

Annually resolved $\delta^{13}\text{C}_{\text{shell}}$ chronologies of long-lived bivalve mollusks (*Arctica islandica*) reveal oceanic carbon dynamics in the temperate North Atlantic during recent centuries

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ABSTRACT

The ability of the ocean to absorb carbon dioxide is likely to be adversely affected by recent climate change. However, relatively little is known about the spatiotemporal variability in the oceanic carbon cycle due to the lack of long-term, high-resolution dissolved inorganic carbon isotope ($\delta^{13}\text{C}_{\text{DIC}}$) data, especially for the temperate North Atlantic, which is the major oceanic sink for anthropogenic CO_2 . Here, we report shell carbon isotope values ($\delta^{13}\text{C}_{\text{shell}}$), a potential proxy for $\delta^{13}\text{C}_{\text{DIC}}$, of old-grown specimens of the long-lived bivalve mollusk, *Arctica islandica*. This paper presents the first absolutely dated, annually resolved $\delta^{13}\text{C}_{\text{shell}}$ record from surface waters of the North Atlantic (Iceland, Gulf of Maine) covering the time interval between 1753 and 2003. According to our results, the $\delta^{13}\text{C}_{\text{shell}}$ data were unaffected by trends related to ontogenetic age. However, the shell carbonate was precipitated with a constant offset from expected equilibrium by -1.54 to $-2.7 \pm 0.2\%$ corresponding to a 6.2 to $10.8 \pm 0.8\%$ contribution of respiratory CO_2 (-25%). The offset did not appear to vary through the lifetime of individual specimens and among specimens. Therefore, the $\delta^{13}\text{C}_{\text{shell}}$ data of this species can very likely be used as a measure of $\delta^{13}\text{C}_{\text{DIC}}$.

Furthermore, shell stable carbon isotope chronologies exhibited habitat-specific differences and a significant inter-annual and decadal variability related to the natural carbon cycle. In addition, a distinct negative $\delta^{13}\text{C}_{\text{shell}}$ shift was found reflecting the oceanic Suess effect, i.e. the admixture of anthropogenic CO_2 . However, this shift only occurred after the early 1920s when a major climate regime shift led to a northward movement of the oceanic Polar Front in the Nordic Seas and a large-scale reorganization of atmospheric and oceanic currents in the North Atlantic. This likely resulted in a reduced admixture of cold Polar water onto the North Icelandic shelf (through the East Iceland Current) and the Gulf of Maine (through the Labrador Current) with an increased volume of warmer, isotopically well-equilibrated Atlantic waters. Our shell-based $\delta^{13}\text{C}_{\text{DIC}}$ proxy record provides the basis to quantitatively assess natural and anthropogenically induced patterns of carbon uptake in the North Atlantic.

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1. Introduction

Approximately $118 \pm 19 \text{ Pg C}$ ($1 \text{ Pg C} = 10^{15} \text{ g C} = 1 \text{ Gt carbon}$), i.e. ca. 30% of the total carbon dioxide emitted to the atmosphere by human activity between 1800 and 1994 has been absorbed by the oceans (Sabine et al., 2004) in the form of dissolved inorganic carbon (DIC). Carbon dioxide (CO_2) resulting from the combustion of fossil energy sources, deforestation and changes in land use is depleted in

^{13}C (Tans, 1981). During the last 200 years the stable carbon isotope ratio of atmospheric CO_2 ($\delta^{13}\text{C}_{\text{atm}}$) has thus changed from values of ca. -6.3 to -8.1% (Friedli et al., 1986; Francey et al., 1999; Keeling et al., 2005). Furthermore, the admixture of anthropogenic CO_2 has led to a significant negative shift of the stable carbon isotope ratio of the oceanic DIC ($\delta^{13}\text{C}_{\text{DIC}}$) (Nozaki et al., 1978; Druffel and Benavides, 1986; Böhm et al., 1996; Swart et al., 1998; Lazareth et al., 2000; Moore et al., 2000; Böhm et al., 2002), also known as the oceanic Suess effect (Gruber et al., 1999). The rate of change of the $\delta^{13}\text{C}_{\text{DIC}}$ signature can be used to estimate the oceanic uptake rate of atmospheric CO_2 (Gruber et al., 2002; Quay et al., 2003, 2007). This uptake rate, however, underlies significant spatiotemporal variations which are poorly

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understood (Brix et al., 2004). Quantification of such fluctuations is fundamentally important for climate modeling, because changes in the strength of the oceanic carbon sink are inversely correlated to the CO₂ concentration in the atmosphere.

Existing studies on the inter-annual variability of the oceanic carbon inventory rely upon relatively short-term field observations of DIC and $\delta^{13}\text{C}_{\text{DIC}}$ starting in the late 1970s (Gruber et al., 2002). Such data are insufficient and far too brief to fully understand the nature of the oceanic carbon cycle either in terms of identifying the underlying processes impacting the preindustrial variability or in comprehending and predicting future changes under different climate forcings. While the stable carbon isotope data of corals and sclerosponges in particular have been employed to extend the $\delta^{13}\text{C}_{\text{DIC}}$ record in tropical settings beyond the instrumental era (Nozaki et al., 1978; Druffel and Benavides, 1986; Böhm et al., 1996; Swart et al., 1998; Lazareth et al., 2000; Moore et al., 2000; Böhm et al., 2002), very little is known from extratropical regions prior to direct measurements.

Stable carbon isotope data from shells ($\delta^{13}\text{C}_{\text{shell}}$) of the bivalve mollusk, *Arctica islandica*, can likely provide the missing information. This species is particularly suitable to reconstruct the oceanic carbon history for the following reasons.

- (1) The ocean quahog is the longest-lived (non-colonial) animal reaching live-spans of up to 374 or 407 years (Schöne et al., 2005a; Wanamaker et al., 2008a).
- (2) Annual growth interruptions result in the formation of distinct growth lines which provide an ideal means of precise calendar dating (Jones, 1980; Marchitto et al., 2000; Schöne et al., 2005b). In surface waters, growth line formation (= retardation of shell growth) in this species occurs during a time interval of about two months (September/October). It starts about a month after the seasonal temperature maximum has been attained. In deeper waters, maximum temperature only occurs in winter when the thermocline disrupts, and warm surface waters are mixed downward. Accordingly, annual growth lines of specimens living below the thermocline form between December and February (Schöne, 2008). It is currently assumed that growth line formation in *A. islandica* is triggered by spawning (Jones, 1980). Pre-mature specimens (i.e. before an age of 10 to 13; Thompson et al., 1980a; Rowell et al., 1990), however, also form annual growth lines at the exact same season of the year. According to Thompson et al. (1980b), juvenile *A. islandica* specimens mimic reproduction during pre-maturity.
- (3) Unlike many short-lived bivalves, *A. islandica* does not seem to exhibit age-related trends in $\delta^{13}\text{C}_{\text{shell}}$, but probably forms its shell with a constant offset from expected equilibrium with the DIC of the ambient water (Erlenkeuser, 1976; Schöne et al., 2005a).
- (4) Furthermore, *A. islandica* inhabits the entire northern North Atlantic (Nicol, 1951), i.e. the largest oceanic sink – relative to the size of this ocean – for atmospheric CO₂ (Gruber et al., 2002).

In the present study, we investigated the potential of $\delta^{13}\text{C}_{\text{shell}}$ chronologies of *A. islandica* as recorders of the $\delta^{13}\text{C}_{\text{DIC}}$ history of the temperate North Atlantic. Particular questions included: Are the $\delta^{13}\text{C}_{\text{shell}}$ time-series affected by vital effects? Are variations of the natural carbon cycle recorded in the shells? Is the long-term oceanic Suess effect preserved in the shell records of *A. islandica* as recently suggested by Butler et al. (2009), and does this trend differ from the $\delta^{13}\text{C}$ trend in tropical surface waters and the atmosphere in regard to timing and strength? Our results were contrasted to sclerosponge records (Böhm et al., 1996, 2002) from tropical settings, to atmospheric data and to sparsely available direct $\delta^{13}\text{C}_{\text{DIC}}$ measurements. Results of this study can provide an important building block toward a better understanding of spatiotemporal differences of the

ocean's capacity for absorbing anthropogenic CO₂ and to evaluating the potential consequences for future climate change and ecosystems.

2. Material and methods

Four shells of the ocean quahog, *A. islandica*, were collected alive by dredging from surface waters (ca. 30 m water depth) in the North Atlantic Ocean. Three specimens came from Icelandic waters, while one came from the Gulf of Maine (see Wanamaker et al., 2008b for complete details) (Fig. 1). Two of the Iceland shells ('Langanes 5' and 'Langanes 9'; live-collected in November 2003) lived offshore of Langanes (N66°16', W14°55.20'), northeastern Iceland, and were largely influenced by the cold East Iceland Current (EIC; Fig. 1). The third Iceland shell, however, grew in a biologically more productive nearshore environment near Flatey Island (ca. N66°11', W77°51'; live-collected in 1986), north Iceland, which is primarily controlled by the Irminger Current (IC), a warmer branch of the North Atlantic Current (NAC; Fig. 1). The Western Gulf of Maine shell (N43°39' 22.14", W69°48'6.01") was exposed to a mixture of the cold Labrador Current (LC) and relatively warm water masses derived from the Gulf Stream (Gatien, 1976; Wanamaker et al., 2008b). Selection of different localities and environmental settings enabled the identification of potential spatiotemporal incoherencies of the oceanic carbon sink and/or differences in the natural carbon cycle.

