

Interdecadal variation in seawater $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ recorded in fish otoliths

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Abstract

Stable carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) in the otolith cores of Atlantic bluefin tuna (*Thunnus thynnus*) vary temporally, with changes that quantitatively follow interdecadal variation in atmospheric and oceanic reservoirs. Both carbon and oxygen isotopic signatures vary significantly by year of birth over the range investigated (1947–2006), with $\delta^{13}\text{C}$ decreasing and $\delta^{18}\text{O}$ increasing ($-2.56 \times 10^{-2}\text{‰}$ and $4.3 \times 10^{-3}\text{‰ yr}^{-1}$, respectively). The rate of change in otolith $\delta^{13}\text{C}$ was similar to reported rates of atmospheric $\delta^{13}\text{C}$ depletion, attributed to deforestation and the burning of fossil fuels (referred to as the Suess effect), suggesting a close link between atmospheric and oceanic carbon pools. Increases in otolith $\delta^{18}\text{O}$ were evident but less pronounced, with observed variation possibly attributable to changing salinity in the Atlantic Ocean. Otolith cores of bluefin tuna effectively track interdecadal trends and record past seawater $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$.

Atmospheric and oceanic (seawater) reservoirs of stable carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) isotopes are known to fluctuate over time because of natural and anthropogenic processes (Quay et al. 1992; Delaygue et al. 2000). Over the last century, atmospheric $\delta^{13}\text{C}$ has decreased significantly because of increased inputs of isotopically light carbon from both the burning of fossil fuels and the reduction of forest and soil carbon reservoirs (the Suess effect; Verburg 2007). This effect has accelerated in recent decades and translates into parallel shifts in animal tissue $\delta^{13}\text{C}$ within terrestrial (Bump et al. 2007) and aquatic ecosystems, with decreasing $\delta^{13}\text{C}$ detected in producers (phytoplankton; Bauch et al. 2000) and low-level consumers (sponges; Druffel and Benavides 1986). Still, shifts in $\delta^{13}\text{C}$ are seldom studied beyond the base of the food web, and no link to the Suess effect has been documented in marine vertebrates. Similarly, atmospheric and oceanic $\delta^{18}\text{O}$ reservoirs appear to be coupled (Jouzel et al. 2002), and carbonates precipitated in equilibrium with these reservoirs are affected by ambient concentrations as well as physicochemical conditions (Kim and O'Neil 1997; Thorrold et al. 1997). Although historical temperature records have been reconstructed using $\delta^{18}\text{O}$ in biogenic carbonates (shells, coral, otoliths; Schöne et al. 2005; Sun et al. 2005; Surge and Walker 2005), few studies have attempted to describe short-term (i.e., decadal) changes in modern seawater $\delta^{18}\text{O}$ using these structures.

Stable isotopic signatures in the otoliths (ear stones) of marine fishes are often linked to water mass properties, and as with other biogenic carbonates, chemical information contained in these structures has been used to reconstruct past climates and environmental conditions (Gao and Beamish 1999; Surge and Walker 2005). Temperature, salinity, and ambient ocean isotope concentration have all been linked to changes in otolith $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Kalish 1991; Thorrold et al. 1997; Elsdon and Gillanders 2002),

and can lead to variability of otolith isotope signatures within and across years. Although otolith composition is also regulated by metabolic and physiological processes (Radtke et al. 1987; Kalish 1991), these properties still yield consistent isotope signatures in otolith cores over annual time periods, justifying their use as natural tracers for specific water masses (Kerr et al. 2007; Rooker et al. 2008). Given the potential usefulness of otolith $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for historical reconstructions (i.e., climate, physicochemical) and as natural tracers, evaluating the temporal variability of these signatures over decadal periods is critically needed.

Here, we examined temporal variation in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the otolith cores (representing the first year of life) of a pelagic fish, Atlantic bluefin tuna (*Thunnus thynnus*), over five decades. This species represents an ideal model for evaluating decadal changes in seawater $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ because juveniles frequent the upper mixed layer of the water column during the first year of life (90% time in less than 15 m; Brill et al. 2002), and archived otoliths comprised of individuals from year classes spanning 60 yr were available. This study is based on the hypothesis that trends in otolith core composition correspond to changes in ambient seawater $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the Gulf of Mexico and western Atlantic (i.e., the Gulf Stream) from 1947 to 2006.

