value from all our collections (1995 to 2003). Shell $\delta^{18}\text{O}$ values are taken from Figure 8a, interpolating values when data do not exist for a specific fortnight. The proportions are then converted to flow amounts using Eqn. 2. The calculated flow amounts match the amount of released water very well (Fig. 12b), although our calculations are for fortnights and the release data is only provided as a monthly record. The controlled releases totaled $3.10 \times 10^9 \text{ m}^3$ from mid-March to mid-December; our estimate is $2.51 \times 10^9 \text{ m}^3$.

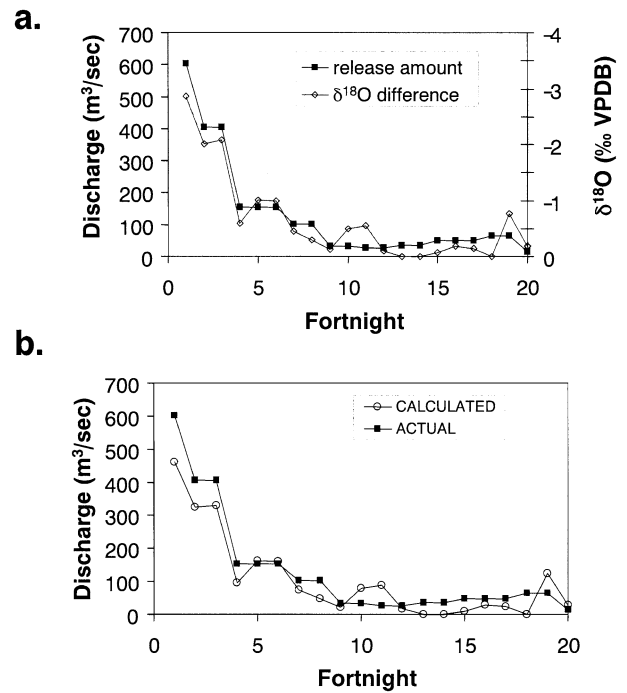


Fig. 12. (a) The $\delta^{18}\text{O}$ difference between 1993 shell and the no-flow record parallels the amount of river water released. Amount released from Bureau of Land Reclamation, Yuma office, US Department of the Interior: Carol Grimes, personal comm. Monthly release data is divided into fortnights as in Table 2. (b) Calculated flow vs. actual flow during 1993.

The second example is from a subfossil shell collected from a chenier at Sacatosa (Fig. 7b). Amino-acid racemization dating, calibrated to the ^{14}C time scale, was used to acquire an age of $1075 \text{ AD} \pm 50 \text{ yr}$ for this shell (Kowalewski et al., 1998). The equations for conditions at Sacatosa (Eqn. 3 and 4) are used for this specimen. This results in a calculated total discharge of $9.11 \times 10^9 \text{ m}^3$ during the 20 fortnights present in the shell. To account for the remaining 6 fortnights (as discussed in section 3.1, above) this amount is increased by 12% to $1.02 \times 10^{10} \pm 6.1 \times 10^8 \text{ m}^3$ for the year plotted in Figure 7b.

5.4. Assumptions and Uncertainties

When applying the above calculations to the subfossil shells of the last 1000 yr, three conditions are assumed to remain constant and variability may contribute to uncertainty in the calculation of river discharge. We assume that the seasonal temperature cycle, the spatial relationships used as a basis for our calibration, and the end-member $\delta^{18}\text{O}$ values of waters remain unchanged. In addition we will comment on the effect that intertidal micro-environments may have on our calculations.

We assume that the temperature of any numbered fortnight is the same in all shells. Undoubtedly interannual variability occurs in fortnightly temperatures. However, because temperature controls the onset of growth, there may be some physiologic moderation of temperature variation from year to year. It is important to keep in mind that the shell $\delta^{18}\text{O}$ response to temperature is approximately 1‰ for each 4.6°C (Grossman

and Ku, 1986). Therefore $\pm 1^\circ\text{C}$ variations lead to only $\pm 0.2\%$ errors in the calculated change in the $\delta^{18}\text{O}$ of mixing zone water.