2.1. Shell preparation

In preparation for annual growth pattern and isotope analyses, one valve of each specimen was mounted on a plexiglass block and a quick-drying epoxy resin (JB KWIK-Weld) applied to the valve surface. Two immediately adjacent, three-millimeter-thick sections were cut from the valves along the height axis and perpendicular to the annual growth lines, with a Buehler Isomet 1000 low-speed precision saw using a 0.4 mm thick low concentration-diamond wafering blade (LC15). The shell slabs were subsequently mounted on

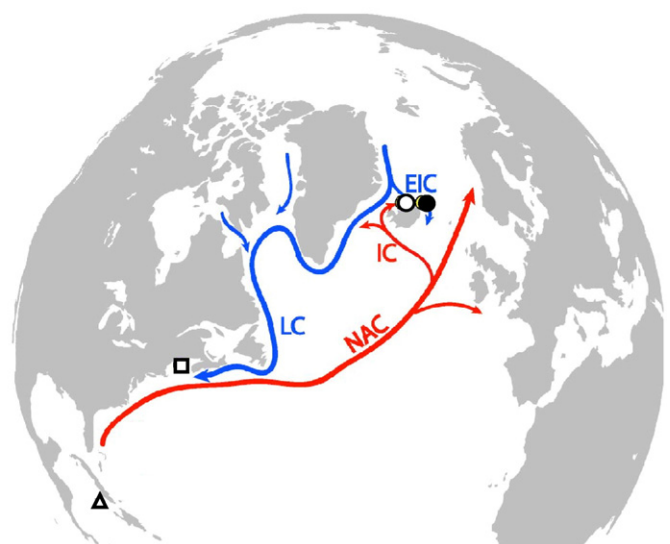


Fig. 1. Map showing major warm (NAC = North Atlantic Current; IC = Irminger Current) and cold (LC = Labrador Current; EIC = East Iceland Current) currents in the North Atlantic and sampling localities of the biogenic hard parts (bivalve shells and sclerosponges) that were used for analyses of stable carbon isotopes. The shell from Flatey (open circle) was exposed to stronger influence of the warm IC, a branch of the NAC, whereas the two specimens from Langanes (filled circle) and the shell from the Gulf of Maine (open square) received relatively larger amounts of cold water from the Polar region (LC, EIC). Tropical sclerosponge (Jamaica; open triangle) carbon isotope data (Böhm et al., 1996, 2002) were taken from the literature for comparison with the new bivalve record.

glass slides, ground with 800 and 1200 SiC grit powder and polished with 1 μm Al_2O_3 powder. Any adhering grinding powder was removed from the shell cross-sections by ultrasonic rinsing after each grinding and polishing step. All samples were then cleaned with 99.5% ethyl alcohol and air-dried.

2.2. Growth pattern analysis

In order to resolve annual growth patterns (Fig. 2) in the outer ostracal layer of the shells, one polished section of each specimen was treated with Mutvei's solution (Schöne et al., 2005c). After the dying process, the cross-sections were gently rinsed with de-ionized water and air-dried. Mutvei's solution simultaneously etches the shell and preserves and stains inter- and intracrystalline organics (i.e., chitin, mucopolysaccharides, and glucosamids; Schöne et al., 2005c). Annual growth lines are richer in organics and therefore stain dark blue and are more etch-resistant. In contrast, the growth increments between two consecutive growth lines are more strongly etched and appear light blue. To analyze shell growth patterns, digital images of the cross-sections were taken with a Nikon Coolpix 995 camera attached to a binocular microscope (Wild Heerbrugg M3Z). Annual growth increments were counted using the image analysis software Panopea (© Peinl & Schöne).

2.3. Stable isotope analysis

For determination of $\delta^{13}\text{C}_{\text{shell}}$ values, a total of 3532 powder samples were obtained from the shells. Following the shape of the microgrowth increments, CaCO_3 powder was milled from the outer shell layer (Fig. 2) under a stereomicroscope at 10 to 20 \times magnification (Schöne et al., 2005a). The cylindrical diamond drill bit measured 1 mm in diameter and was firmly mounted on a Rexim Minimo drill. The widths of the milling steps ranged between 20 and 300 μm in the direction of shell growth and represented ca. 1 to 45 weeks of growth. The shell from Flatey was sampled from age one onward, whereas sampling in specimens Langanes 5 and 9 started at ontogenetic ages 18 and 28, respectively, and sampling in the Gulf of Maine shell started at age 26. Each milling yielded approximately 40 to 120 μg of aragonite powder. These samples were analyzed with a Finnigan MAT 253 continuous-flow mass spectrometer equipped with a Gas Bench II. Stable carbon isotope values are reported relative to the Vienna Pee-Dee Belemnite

(VPDB) standard based on a NBS-19 calibrated Carrara marble value of +2.01‰. On average, replicated precision (1σ) was better than $\pm 0.03\text{‰}$. Annually averaged data are given in the Appendix A.

2.4. Spectral analysis

Comparison with other $\delta^{13}\text{C}$ records first required calculation of weighted annual $\delta^{13}\text{C}_{\text{shell}}$ averages (Schöne et al., 2004). Because the shell is not growing at the exact same rates throughout the year, each shell portion represents different amounts of time. The time-averaging of samples taken from fast growing shell portions is lower than that of slow-growing shell portions. Rather than arithmetically averaging $\delta^{13}\text{C}$ data, each sample was weighted based on seasonal shell growth data so that samples from fast growing periods of the year were underweighted relative to slower growing periods. All series were normally distributed.

In order to discover temporal dynamics in the shell stable carbon isotope chemistry, eigenmode filtering and reconstruction was applied to all $\delta^{13}\text{C}$ time-series. This enabled extraction of long-term trends and decadal oscillations, respectively. To retain long-term trends, the strongest oscillatory components (= trends), i.e. eigenmodes 1 and 2, were isolated. Conversely, these long-term trends were removed from the original time-series to study the decadal-scale variability by means of spectral analysis. Furthermore, the detrended chronologies were pre-whitened with first-order autoregressive (AR-1) modeling (Box and Jenkins, 1976). This approach removed lag-1 autocorrelation from the time-series. AR-1 coefficients (α) ranged from 0.10 (Langanes 9) to 0.58 (Langanes 5).

Then, continuous wavelet transformation was applied to the four $\delta^{13}\text{C}_{\text{shell}}$ chronologies (Fig. 4). In the present study we used a Morlet wavelet with wave number six ($\omega_0=6$). The continuous wavelet transform (CWT) resolves the localized frequency and intensity patterns of a signal, i.e. it can resolve if and how the strength of a signal changed over time; it can analyze intermittently stronger or weaker periods of the signal. 5% statistical significance levels were estimated by using the red noise background spectra (Torrence and Compo, 1998).

In order to identify high common spectral power, we followed Grinsted et al. (2004) and computed cross-wavelet transforms (XWTs) from sets of two CWTs (Fig. 5). 5% significance levels were again given against red noise. Relative phase relationships between CWTs (phase angle θ given in degree) are indicated by arrows and permit to

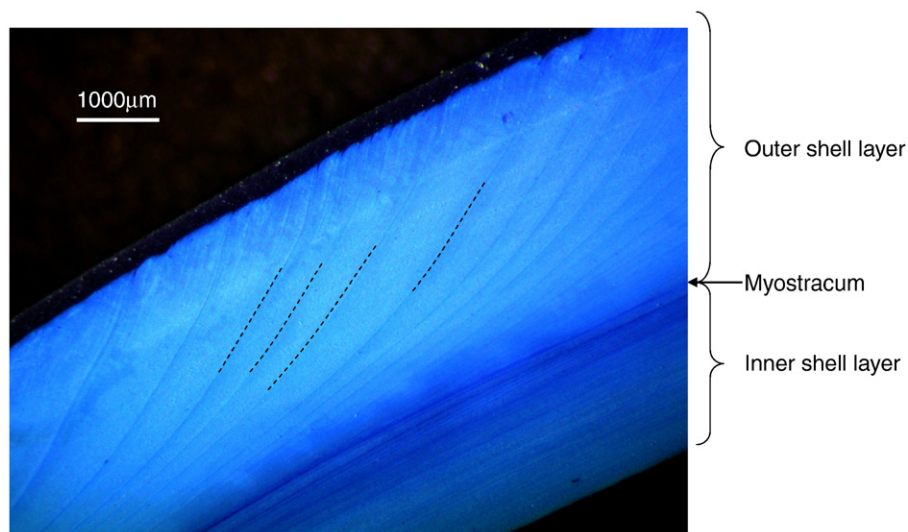


Fig. 2. Cross-section of an *Arctica islandica* shell ('Flatey' specimen, HM-Fla86-A1L ca. N66°11', W77°51'; live-collected in 1986, kindly provided by Harry Mutvei) treated with Mutvei's solution. Distinct annual growth lines (dashed lines) are easily discernible in the outer shell layer enabling precise calendar dating of each shell portion and of isotope samples taken from the shell. In surface waters, the growing season of this species is typically from November of the current through September of the next calendar year. Annual growth lines are formed during reproduction approximately four weeks after summer temperature maximum (Schöne, 2008). o = outer shell layer; i = inner shell layer.

recognize if the series were in-phase ($\theta = 0^\circ$) or anti-phase ($\theta = 180^\circ$) or if one series lead or lags the other ($\theta = 1$ to 179° and $\theta = -1$ to -179°) (Fig. 5). It should be noted that interpreting the phase angle in terms of lead or lag is difficult, because, for example, a lag of 90° equals a lead of 270° .

Finally, wavelet coherence (WTC) of the XWT in the time-frequency space was analyzed (Grinsted et al., 2004). This method compares well to traditional regression analyses and given values comparable to correlation coefficients (Fig. 6). Unlike XWT, WTC can find agreement between two CTWs even if the common power is low. Statistical significance test of WTC employed Monte Carlo techniques, i.e. based on the AR-1 coefficients of the $\delta^{13}\text{C}_{\text{shell}}$ chronologies an ensemble of 1000 surrogate data pairs was generated. Phase relationships between XWTs are indicated by arrows (Fig. 6).