Methods

Otoliths used here were collected from three regions at different time periods: (1) yearlings ($n = 103$) in the U.S. Atlantic from 1999 to 2004 and 2006 to 2007, (2) adults from the spawning area in the Gulf of Mexico ($n = 42$) from 1999 to 2002 and 2007, and (3) adults from a foraging ground in the Gulf of St. Lawrence ($n = 224$) from 1975 to 1984 and 2006 to 2007. After extraction, otoliths were cleaned and stored in dry containers. Based on Rooker et al. (2008), individuals from the selected areas were comprised almost exclusively of the western population of bluefin tuna (i.e., no mixing of migrants from the

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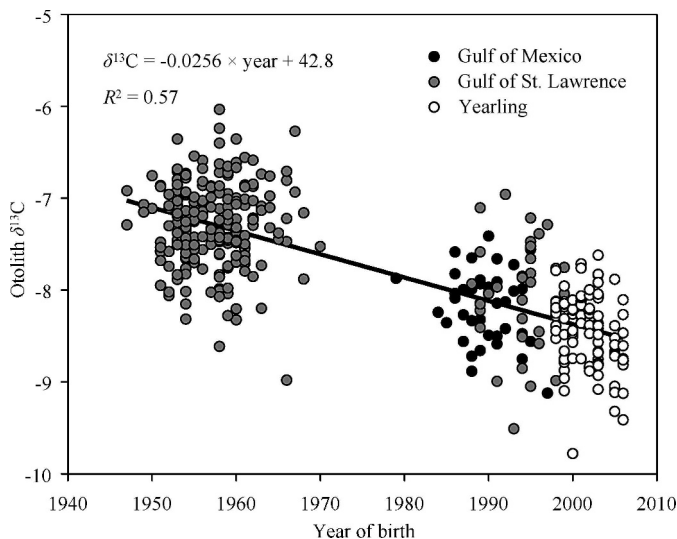


Fig. 1. Linear regression of $\delta^{13}\text{C}$ in milled otolith cores from Atlantic bluefin tuna (*Thunnus thynnus*) against year of birth from 1947 to 2006 ($n = 369$). Bluefin tuna were collected from the western Atlantic, with ages derived from annuli counts (Secor et al. 2008) or length-to-age conversion (Rooker et al. 2007).

Mediterranean Sea). Therefore, all bluefin tuna were assumed to have originated from western Atlantic nurseries, spending time in the Gulf of Mexico and associated Gulf Stream through age 1 yr. For yearling bluefin tuna collected in 1999 to 2004, the entire otolith was powdered using a mortar and pestle to obtain material representative of the first year of life. Otoliths of yearlings from 2006–2007 and all adults were sectioned and the core milled using a New Wave Research micromill (no difference between methods; Rooker et al. 2008). The region corresponding to the first year of life, as identified from measurements of transverse sections of yearling bluefin tuna otoliths, was powdered using a series of drill passes over a preprogrammed drill path by a 500- μm -diameter Brasseler carbide bit until approximately 750- μm depth was reached. Age assignments of adult bluefin tuna were based on counts of annual growth increments when available (85% of samples), or approximated using a length to age conversion (Rooker et al. 2007). Otolith powder was analyzed for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ using an automated carbonate preparation device coupled to an isotope-ratio mass spectrometer (Rooker et al. 2008). Powdered samples were reacted with dehydrated phosphoric acid under vacuum at 70°C. Analytical precision of the mass spectrometer was $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 0.06\text{‰}$ for $\delta^{13}\text{C}$. Isotope ratio measurements were calibrated based on repeated measurements of National Bureau of Standards (NBS)-19 and NBS-18 and reported relative to the Pee Dee Belemnite standard.