Climate change may have occurred within the time interval represented by shells in the cheniers of the Colorado River delta. The most prominent climatic variation of the last 1000 yr is the shift from a warmer climate in the earlier part of the last millennium to a cooler climate in the latter half, often characterized as the Medieval Warm Period and the Little Ice Age respectively. In the southwest this variation is thought to have been relatively small, less than 1°C if present at all (Hughes and Diaz, 1994; Davis, 1994; Dean, 1994). We can calculate the effect that a 1°C change would have on the total annual discharge calculated for the example shell from 1075 AD (Fig. 7b). If the temperature was 1°C warmer throughout the entire year the $\delta^{18}\text{O}$ of the fossil shell would be reduced by 0.22% . Subtracting this amount from the $\delta^{18}\text{O}_{\text{fossil shell}}$ values for each fortnight leads to an increase in the calculated discharge of $1.08 \times 10^9 \text{ m}^3/\text{yr}$. A uniform 1°C cooler temperature leads to a reduction in total annual discharge of the same magnitude.

The spatial relationship between the mouth of the river and shell collection localities is also assumed to be constant during the time interval under investigation. Changes in the location of the river mouth can occur during storm events or due to flooding and a study covering a long time interval must address the possibility of significant movement of the river's channel. Note, however, that the difference in the stable isotope response near the mouth of the river (at Isla Montague) and at Sacatosa is not large. A comparison of Eqn. 2 and 4 reveals a 12% difference in response over a distance of 30km. This suggests that small changes in the location of the river mouth would not have a large impact on the calculation of discharge.

The end-member values of the $\delta^{18}\text{O}$ of sea and river water probably vary from year to year. The $\delta^{18}\text{O}$ of seawater is more positive than average seawater due to evaporation enhanced by the large tidal range and the high temperatures of the northern Gulf of California. Climate has not changed dramatically in this region over the last 1000 yr, and we expect that evaporative effects were similar throughout this interval. The river water end-member has probably been much more variable. The $\delta^{18}\text{O}$ cycle was driven by the isotopic composition of sparse rainfall in the lower Colorado River basin in the fall, winter and spring, and by the melt of the Rocky Mountains snow pack in the early summer. From year to year the $\delta^{18}\text{O}$ of accumulated snow in any one region will have somewhat different $\delta^{18}\text{O}$ values. However, the Colorado River watershed integrates a very large area and this would dampen the variation from year to year. This suggestion is supported by the shell $\delta^{18}\text{O}$ cycle measured in the predam fresh-water bivalves, which is very similar for three different years (Fig. 9). The most negative $\delta^{18}\text{O}$ value inferred from these fresh-water bivalve shell analyses also agrees well with the $\delta^{18}\text{O}$ of groundwaters thought to be recharged by predam flood-stage Colorado River water (-17% SMOW) (Robertson, 1991; Guay et al., in press).

Finally, specimens may grow in micro-environments that are significantly different from open marine conditions. For example, *Chione* specimens may live high in the intertidal zone, in seawater that is sometimes more saline than the seawater end-member. This would result in underestimation of the calculated discharge. Specimens that lived high in the intertidal zone can

be identified and culled from a study by examining the variance of the $\delta^{18}\text{O}$ signal on short time scales. An animal living high in the intertidal zone would be stranded in a tide pool frequently throughout the year. Evaporative enrichment of the ^{18}O content of tide pool water should be recorded in shell $\delta^{18}\text{O}$, and will occur on a fortnightly basis due to the tidal cycle (Goodwin et al., 2001). Thus, sampling within the tidal bundles will help identify shells that frequently undergo tidal stranding and evaporation. Animals living in the subtidal or low intertidal zone have much less noisy stable isotope profiles and are much better suited for study of river discharge because they are not greatly affected by highly localized $\delta^{18}\text{O}$ anomalies created by evaporation.

6. CONCLUSIONS

By adopting sclerochronological techniques to guide the sampling of seasonal $\delta^{18}\text{O}$ cycles in *Chione* shells from the Colorado River delta, we are able to produce records of ancient river flow and paleosalinity with fortnightly to seasonal resolution. Because these records are based on fortnightly comparisons between shells grown in no-flow and river-flow conditions, the uncertainties due to the seasonal temperature cycle are minimized. This approach allows us to account for seasonal changes in the $\delta^{18}\text{O}$ of the fresh-water and seawater end-members throughout this record. Finally, releases of known amounts of water have allowed us to calibrate the stable isotope signals with actual river flow rates. This is a powerful approach for reconstructing long-term records of river flow.

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