2.5. Instrumental data

Annual $\delta^{13}\text{C}_{\text{atm}}$ data were assembled from direct meteorological observations (Keeling et al., 2005) and air inclusions in ice (Friedli et al., 1986; Francey et al., 1999). The $\delta^{13}\text{C}_{\text{DIC}}$ measurements were taken at different seasons from surface waters (3–12 m) of 45° – 59°N and 0° – 59°W (Keeling and Guenther, 1994) and cover the time interval between 1979 and 2001. An additional $\delta^{13}\text{C}_{\text{DIC}}$ measurement was completed on 17 August 2006 (5 p.m.) in Distillfjörður SW þórshöfn, southwestern tip of Langes peninsula ($N66^\circ11'22.26''$, $W15^\circ21'9.54''$) in ca. 15 m water depth. This $\delta^{13}\text{C}_{\text{DIC}}$ value ($+0.36\text{‰}$) was not depicted in Fig. 3.

3. Results

The four uninterrupted, annually resolved $\delta^{13}\text{C}_{\text{shell}}$ chronologies of *A. islandica* cover the time interval between AD 1753 and 2003 (Fig. 3A). Prior to 1887, only one shell record (Flatey) was available.

3.1. Offsets among $\delta^{13}\text{C}_{\text{shell}}$ curves

In comparison to the Langes and Gulf of Maine shells, the specimen from Flatey showed a strong enrichment in ^{13}C . Between 1889 and 1986, average $\delta^{13}\text{C}_{\text{shell}}$ values of the Flatey specimen (2.78‰) were 0.83 to 1.03‰ more positive than those of the three remaining specimens (Gulf of Maine = 1.75‰ ; Langes 5 = 1.95‰). Conversely, the average isotope records of the specimens from Langes and the Gulf of Maine deviated only by 0.2‰ from each other. According to the high-pass filtered data (Fig. 3B), however, even isotope records from specimens living in close distance (few tens of meters) from each other (Langes shells) did not perfectly match (see also Table 1).

3.2. Trends in the stable carbon isotope curves

Until the early 1920s, none of the shells showed a distinct and directed shift in their $\delta^{13}\text{C}_{\text{shell}}$ values (Fig. 3, Table 1). During the first 170 years of its life, the shell stable carbon isotope values of the Flatey specimen fluctuated around 3.1‰ , while the average $\delta^{13}\text{C}_{\text{shell}}$ values of the shells from Langes and the Gulf of Maine remained about 0.9 and 1.2‰ more negative, respectively (Fig. 3B). This is in sharp contrast to the $\delta^{13}\text{C}_{\text{atm}}$ values and carbon isotope records of tropical sclerosponges ($\delta^{13}\text{C}_{\text{sponge}}$) (Böhm et al., 1996, 2002) that both declined by ca. -0.003‰ yr^{-1} (-0.42‰ and -0.35‰ , respectively) between 1790 and 1920 (Fig. 3, Table 1). However, between ca. 1920 and 1986, $\delta^{13}\text{C}_{\text{shell}}$ values of all studied bivalves changed, on average, by about -0.010‰ yr^{-1} or -0.73‰ (Table 1). During the same time interval, $\delta^{13}\text{C}_{\text{atm}}$ values exhibited a more pronounced shift of -0.014‰ yr^{-1} (-0.95‰), whereas sclerosponges reflected a lower negative change of only -0.008‰ yr^{-1} (-0.53‰ ; Fig. 3B, Table 1).

Notably, shell and atmospheric stable carbon isotope values often decoupled from each other. For example, between 1920 and 1955, the

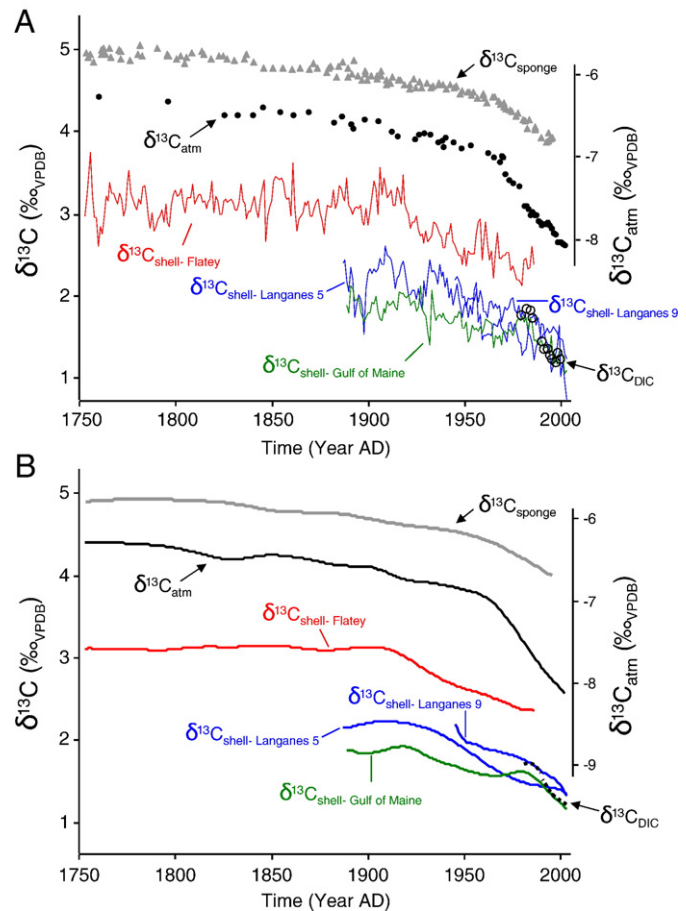


Fig. 3. Annual stable carbon isotope curves from instrumental records [atmospheric carbon dioxide (filled circles) (Friedli et al., 1986; Francey et al., 1999; Keeling et al., 2005); oceanic dissolved inorganic carbon (open circles) (Keeling and Guenther, 1994) between 45° and 59°N and 0° – 59°W and biogenic hard parts [bivalve shells from temperate North Atlantic; tropical sclerosponges (Böhm et al., 1996, 2002)]. (A) Declining values resemble the oceanic Suess effect and enrichment in ^{12}C . Shells of *Arctica islandica* are precipitated with a constant offset of ca. -1.54 to $-2.7 \pm 0.2\text{‰}$ from expected carbon isotope equilibrium. (B) After removal of high-frequency oscillations, the negative shift in stable carbon isotopes appears more distinct. Note the decoupled decline of the records. Atmospheric ($\delta^{13}\text{C}_{\text{atm}}$) and tropical sclerosponge carbon isotope values ($\delta^{13}\text{C}_{\text{sponge}}$) show a negative shift after the late 18th century to present, whereas bivalve data ($\delta^{13}\text{C}_{\text{shell}}$) only decreased after the early 1920s concurrent with a major regime shift in North Atlantic climate. Decline of $\delta^{13}\text{C}_{\text{shell}}$ during 1920–1955 is more severe than that of $\delta^{13}\text{C}_{\text{atm}}$ and $\delta^{13}\text{C}_{\text{sponge}}$ reflecting increased influence of warm Atlantic waters in Nordic Seas. Right y-axis is for $\delta^{13}\text{C}_{\text{atm}}$ values, left y-axis for all other isotope data. Shorter record from 'Langes' is from specimen "Langes 9", longer record from specimen "Langes 5".

$\delta^{13}\text{C}_{\text{shell}}$ values of the specimen from Flatey dropped by -0.43‰ (-0.012‰ yr^{-1}), i.e. nearly three times as fast as atmospheric values (-0.16‰ or -0.004‰ yr^{-1}) or tropical sclerosponge records (-0.15‰ or -0.004‰ yr^{-1} ; Fig. 3B, Table 1). During the same time interval, shells from Langes and the Gulf of Maine decreased, on average, by -0.010‰ yr^{-1} or -0.36‰ (Fig. 3B, Table 1). Conversely, atmospheric and sclerosponge $\delta^{13}\text{C}$ values shifted by ca. -0.88‰ and -0.41‰ (-0.028‰ yr^{-1} and -0.013‰ yr^{-1}), respectively, between 1960 and 1990, whereas only a -0.27‰ (-0.009‰ yr^{-1}) change was observed in the Iceland shells. In the Gulf of Maine, these changes were even smaller: -0.12‰ or -0.004‰ yr^{-1} (Fig. 3B, Table 1).

3.3. DIC and skeletal $\delta^{13}\text{C}$ values

Oceanic $\delta^{13}\text{C}_{\text{DIC}}$ values of the northern North Atlantic stretching over multiple consecutive years were only available for 1979–2001

Table 1

Comparison of stable carbon isotope ($\delta^{13}\text{C}$) data from instrumental records [atmospheric CO_2 (Friedli et al., 1986; Francey et al., 1999; Keeling et al., 2005), oceanic dissolved inorganic carbon, DIC (Keeling and Guenther, 1994)] and biogenic hard parts [sclerosponges (Böhm et al., 1996, 2002); bivalves]. For original values see Supplementary information.

