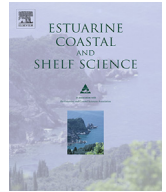




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# Drought and flood signals in subtropical estuaries recorded by stable isotope ratios in bivalve shells

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## ABSTRACT

Isotope ratios of carbon and oxygen recorded in biogenic carbonates can be effective proxies for ambient conditions in estuaries including salinity and temperature. Together, they have the potential to allow periods of drought and flooding to be identified in subtropical estuaries that receive stochastic and a periodic delivery of freshwater inflow. We investigated the ability of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values in shell increments from the eastern oyster *Crassostrea virginica* sampled from subtropical estuaries in the western Gulf of Mexico to indicate differences in temperature and salinity dynamics at fine spatial scales. Oyster shells at locations that experienced both hypersalinity during droughts and dramatic decreases in salinity during floods showed distinct depletions in shell  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values that reflected local salinity conditions. In contrast, oysters at sites where no major salinity fluctuation occurred showed only seasonal fluctuations in isotopes reflecting temperature and possibly feeding patterns. Further, similar isotopic patterns were observed across multiple individuals from each site. Our results show that  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values in shells measured together provide a powerful method to identify droughts and floods in subtropical estuaries and therefore extend records of dynamic inflow to these stressed ecosystems.

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## 1. Introduction

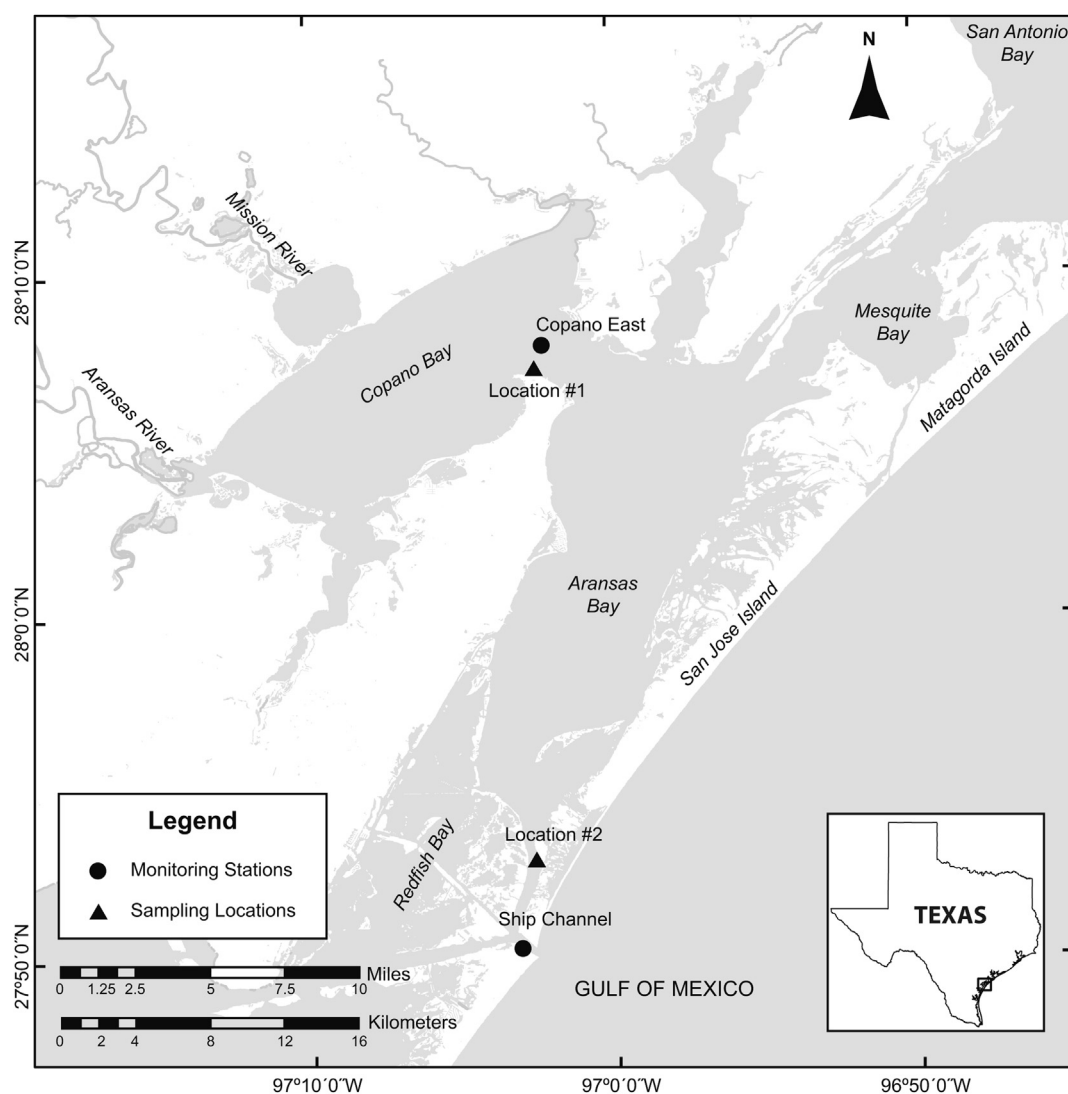
Subtropical estuaries in the western Gulf of Mexico are complex systems that often endure periods of extended drought followed by stochastically occurring floods that dramatically alter physico-chemical attributes across estuarine gradients (Bianchi et al., 1999; Nielsen-Gammon et al., 2005). While droughts are typically characterized by gradually intensifying environmental parameters such as salinity, floods may induce rapid and potentially extreme reversions, delivering a majority of the annual nutrient load in a short amount of time (Eyre and Pont, 2003; Arismendez et al., 2009). Ecological stress and disturbance may thus take the form of either punctuated “pulses” or extended “presses” (Glasby and Underwood, 1996) that can have equally dramatic effects on ecological processes such as nutrient cycling, productivity, and nursery habitat function (Gillanders and Kingsford, 2002; Gillson, 2011). Quantifying the spatiotemporal dynamics of both floods and droughts in subtropical estuaries is integral to understanding