Results and Discussion

A significant relationship was detected by a linear regression of otolith $\delta^{13}\text{C}$ against year of birth with a slope of -2.56×10^{-2} ($n = 369$, $R^2 = 0.57$, $p < 0.05$; Fig. 1), corresponding to an approximate 1.51‰ depletion

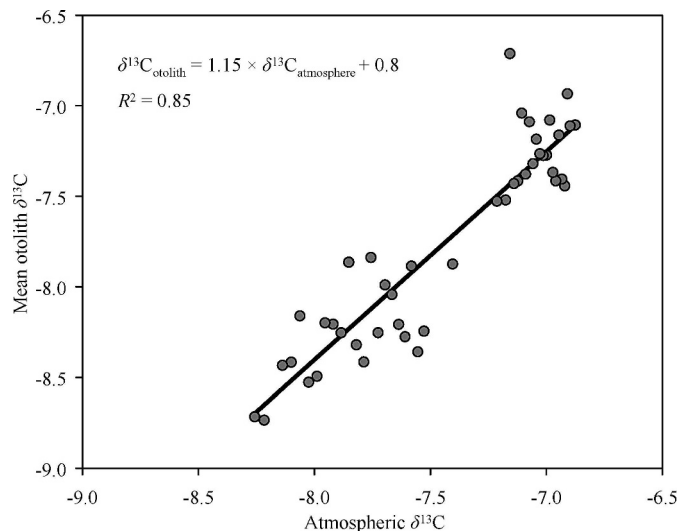


Fig. 2. Mean $\delta^{13}\text{C}$ (grouped by year of birth) in milled otolith cores from Atlantic bluefin tuna (*Thunnus thynnus*) collected in the western Atlantic compared to atmospheric $\delta^{13}\text{C}$ for years from 1947 to 2006. Atmospheric $\delta^{13}\text{C}$ derived from Verburg's (2007) polynomial estimator of $\delta^{13}\text{CO}_2$.

in $\delta^{13}\text{C}$ over the 59-yr period investigated (1947–2006). Despite the ability of physicochemical factors (i.e., temperature and salinity) to affect seawater $\delta^{13}\text{C}$ (Thorrold et al. 1997; Elsdon and Gillanders 2002), they do not appear linked to the observed decadal shift in otolith $\delta^{13}\text{C}$. Changes in oceanic temperature and salinity have been documented over the approximate time period analyzed (1950s–1990s). The largest mean temperature anomaly was found to be 0.37°C for the 0–300-m-depth layer of the North Atlantic Ocean (Levitus et al. 2000). However, using the relationship between otolith $\delta^{13}\text{C}$ and temperature from Thorrold et al. (1997) and assuming constant seawater $\delta^{13}\text{C}$, this temperature change would account for a decrease in otolith $\delta^{13}\text{C}$ of approximately 0.067‰, only 4% of the observed change. An increase in salinity of 0.1 to 0.4 occurred for subtropical Atlantic waters south of 35°N concentrated around the Gulf Stream (Curry et al. 2003). The increase in salinity would result in increased otolith $\delta^{13}\text{C}$ (Elsdon and Gillanders 2002), rather than the decreasing trend in this study. Therefore, temperature and salinity do not appear to be the predominant factors controlling the observed $\delta^{13}\text{C}$ shift in otoliths.

Decreasing seawater $\delta^{13}\text{C}$ has been attributed to the combined effect of the burning of fossil fuels and deforestation, which has increased the proportion of ^{13}C -depleted CO_2 in the atmosphere over the past century (Quay et al. 1992). Studies on phytoplankton and sclerosponge skeletons have recorded decreases in $\delta^{13}\text{C}$ values between approximately -0.50‰ and -0.90‰ because of the influx of isotopically light CO_2 over different 150-yr periods (Druffel and Benavides 1986; Bauch et al. 2000), and evidence from this study suggests that the same effect also influences otolith $\delta^{13}\text{C}$ in marine vertebrates. Sharp declines in atmospheric $\delta^{13}\text{C}$ first began in the early 1900s, and have since resulted in a total depletion of 1.38‰