Data set	Inter-annual (‰yr^{-1}) and long-term $\delta^{13}\text{C}$ change (‰)				Average inter-annual $\delta^{13}\text{C}$ variability ^a (‰)	Average $\delta^{13}\text{C}$ (‰)	
	1790–1920	1920–1955	1920–1986	1960–1990		1979–1986	1979–1999
Atmospheric CO_2	–0.0032 –0.42	–0.004 –0.16	–0.014 –0.95	–0.028 –0.88	0.013 \pm 0.020	–7.56	–7.77
Oceanic DIC					0.047 \pm 0.031	1.79	1.52
Sclerosponges	–0.0027 –0.35	–0.004 –0.15	–0.008 –0.53	–0.013 –0.41	0.024 \pm 0.025	4.12	4.05
Bivalves							
Flatey	–0.0007 –0.09	–0.012 –0.43	–0.010 –0.66	–0.008 –0.23	0.134 \pm 0.120	2.37	
Langanes 9			(–0.012)	–0.009 –0.29	0.078 \pm 0.055	1.74	1.64
Langanes 5	(0.0018)	–0.011 –0.39	–0.011 –0.76	–0.010 –0.30	0.132 \pm 0.111	1.47	1.44
Gulf of Maine	(0.0016)	–0.009 –0.32	–0.006 –0.37	–0.004 –0.12	0.089 \pm 0.093	1.60	1.47

Values in parentheses represent average values over shorter time interval than given in header of column. Prior to calculation of inter-annual and long-term changes, high-frequency oscillation was removed.

^a Errors given in standard deviations (1σ).

(Fig. 3A) (Keeling and Guenther, 1994). During this time interval, the carbon isotope chemistry shifted by about -0.032‰yr^{-1} . Remarkably, the average $\delta^{13}\text{C}_{\text{DIC}}$ (1979–1999: 1.52‰; 1979–1986: 1.79‰) and contemporary $\delta^{13}\text{C}_{\text{shell}}$ values (average of Langanes and Gulf of Maine shells; 1979–1999: 1.50‰; 1979–1986: 1.60‰) were nearly identical (Fig. 3; Table 1). The specimen from Flatey, however, was 0.58‰ (1979–1986) more positive than the average observed $\delta^{13}\text{C}_{\text{DIC}}$ value. An even stronger positive offset of 2.33‰ (1979–1986) and 2.53‰ (1979–1999) from oceanic $\delta^{13}\text{C}_{\text{DIC}}$ data from Keeling and Guenther (1994) was observed in the case of sclerosponges (Fig. 3B, Table 1).

A water sample taken in Distillfjörður, Langanes peninsula in August 2006 returned a $\delta^{13}\text{C}_{\text{DIC}}$ value of 0.36‰, i.e. ca. 1 per mil more negative than the 1999 value (1.22‰) from dataset by Keeling and Guenther (1994).

3.4. Inter-annual and decadal $\delta^{13}\text{C}$ variability

Other than the atmospheric, oceanic and sclerosponge carbon isotope chronologies, the $\delta^{13}\text{C}_{\text{shell}}$ time-series exhibited a distinct inter-annual variability of up to 0.76‰ (Fig. 3A). Average year-to-year $\delta^{13}\text{C}$ changes ranged from 0.08 to 0.13‰ in the case of bivalves, but were as small as 0.05 and 0.01‰ in the case of oceanic and atmospheric carbon isotope values, respectively (Fig. 3A, Table 1). Temporal resolution of the $\delta^{13}\text{C}_{\text{sponge}}$ data was not sufficient to compute inter-annual variability.

Furthermore, CTWs revealed lower-frequency variations in the $\delta^{13}\text{C}_{\text{shell}}$ chronologies (Fig. 4). Significant spectral power occurred at frequencies corresponding to periods of 2–3, 4–6, 7–12, 14–16 and 25–31 years (Fig. 4). However, not all of these spectral densities reached statistical significance in each of the studied $\delta^{13}\text{C}_{\text{shell}}$ chronologies. For example, the 7–9 year band was only weakly developed in the Flatey time-series series, but stronger in the specimens from the Gulf of Maine and Langanes.

Common spectral features observed by visual comparison of the CWTs were confirmed by cross-wavelet and wavelet coherence spectra (Figs. 5 and 6). However, not all significant common spectral power was phase-locked. For example, 2–3 year oscillations occurred in all four chronologies, but showed only in-phase behavior between 1955 and 1965. Significant common spectral power in the 7–12 year band was in-phase among the Langanes time-series, but in anti-phase (i.e., ~3 to 6 years shifted) or slightly out-of-phase between Langanes and the Gulf of Maine. 15–16-year and 25–31-year periods were in-phase among all chronologies from Iceland, but the Gulf of Maine

specimen was leading the three Icelandic specimens by 90° (i.e., ~4 and 6–8 years).

Because of poor temporal resolution, such variations and phase relationships were difficult to detect in either the sclerosponge, oceanic DIC or the atmospheric carbon isotope curves.

4. Discussion

According to numerous previous studies the stable carbon isotope values of bivalve shells (species without photosymbionts) are affected by vital effects and exhibit strong ontogenetic trends which limits their use for $\delta^{13}\text{C}_{\text{DIC}}$ reconstructions: With increasing ontogenetic age the amount of respiratory CO_2 increases and drives the $\delta^{13}\text{C}_{\text{shell}}$ values toward the negative end (e.g., Jones et al., 1983; Tanaka et al., 1986; Krantz et al., 1987; Barrera et al., 1994; Elliot et al., 2003; Lorrain et al., 2004; Gillikin et al., 2006). On the contrary, Gillikin et al. (2005) found a slightly positive $\delta^{13}\text{C}_{\text{shell}}$ trend through ontogeny in *Saxidomus gigantea*. Likewise, Brey and Mackensen (1997) reported a trend toward more positive $\delta^{13}\text{C}_{\text{shell}}$ values with increasing ontogenetic age in a 15-year-old shell of *Laternula elliptica*. Notably, conclusions on directed $\delta^{13}\text{C}_{\text{shell}}$ shifts through lifetime were predominantly drawn from relatively short-lived bivalves (see references above) or from the youth portions of long-lived species (Foster et al., 2009). How was it assured that the alleged ontogenetic trends observed over a time interval of five, ten or twenty years were not actually – at least in part – influenced by environmental forcings, which remained unexamined and fluctuated on decadal time scales? For example, Foster et al. (2009) attributed a negative $\delta^{13}\text{C}_{\text{shell}}$ shift¹ within the last nine years of a 21-year-old *A. islandica* as a “strong ontogenetic effect” without considering that this bivalve lived in a habitat which is greatly influenced by the North Atlantic Oscillation (NAO) and associated decadal-scale biogeochemical cycles (Hurrell and van Loon, 1997; Kröncke et al., 2001). For example, during positive NAO years, primary productivity increases and $\delta^{13}\text{C}_{\text{DIC}}$ values in surface waters should become more positive.

Results of the present study provide strong evidence against ontogenetic age-related shifts of the $\delta^{13}\text{C}_{\text{shell}}$ values in *A. islandica*. Samples were taken at subannual resolution (~1 to 45 weeks per

¹ Foster et al. (2009) claim that stable isotope measurements were done on shell material obtained from the prismatic layer. However, the outer shell layer of the ocean quahog consists almost exclusively of cross-acicular crystal fabrics. Only the annual growth lines consist of irregular simple prisms (Ropes et al., 1984; Schöne et al., 2010).

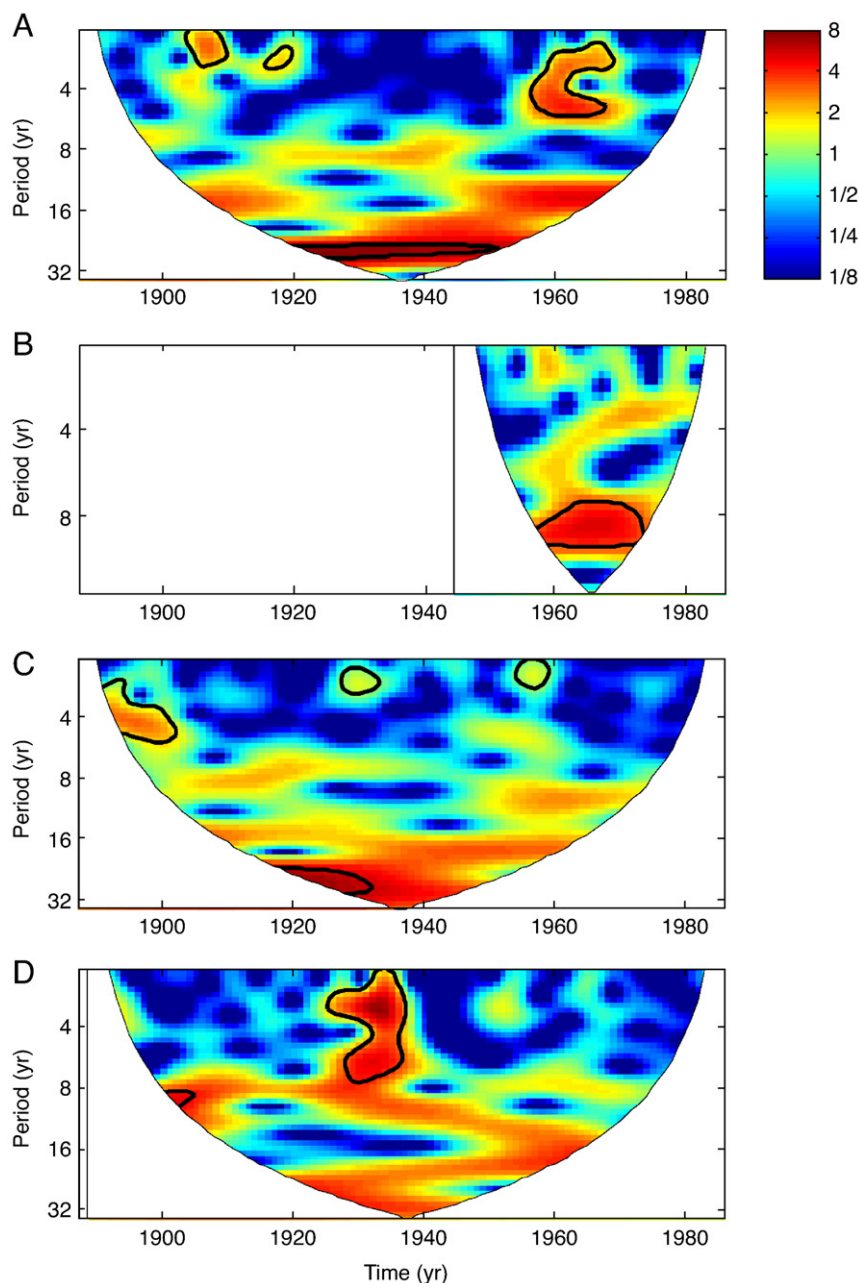


Fig. 4. Continuous wavelet power spectra of the pre-whitened and standardized $\delta^{13}\text{C}_{\text{shell}}$ time-series (A = Flatey; B = Langes 9; C = Langes 5; D = Gulf of Maine). For comparison with one another, only the time interval between 1887 and 1986 was spectrally analyzed. Low-frequency trend caused by oceanic Suess effect was removed prior to the analysis. Zero padding has been applied to reduce the variance. Legend indicates relative power units. Black contour within cone of influence (portion outside cone is not shown because these may be distorted by edge effects) is the 5% significance level, using a red noise (autoregressive lag1) background spectrum. Diagrams were produced with Matlab routine provided by Grinsted et al. (2004). Note common power occurred at periods of 2–3, 4–6, 7–12, 14–16 and 25–31 years. However these spectral densities did not reach statistical significance in all specimens.