system-level responses to dynamic and often unpredictable climates.

Chemical records in biogenic structures have been usefully employed to reconstruct environmental conditions in a wide variety of habitats worldwide. Many of these endeavors probe biogenic carbonate structures with chronological layers such as coral skeletons (McCulloch et al., 2003; Gaetani et al., 2011), fish otoliths (Dufour et al., 2008; Walther and Limburg, 2012), and bivalve shells (Surge et al., 2003; Dettman et al., 2004; Harding et al., 2010; Goodwin et al., 2013). Effective reconstructions of temperature and salinity can be accomplished through analysis of stable isotope ratios that either directly reflect ambient properties or whose kinetic or equilibrium fractionation dynamics are well constrained (McConnaughey and Gillikin, 2008). In estuarine systems, these reconstructions are made possible by significant differences in marine and freshwater endmembers of ambient constituents that define mixing curves across salinity gradients. Freshwater endmembers of  $\delta^{13}\text{C}$  of DIC and  $\delta^{18}\text{O}$  are both typically isotopically depleted (or lighter) than their marine counterparts, leading to positive relationships between isotopic ratios and salinity, particularly for well-flushed estuaries (Tan, 1989; Fry, 2002). Both of these isotope ratios are effectively recorded by biogenic carbonate structures, making them attractive proxies for chronological

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**Fig. 1.** Map of the collection locations in the Aransas-Copano Bay system on the southern Texas coast. Symbols indicate oyster shell sampling locations (triangles) and continuous temperature and salinity monitoring stations (circles) maintained by the Mission-Aransas National Estuarine Research Reserve (MANERR).

reconstructions of environmental change. Although bivalve shell isotope ratios have been used to identify periods of drought in temperate systems (Harding et al., 2010), they have not yet been investigated in subtropical estuaries that experience extended inter-annual droughts.

Values of  $\delta^{18}\text{O}$  in carbonates are primarily driven by two factors: (1) source water  $\delta^{18}\text{O}$  values and (2) temperature (Sharp, 2007). Assuming source water composition is constant, temperature-driven equilibrium fractionation between water and carbonate leads to an inverse relationship between temperature and carbonate  $\delta^{18}\text{O}$  values (Epstein et al., 1953). That is, lower temperatures result in higher (or heavier)  $\delta^{18}\text{O}$  values. However, water  $\delta^{18}\text{O}$  composition is not always constant, particularly in coastal and estuarine environments (Gat, 1996). The two primary drivers of water  $\delta^{18}\text{O}$  composition in coastal environments are evaporative loss and freshwater inflow, both of which can affect the salinity regimes of estuaries (Corlis et al., 2003; Price et al., 2012). Evaporative loss can preferentially remove light molecules, leaving the remaining water saltier and isotopically heavier, although the magnitude of this effect is modified by factors such as relative humidity and ambient temperatures (Horita and Wesolowski, 1994; Luz et al., 2009). In addition, freshwater endmembers of modern  $\delta^{18}\text{O}$  values are typically

lower than those in marine waters (Bowen and Revenaugh, 2003; Dutton et al., 2005; LeGrande and Schmidt, 2006; McMahon et al., 2013). As a result, influx of fresh water to estuarine habitats reduces salinity and ambient water  $\delta^{18}\text{O}$  values, the magnitude of this shift depending on the freshwater endmember of the tributary in question. For biogenic carbonates that are precipitated in equilibrium with ambient water, these combined effects result in a positive relationship between salinity and carbonate  $\delta^{18}\text{O}$  values (Andrus and Crowe, 2000; Goodwin et al., 2010; Versteegh et al., 2012). A significant flood event should therefore result in a dramatic decrease in carbonate  $\delta^{18}\text{O}$  values (Dettman et al., 2004). Provided the freshwater endmember is substantially different than the marine endmember, this influx should dominate any temperature-related fractionation associated with the flood.

Values of  $\delta^{13}\text{C}$  in biogenic carbonates such as mollusk shells are primarily driven by two factors as well: (1) ambient dissolved inorganic carbon (DIC) isotope ratios and (2) "vital effects" consisting of metabolic alteration of the internal DIC pool and kinetic fractionation (McConnaughey et al., 1997). Any process that alters ambient DIC  $\delta^{13}\text{C}$  values should be reflected in accreted carbonate  $\delta^{13}\text{C}$  values. In coastal systems, DIC  $\delta^{13}\text{C}$  values strongly correlate with salinity (Chanton and Lewis, 1999; Fry, 2002; Atekwana et al.,

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