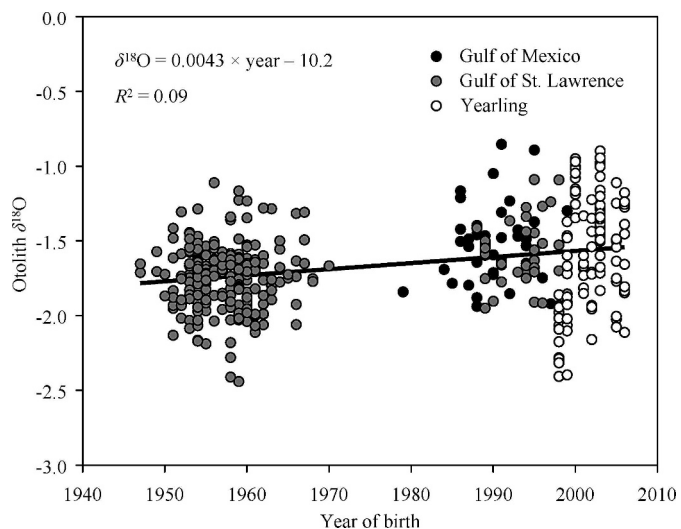


Fig. 3. Linear regression of $\delta^{18}\text{O}$ from milled otolith cores of Atlantic bluefin tuna (*Thunnus thynnus*) against year of birth from 1947 to 2006 ($n = 369$). Bluefin tuna were collected from the western Atlantic, with ages derived from annuli counts (Secor et al. 2008) or length-to-age conversion (Rooper et al. 2007).

over the time period examined (1947–2006; based on the polynomial $\delta^{13}\text{C}$ estimator in Verburg 2007), which is very similar to the observed 1.51‰ decline in bluefin tuna otoliths (higher value because of aforementioned minor effect of temperature on otolith $\delta^{13}\text{C}$). Direct comparison of the shift in mean otolith $\delta^{13}\text{C}$ by year of birth vs. the change in atmospheric $\delta^{13}\text{C}$ yielded a nearly one-to-one slope (slope = 1.15, $R^2 = 0.85$; Fig. 2), indicating that otoliths of bluefin tuna effectively track atmospheric changes in $\delta^{13}\text{C}$.

Results from a linear regression of otolith $\delta^{18}\text{O}$ against year of birth suggested that a minimal, yet significant, change occurred ($n = 369$, $R^2 = 0.09$, $p < 0.05$; Fig. 3). Otolith $\delta^{18}\text{O}$ increased by $4.3 \times 10^{-3}\text{‰ yr}^{-1}$, with an overall change of 0.25‰ from 1947 to 2006. It is commonly accepted that $\delta^{18}\text{O}$ accretion in otoliths is related to seawater $\delta^{18}\text{O}$, which is closely linked to temperature and salinity. However, adjusting for temperature changes (0.37°C increase; Levitus et al. 2000) and using established temperature– $\delta^{18}\text{O}$ relationships would result in a depletion of otolith $\delta^{18}\text{O}$ (0.08‰, Kalish 1991; 0.12‰, Thorrold et al. 1997), not an enrichment. Shifts in salinity such as those reported around the Gulf Stream (0.1–0.4 increase; Curry et al. 2003) would increase seawater $\delta^{18}\text{O}$ up to 0.24‰ over the time period investigated (Delaygue et al. 2000). Therefore, the observed enrichment in otolith $\delta^{18}\text{O}$ is likely due in part to salinity changes over time, suggesting that salinity plays a more important role in otolith $\delta^{18}\text{O}$ composition than previously assumed. Mixing of Gulf Stream and other North Atlantic water masses may also affect seawater $\delta^{18}\text{O}$ over time, but this effect has been investigated only on a smaller spatial scale (Fairbanks 1982).

The change of ambient $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures in the atmosphere and ocean over the past several decades emphasizes the need to understand decadal shifts in isotope

ratios for recreating past climate records and physicochemical conditions. The ability of otoliths to record these interdecadal trends highlights their role as environmental archives, and supports the premise that otolith chemistry is a powerful tool to investigate environmental histories. Further, because of temporal variation in both otolith $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, using these markers as natural tracers will require adjustments when examining samples spanning multiple decades.

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