sample) across four old-grown specimens. Through this it has been possible to construct the first, precisely (absolutely) dated, annually resolved, multi-century $\delta^{13}\text{C}_{\text{DIC}}$ record of extratropical settings. As will be demonstrated below, our data indicate that it will be possible to reconstruct the oceanic Suess effect and decadal-scale, natural biogeochemical dynamics in the $\delta^{13}\text{C}_{\text{DIC}}$.

4.1. $\delta^{13}\text{C}_{\text{shell}}$ data and vital effects: no ontogenetic trend, but constant metabolic offset

According to Fig. 3, the $\delta^{13}\text{C}_{\text{shell}}$ chronologies of *A. islandica* did not exhibit trends related to ontogenetic age and associated changes in the amount of respired CO_2 used to build the shell carbonate.

Although the bivalves studied here started growing at different times during the last 250 years and were of different ontogenetic age, all $\delta^{13}\text{C}_{\text{shell}}$ curves showed an abrupt and synchronous negative shift during the early 1920s (Fig. 3). Prior to that time, the curves fluctuated around a long-term mean without exhibiting any directed change (Table 1). In the extreme case of the specimen from Flatey, carbon isotope values remained nearly unchanged during the first 170 years of its life. These observations support previous findings (Schöne et al., 2005a) suggesting that $\delta^{13}\text{C}_{\text{shell}}$ values of *A. islandica* were unaffected by ontogenetic age (also see Butler et al., 2011–this issue).

Although no age-related $\delta^{13}\text{C}_{\text{shell}}$ trends were observed, shells of the ocean quahog were most likely precipitated with a constant offset

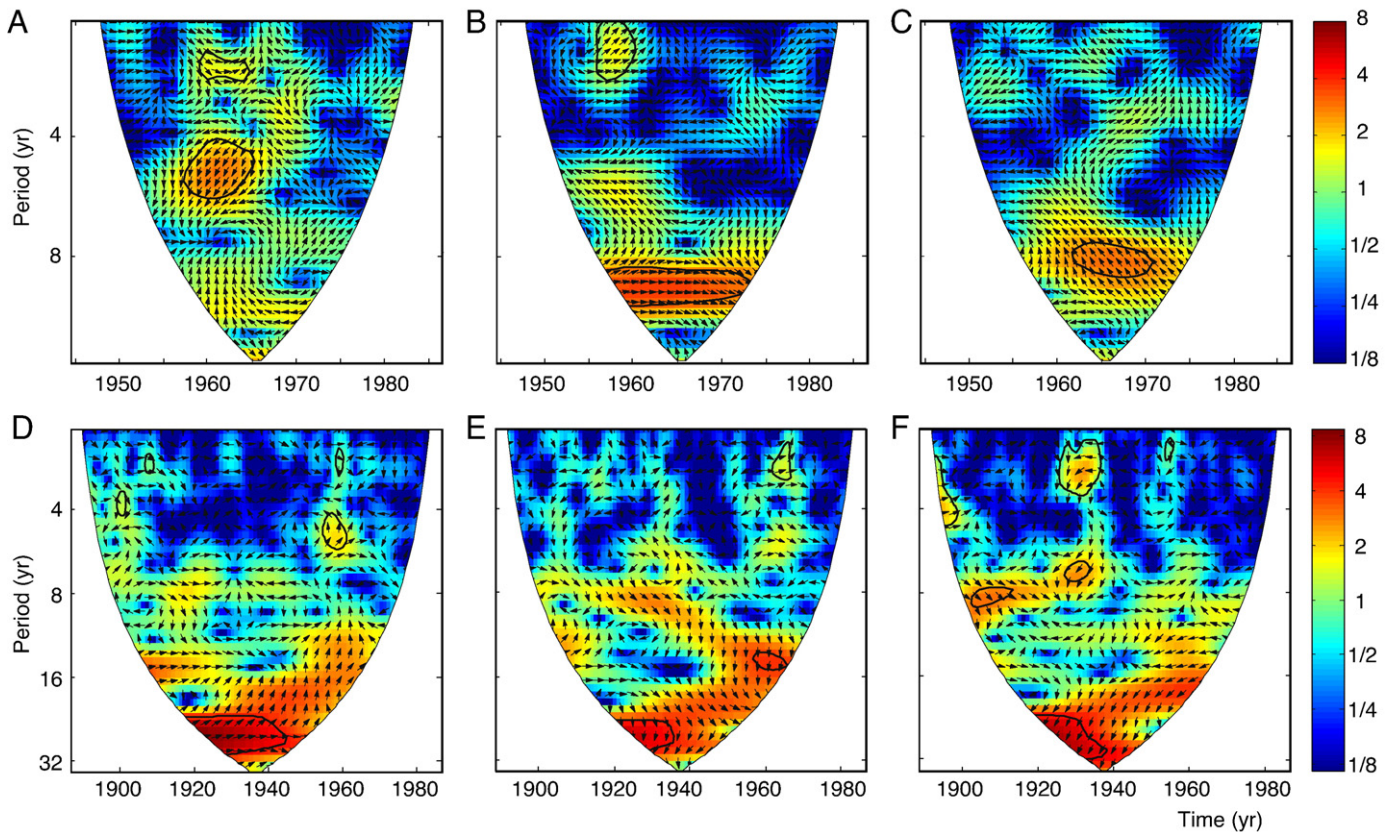


Fig. 5. Cross-wavelet power spectra of the pre-whitened and standardized $\delta^{13}\text{C}_{\text{shell}}$ time-series (A = Flatey vs. Langanes 9; B = Langanes 9 vs. Langanes 5; C = Langanes 9 vs. Gulf of Maine; D = Flatey vs. Langanes 5; E = Flatey vs. Gulf of Maine; F = Langanes 5 vs. Gulf of Maine). Low-frequency trend caused by oceanic Suess effect was removed prior to the analysis. Legend indicates relative power units. The 5% significance level against red noise is shown as a thick contour. Relative phase relationships are depicted as arrows (in-phase pointing right; anti-phase pointing left; any other direct = out-of-phase). Diagrams were produced with Matlab routine provided by Grinsted et al. (2004). Note that not all significant spectral power was phase-locked. For example, the 7–12 year band was in-phase among the Langanes time-series, but in anti-phase (i.e., ~3 to 6 years shifted) or slightly out-of-phase between Langanes and the Gulf of Maine.

from expected equilibrium with the $\delta^{13}\text{C}_{\text{DIC}}$ values of the ambient water. This offset likely remained nearly unchanged over lifetime. Between 1979 and 1999, average $\delta^{13}\text{C}_{\text{shell}}$ values (Langanes and Gulf of Maine) were nearly identical to the $\delta^{13}\text{C}_{\text{DIC}}$ values (1.52‰; Table 1). Taking the fractionation factor ε between aragonite and HCO_3^- of $2.7 \pm 0.2\%$ into account (Romanek et al., 1992), *A. islandica* formed its shell $-2.7 \pm 0.2\%$ away from isotopic equilibrium with the ambient DIC pool. Assuming a $\delta^{13}\text{C}$ value of -25% , which is typical for soft tissues of marine bivalve mollusks (McConnaughey et al., 1997) and close to values of the potential food source, i.e. particulate organic matter, POM (Goericke and Fry, 1994), this offset translates into a contribution of respiratory CO_2 to the shell carbonate of about $10.8 \pm 0.8\%$, a value that is in good agreement with previous observations (Gillikin et al., 2006; McConnaughey and Gillikin, 2008).

Available instrumental $\delta^{13}\text{C}_{\text{DIC}}$ measurements from the North Atlantic may be not representative of the actual $\delta^{13}\text{C}_{\text{DIC}}$ signature at the localities where the bivalves lived. For example, the single value from the southwestern tip of Langanes suggests that these waters were nearly 1.2‰ more negative than the basin-wide average. If the local Langanes $\delta^{13}\text{C}_{\text{DIC}}$ value of 0.36‰ is used, the (Icelandic) shells would only have formed $-1.54 \pm 0.2\%$ away from the expected isotopic equilibrium, and the contribution of metabolic carbon to the biomineral would decrease to ca. $6.2 \pm 0.8\%$. Note that this figure is a minimum estimate, because due to the oceanic Suess effect (see below) the average $\delta^{13}\text{C}_{\text{DIC}}$ value during 1979–1999 at Langanes was most likely slightly more positive than in 2006.

In summary, the $\delta^{13}\text{C}_{\text{shell}}$ values of *A. islandica* provide a measure of oceanic $\delta^{13}\text{C}_{\text{DIC}}$ values. However, this relationship is not a one-to-one

relationship, because of a metabolic offset which does not appear to change through lifetime.

4.2. Habitat-specific $\delta^{13}\text{C}_{\text{shell}}$ records

The $\delta^{13}\text{C}_{\text{shell}}$ curves of specimens from different localities were parallel offset from one another (Fig. 3A, Table 1). It appears unlikely that these differences were caused by individual differences in the (ontogenetically unchanged) metabolic CO_2 contribution to the shell carbonate, because shells that lived in close proximity (Langanes shells) were more similar to each other in respect to carbon isotope values than shells from different settings (specimens from the Gulf of Maine and Flatey). We rather assume that differences in the local isotope signature (background $\delta^{13}\text{C}_{\text{DIC}}$ value) of the water caused the observed $\delta^{13}\text{C}_{\text{shell}}$ variability, e.g. differences in the biological activity and remineralization of organic matter, riverine influx (depleted in ^{13}C), as well as vertical mixing of the water column. For example, elevated primary productivity results in more positive $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{shell}}$ values, whereas oxidation of organic material causes the opposite. The Flatey specimen lived in a highly productive nearshore environment. Therefore, the ambient water was probably enriched in ^{13}C which resulted in more positive $\delta^{13}\text{C}_{\text{shell}}$ values than the remaining specimens. In addition, specimens living at different sites (even the two bivalves from Langanes) may have eaten isotopically slightly different food. Note that the figure of -25% for soft tissue and POM given above is only an average value and can change by as much as 5% (Goericke and Fry, 1994). Further studies are, however, required to confirm our interpretation that individual differences in respiratory

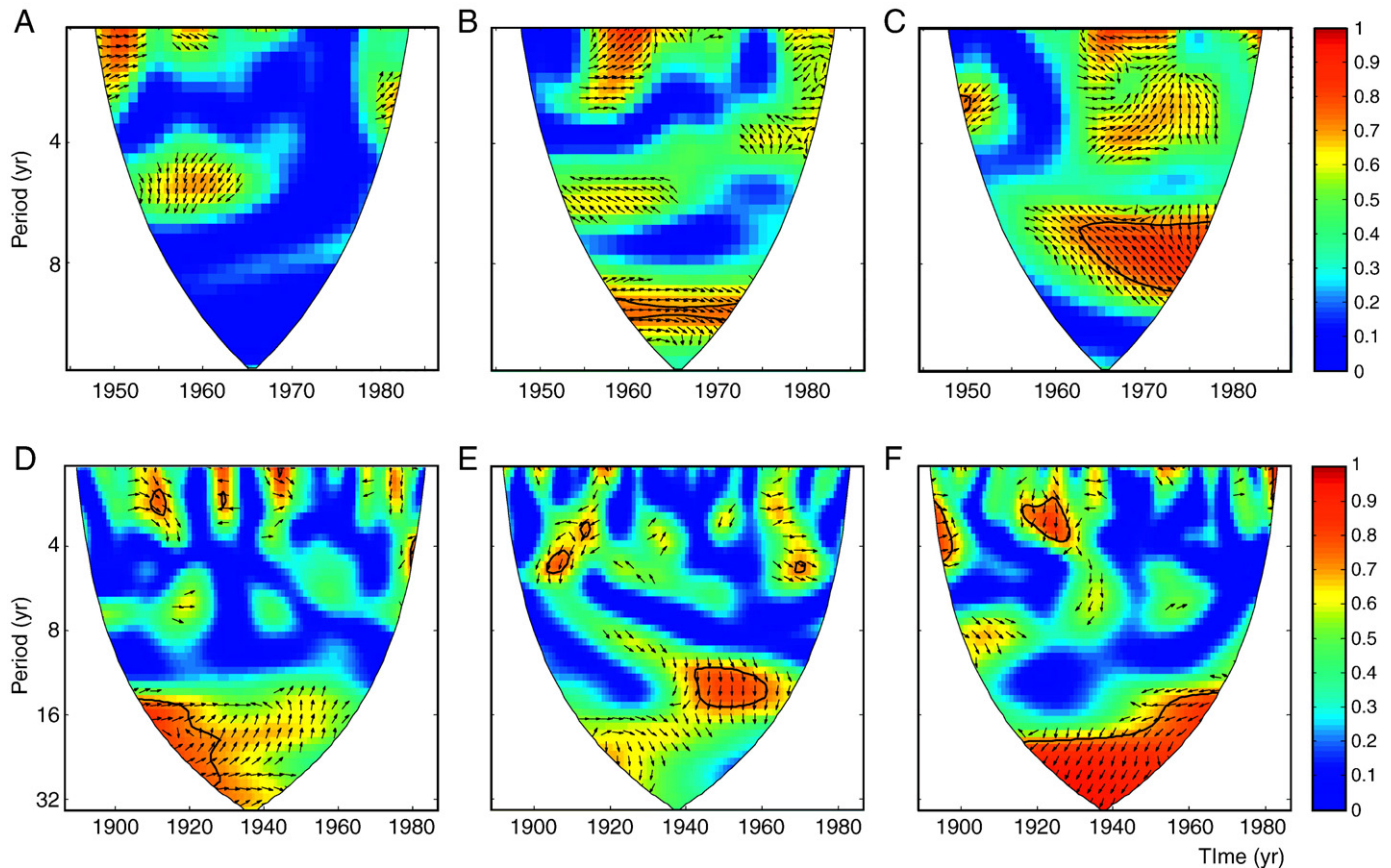


Fig. 6. Squared wavelet coherence spectra of the pre-whitened and standardized $\delta^{13}\text{C}_{\text{shell}}$ time-series (A = Flatey vs. Langanes 9; B = Langanes 9 vs. Langanes 5; C = Langanes 9 vs. Gulf of Maine; D = Flatey vs. Langanes 5; E = Flatey vs. Gulf of Maine; F = Langanes 5 vs. Gulf of Maine). Low-frequency trend caused by oceanic Suess effect was removed prior to the analysis. Legend indicates coherence between series, similar to read as correlation coefficient (0 = no coherence; 1 = strong coherence). The 5% significance level against red noise is shown as a thick contour. Relative phase relationships are depicted as arrows (in-phase pointing right; anti-phase pointing left; any other direct = out-of-phase). Diagrams were produced with Matlab routine provided by Grinsted et al. (2004).

CO_2 incorporation into the shell carbonate of the ocean quahog are negligibly small.

4.3. Inter-annual variability of the $\delta^{13}\text{C}_{\text{shell}}$ record

Microenvironmental differences between the coastal settings in which the bivalves lived may also have caused the lack of a strong year-to-year running similarity between the four $\delta^{13}\text{C}_{\text{shell}}$ time-series (Fig. 3A). At each locality, primary productivity, remineralization of organic matter, temperature and salinity underlie perpetual changes.

Furthermore, the inter-annual variability of the carbon isotope ratios from bivalve shells was significantly larger than that of sclerosponges, oceanic DIC or the atmosphere (Fig. 3A). We attribute this finding to a significantly improved temporal resolution of the shell time-series compared with existing instrumental or proxy DIC records. Currently available instrumental $\delta^{13}\text{C}_{\text{DIC}}$ data are snapshot measurements and in fact, the seasonal variability of $\delta^{13}\text{C}_{\text{DIC}}$ can be up to 1‰ in higher latitudes (Tanaka et al., 2003). Averages of instrumental snapshots may represent the annual average. In the case of sclerosponges, year-to-year variations of carbon isotope ratios are attenuated by time-averaging issues. The lack of annual bandings precludes precise temporal control during sampling as well as calendar dating of individual samples. These samples are highly time-averaged and the time represented by each sample remains unknown (Schöne et al., 2004).

4.4. Decadal-scale variability of the $\delta^{13}\text{C}_{\text{shell}}$ record

Aside from year-to-year fluctuations, the shell stable carbon isotope curves revealed statistically significant decadal variability.

Common low-frequency $\delta^{13}\text{C}_{\text{shell}}$ oscillations among specimens from the same site or even among all specimens (Figs. 4–6) suggest external forcings of the carbon isotope ratios, for example by the NAO (6–10 years, reduced power at 3 and 10–20 years; Hurrell and van Loon, 1997) and large-scale lower-frequency fluctuations (e.g., 12–16 years) of sea surface temperature in the North Atlantic (Deser and Blackmon, 1993). These climate oscillations may exert a direct control over primary productivity, air–sea exchange, precipitation (riverine influx) and fractionation between DIC and atmospheric CO_2 .

However, the observed periodic variations were not always phase-locked among the studied shells (Figs. 5 and 6). For example, the 7–12, 15–16 and 25–31-year periods were mainly in-phase among specimens from Iceland (Langanes shells or Langanes + Flatey shells, respectively), but strongly out-of-phase between the specimens from Iceland and the Gulf of Maine. These phase shifts probably reflect the propagation of climate signals across the North Atlantic. Following Sutton and Allen (1997) it may take up to nine years for a signal to travel from the equator to Iceland. In turn, carbon isotope signals of the polar water may arrive at the Gulf of Maine with a significant time lag (compare Fig. 1).

4.5. Oceanic Suess effect recorded by $\delta^{13}\text{C}_{\text{shell}}$

A recent study by Butler et al. (2009) suggested that stable carbon isotope values of the long-lived *A. islandica* may provide a potential means to estimate the oceanic Suess effect. However, their interpretation was based on 37, strongly time-averaged isotope data (with a precision error of $\pm 0.14\%$) covering the last four centuries.

Furthermore, their time-series was based on one ventral margin sample per shell which exacerbated the recognition of potential ontogenetic trends. Results of the present study, however, provided strong support for the findings by Butler et al. (2009). All four $\delta^{13}\text{C}_{\text{shell}}$ time-series exhibited a nearly synchronous negative shift starting around the early 1920s. On average, the magnitude of this $\delta^{13}\text{C}_{\text{shell}}$ shift (-0.71‰) was slightly lower than the decline of atmospheric stable carbon isotope values (-0.95‰), but slightly higher than $\delta^{13}\text{C}_{\text{sponge}}$ values from the tropics (-0.53‰) during the same time interval. The stronger observed 1920 to 1986 isotope shift in the bivalve shells compared to the Caribbean sclerosponge may reflect local conditions, e.g. enhanced isotopic equilibration of the surface water with the atmosphere by stronger wave agitation or climatically forced increase in riverine influx. River water tends to have a more negative carbon isotope signature than the ocean (e.g., Mook and Tan, 1991).

According to the findings of this study, however, the obvious effects of the oceanic Suess effect in extratropical settings of the North Atlantic started more than a century later than in the tropics (Fig. 3). As reflected by declining $\delta^{13}\text{C}_{\text{sponge}}$ values (Böhm et al., 1996, 2002), tropical oceans began absorbing anthropogenic CO_2 almost contemporaneously (Körtzinger et al., 2003) with the starting of the industrialization during the late 18th century and the associated $\delta^{13}\text{C}_{\text{atm}}$ decline (Fig. 3), whereas the $\delta^{13}\text{C}_{\text{shell}}$ values of *A. islandica*, commenced declining only after the 1920s (Fig. 3). This discrepancy can likely be explained by a major regime shift in the North Atlantic (Drinkwater, 2006) at around that time. This regime shift involved a large-scale reorganization of the major wind fields in the North Atlantic sector during which the Westerlies apparently weakened (Rogers, 1985; Meeker and Mayewski, 2002). Furthermore, high-resolution alkenone data from a sediment core taken north of Iceland (near Flatey) indicate a northward retreat of a major water mass boundary, known as the Polar Front, ca. AD 1900 (Sicre et al., 2008). The movement of the Polar Front during the 1920s probably resulted in a reduced admixture of cold Polar water onto the North Icelandic shelf (through the East Iceland Current) and the Gulf of Maine (through the Labrador Current) with an increased volume of warmer Atlantic waters. Because of its long transit time through the North Atlantic gyre, the warmer Atlantic waters (Fig. 1) are isotopically ($\delta^{13}\text{C}$) well-equilibrated with the atmosphere.² On the contrary, polar and arctic waters were only shortly in contact with the atmosphere and may have been temporarily been covered by sea ice. Consequently, these waters are isotopically less well-equilibrated with the atmosphere and typically exhibit a strongly reduced Suess effect (Olsen et al., 2006). The dominance of the arctic and polar waters prior to the 1920s at the sites where the studied bivalves lived likely explains the absence of a measurable negative shift in the shell carbon isotope records.

4.6. $\delta^{13}\text{C}_{\text{shell}}$ values as a measure for oceanic uptake rate of anthropogenic CO_2 ?

Although long-term trends and decadal variability in the carbon chemistry of the ocean can be recognized in the $\delta^{13}\text{C}_{\text{shell}}$ data, it appears unlikely that the studied shells are suitable to estimate changes in the oceanic uptake rate of atmospheric carbon dioxide. This is largely because $\delta^{13}\text{C}_{\text{DIC}}$ signature of the surface water does not immediately respond to changes in the CO_2 absorption by the surface ocean. Whereas the equilibration time of CO_2 between the atmosphere and the surface water is about eight months, the carbon isotopic equilibration takes ca. ten times longer (Broecker and Peng,

1982). Therefore, most open ocean surface waters are close to equilibrium with respect to atmospheric CO_2 . However, only surface waters that have been in contact with the atmosphere for eight years or more exhibit nearly the same isotopic composition of the water (as it has been a decade earlier). In order to estimate the uptake rate of anthropogenic CO_2 by the ocean, bivalves that lived below the thermocline would provide significantly better results. In addition, surface water $\delta^{13}\text{C}_{\text{DIC}}$ values are affected by a variety of local and regional effects such as variable riverine influx, changes in primary productivity, remineralization of organic matter, wave movement, changing ocean currents etc.

5. Summary and conclusions

In this study, we demonstrated that $\delta^{13}\text{C}_{\text{shell}}$ values of the ocean quahog, *A. islandica* provide a measure of the $\delta^{13}\text{C}_{\text{DIC}}$ history (although a rigorous calibration is still required) which can potentially be used to estimate changes of the strength of the oceanic CO_2 sink. Previous assumptions regarding this link were based solely upon short-term observational $\delta^{13}\text{C}_{\text{DIC}}$ records (Gruber et al., 2002). The main findings of our study are as follows.

- (1) The shell stable carbon isotope signature of the long-lived ocean quahog is not affected by ontogenetic age-related changes. However, ca. 6.2 to $10.8 \pm 0.8\%$ of shell carbonate is derived from respiratory CO_2 . Yet, the amount of metabolic carbon incorporated into the shell does not seem to change significantly over lifetime and does not seem to differ significantly among different specimens. Further studies are required to corroborate this assumption and quantify the variability among specimens.
- (2) Shell stable carbon isotope values of specimens from different localities varied by up to ca. 1‰ . This finding is attributed to differences in the local background $\delta^{13}\text{C}_{\text{DIC}}$ signature.
- (3) Due to perpetual changes of the primary productivity, remineralization of organic matter, temperature and riverine influx the annually resolved $\delta^{13}\text{C}_{\text{shell}}$ chronologies exhibited considerable inter-annual and decadal-scale variability.
- (4) The oceanic Suess effect was clearly developed in all studied shells. However, the strong negative shift did not occur before the 1920s. During that time interval major atmospheric and hydrographic changes increased the dominance of isotopically well-equilibrated, subtropical waters at the localities where the bivalves dwelled.

Further studies should assemble $\delta^{13}\text{C}_{\text{shell}}$ chronologies of *A. islandica* from subsurface waters. Such records can potentially reveal how climate change impacts the capability of the ocean to absorb anthropogenic CO_2 . In addition, a rigorous calibration study is required to quantify the metabolic offset of the $\delta^{13}\text{C}_{\text{shell}}$ values and confirm that this offset truly remains invariant through lifetime.

Acknowledgements

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Appendix A

Summary of instrumental and proxy stable carbon isotope data (‰VPDB). Data were annually averaged, weighted averages in the case of bivalves. Atmospheric data were assembled from air inclusions in

² It should be noted that isotopic equilibration between the atmosphere and surface water takes about eight years (Broecker and Peng, 1982).

firn ice and measured CO₂ at Hawaii (Friedli et al., 1986; Francey et al., 1999; Keeling et al., 2005). DIC values came from the temperate North Atlantic (Keeling and Guenther, 1994). Caribbean (Jamaica) sclerosponge record consists of averages of two transects of a specimen from Montego Bay and one transect of a specimen from Rio Bueno (Böhm et al., 1996, 2002).

Year AD ↓	$\delta^{13}\text{C}_{\text{atm}}$	$\delta^{13}\text{C}_{\text{DIC}}$	$\delta^{13}\text{C}_{\text{sponge}}$	$\delta^{13}\text{C}_{\text{shell}}$			
Locality →	Hawaii	N Atlantic	Jamaica	Flatey	Langanes 9	Langanes 5	Gulf of Maine
1753			4.97	2.98			
1754			4.91	3.21			
1755			4.94	3.51			
1756				3.75			
1757			4.86	3.23			
1758				2.95			
1759				2.96			
1760	−6.28			2.60			
1761			4.97	2.85			
1762			5.01	2.75			
1763			4.95	2.95			
1764				3.20			
1765			5.03	3.16			
1766			4.92	3.38			
1767				3.25			
1768				3.25			
1769				3.17			
1770			5.01	3.11			
1771			4.95	3.26			
1772				3.17			
1773				2.98			
1774				3.06			
1775				3.40			
1776			4.88	3.53			
1777				3.24			
1778				3.18			
1779				3.10			
1780			4.95	3.05			
1781			5.05	3.17			
1782			4.93	3.13			
1783				3.33			
1784				3.33			
1785				3.16			
1786				3.00			
1787				2.83			
1788				3.01			
1789				2.80			
1790			5.03	2.84			
1791				2.94			
1792				2.98			
1793				3.05			
1794				2.89			
1795			4.94	3.12			
1796	−6.33		4.93	2.89			
1797				2.84			
1798				3.10			
1799				3.22			
1800			4.90	3.29			
1801				3.20			
1802			4.93	3.23			
1803				3.31			
1804			4.84	3.12			
1805			4.92	3.00			
1806				3.20			
1807				3.20			
1808			4.96	3.20			
1809				3.35			
1810				3.13			
1811				3.18			
1812				3.23			
1813			4.98	3.23			
1814			4.94	3.14			
1815				3.15			
1816				3.07			
1817				3.14			
1818			4.89	3.18			
1819				3.39			

Appendix A (continued)

Year AD ↓	$\delta^{13}\text{C}_{\text{atm}}$	$\delta^{13}\text{C}_{\text{DIC}}$	$\delta^{13}\text{C}_{\text{sponge}}$	$\delta^{13}\text{C}_{\text{shell}}$			
Locality →	Hawaii	N Atlantic	Jamaica	Flatey	Langanes 9	Langanes 5	Gulf of Maine
1820				3.01			
1821				3.21			
1822			4.93	3.16			
1823				2.98			
1824			4.93	2.99			
1825	−6.49			3.16			
1826			4.90	3.18			
1827				3.14			
1828				3.16			
1829				3.17			
1830			4.88	3.14			
1831				3.04			
1832	−6.5			3.04			
1833				3.14			
1834				3.35			
1835			4.89	3.15			
1836			4.95	3.13			
1837				2.93			
1838				3.03			
1839				3.03			
1840	−6.49		4.85	3.12			
1841				3.21			
1842				3.05			
1843				2.96			
1844				3.17			
1845	−6.4		4.78	3.31			
1846				3.41			
1847				2.65			
1848				2.96			
1849				3.09			
1850			4.79	3.16			
1851				3.40			
1852				3.46			
1853				3.43			
1854	−6.45			3.41			
1855			4.78	3.44			
1856				3.38			
1857				3.21			
1858				3.18			
1859				3.20			
1860			4.76	2.97			
1861	−6.49			3.62			
1862				3.07			
1863				2.79			
1864			4.79	2.93			
1865				2.98			
1866				3.00			
1867				3.14			
1868				3.09			
1869	−6.46		4.77	3.15			
1870				2.97			
1871			4.83	2.97			
1872				3.07			
1873			4.79	3.14			
1874				3.18			
1875				3.02			
1876				2.91			
1877				2.74			
1878			4.72	2.93			
1879			4.79	3.10			
1880			4.80	3.09			
1881				3.09			
1882	−6.59			3.28			
1883			4.68	3.07			
1884			4.80	3.14			
1885				3.35			
1886	−6.52		4.86	3.31			
1887				3.19		2.40	
1888				3.16		2.44	
1889			4.73	3.44		2.19	1.89
1890				3.11		2.04	1.79
1891	−6.61		4.71	3.07		2.34	2.12
1892	−6.66		4.88	2.99		2.19	2.09
1893				3.07		1.73	1.93

Appendix A (continued)

Year AD ↓	$\delta^{13}\text{C}_{\text{atm}}$	$\delta^{13}\text{C}_{\text{DIC}}$	$\delta^{13}\text{C}_{\text{sponge}}$	$\delta^{13}\text{C}_{\text{shell}}$			
Locality →	Hawaii	N Atlantic	Jamaica	Flatey 9	Langanes 5	Langanes 5	Gulf of Maine
1894			4.69	3.07	1.91	1.96	
1895				3.06	2.02	1.98	
1896			4.64	3.10	1.96	1.81	
1897				2.90	1.84	1.74	
1898	−6.55		4.73	2.86	1.54	1.68	
1899			4.63	3.06	2.08	1.73	
1900				2.86	2.26	1.79	
1901			4.69	3.03	2.32	1.80	
1902				3.22	2.28	1.91	
1903				3.40	2.32	1.90	
1904			4.67	3.31	2.30	1.99	
1905	−6.56			3.00	2.33	1.82	
1906			4.72	3.56	2.45	1.72	
1907				3.24	2.38	1.69	
1908				3.43	2.39	1.84	
1909			4.61	3.37	2.61	1.79	
1910				3.19	2.50	1.94	
1911			4.59	3.24	2.48	1.88	
1912	−6.69		4.68	3.28	2.44	1.91	
1913				3.10	2.31	1.94	
1914				3.10	2.09	1.87	
1915	−6.75		4.64	3.32	2.21	1.83	
1916			4.64	3.24	2.26	2.05	
1917				3.12	2.36	2.03	
1918			4.57	3.47	2.42	2.02	
1919				3.14	2.35	2.00	
1920				3.04	2.18	1.98	
1921			4.55	3.00	2.02	2.01	
1922				2.82	2.02	1.88	
1923			4.66	2.89	2.06	1.93	
1924	−6.79		4.55	2.91	2.06	1.93	
1925				2.97	1.96	1.81	
1926	−6.74		4.61	2.81	2.09	1.87	
1927			4.54	2.73	1.92	2.13	
1928				2.75	1.82	1.83	
1929	−6.72			2.64	2.19	1.80	
1930			4.59	2.79	1.99	1.75	
1931				2.66	2.24	1.55	
1932	−6.74		4.55	2.70	2.44	1.40	
1933			4.56	2.74	2.29	2.06	
1934				2.89	2.31	1.84	
1935				2.87	2.26	1.70	
1936	−6.83		4.59	2.83	2.15	1.75	
1937				2.75	2.38	1.77	
1938	−6.8		4.57	2.71	2.24	1.73	
1939	−6.88			2.59	2.29	1.79	
1940	−6.78		4.53	2.59	2.10	1.72	
1941				2.78	2.21	1.70	
1942			4.57	2.75	1.98	1.65	
1943				2.89	2.08	1.66	
1944	−6.82		4.54	2.66	1.88	1.69	
1945			4.56	2.61	2.20	1.76	
1946				2.55	2.24	1.15	
1947			4.47	2.50	2.18	1.95	
1948	−6.9		4.51	2.49	2.10	1.82	
1949				2.39	1.98	1.74	
1950				2.58	1.99	1.89	
1951			4.49	2.36	1.86	1.92	
1952			4.48	2.54	1.97	1.74	
1953	−6.87		4.45	2.51	1.96	1.87	
1954			4.49	2.51	1.97	1.77	
1955				2.51	1.94	2.07	
1956			4.41	2.76	2.05	2.16	
1957				2.91	1.91	1.68	
1958				2.93	2.07	1.76	
1959			4.46	2.43	1.95	1.46	
1960			4.41	2.62	1.82	1.52	
1961			4.36	2.89	1.80	1.52	
1962	−6.96			2.64	1.74	1.54	
1963				2.44	1.92	1.53	
1964			4.43	2.54	1.94	1.51	
1965	−7.02		4.44	2.22	1.85	1.65	
1966				2.53	1.91	1.63	
1967			4.38	2.76	1.86	1.63	

Appendix A (continued)

Year AD ↓	$\delta^{13}\text{C}_{\text{atm}}$	$\delta^{13}\text{C}_{\text{DIC}}$	$\delta^{13}\text{C}_{\text{sponge}}$	$\delta^{13}\text{C}_{\text{shell}}$			
Locality →	Hawaii	N Atlantic	Jamaica	Flatey 9	Langanes 5	Langanes 5	Gulf of Maine
1968	−7.07		4.34	2.45	1.88	1.71	1.51
1969	−7			2.45	1.68	1.61	1.40
1970	−7.01		4.34	2.50	1.75	1.59	1.55
1971	−7.21		4.28	2.49	1.87	1.51	1.57
1972				2.53	1.82	1.44	1.54
1973	−7.28		4.26	2.53	1.87	1.66	1.59
1974			4.24	2.31	1.95	1.68	1.57
1975	−7.32			2.36	1.97	1.57	1.51
1976			4.19	2.29	1.82	1.66	1.59
1977			4.23	2.20	1.78	1.54	1.70
1978	−7.37			2.19	1.89	1.43	1.72
1979		1.77		2.16	1.74	1.43	1.70
1980			4.16	2.12	1.81	1.27	1.75
1981	−7.598		4.13	2.44	1.76	1.34	1.67
1982	−7.595	1.85	4.05	2.45	1.74	1.35	1.73
1983	−7.648		4.15	2.33	1.56	1.55	1.58
1984	−7.714	1.83		2.34	1.74	1.51	1.73
1985	−7.677	1.74		2.60	1.73	1.41	1.66
1986	−7.706		4.05	2.37	1.77	1.21	1.46
1987	−7.706				1.64	1.36	1.45
1988	−7.783				1.74	1.46	1.41
1989	−7.809		3.94		1.55	1.47	1.44
1990	−7.837	1.44			1.47	1.65	1.47
1991	−7.824	1.35			1.54	1.64	1.38
1992	−7.829	1.35	3.88		1.56	1.47	1.37
1993	−7.812	1.35	3.94		1.61	1.42	1.38
1994	−7.846	1.28	3.92		1.55	1.36	1.29
1995	−7.888	1.23	3.93		1.57	1.06	1.52
1996	−7.931				1.63	1.14	1.16
1997	−7.956	1.18			1.58	1.27	1.28
1998	−8.038	1.29			1.55	1.38	1.17
1999	−8.041	1.22			1.48	1.64	1.33
2000	−8.049				1.49	1.01	1.32
2001	−8.064				1.46	1.21	1.27
2002	−8.081				1.29	0.96	1.05
2003					1.24	0.74	1.09

References

- Barrera, E., Tevesz, M.J.S., Carter, J.G., McCall, P.L., 1994. Oxygen and carbon isotopic composition and shell microstructure of the bivalve *Laternula elliptica* from Antarctica. *Palaios* 9, 275–287.
- Böhm, F., Joachimski, M.M., Lehnert, H., Morgenroth, G., Kretschmer, W., Vacelet, J., Dullo, W.C., 1996. Carbon isotope records from extant Caribbean and South Pacific sponges: evolution of $\delta^{13}\text{C}$ in surface water DIC. *Earth and Planetary Science Letters* 139, 291–303.
- Böhm, F., Haase-Schramm, A., Eisenhauer, A., Dullo, W.C., Joachimski, M.M., Lehnert, H., Reitner, J., 2002. Evidence for preindustrial variations in the marine surface water carbonate system from coralline sponges. *Geochemistry, Geophysics, and Geosystems* 3, 1019. doi:10.1029/2001GC000264.
- Box, G.E.P., Jenkins, G., 1976. *Time Series Analysis, Forecasting and Control*. Holden-Day, San Francisco. 575 pp.
- Brey, T., Mackensen, A., 1997. Stable isotopes prove shell growth bands in the Antarctic bivalve *Laternula elliptica* to be formed annually. *Polar Biology* 17, 465–468.
- Brix, H., Gruber, N., Keeling, C.D., 2004. Interannual variability of the upper ocean carbon cycle at station ALOHA near Hawaii. *Global Biogeochemical Cycles* 18, GB4019. doi:10.1029/2004GB002245.
- Broecker, W.S., Peng, T.H., 1982. *Tracers in the Sea*. Eldigio Press, Palisades, NY. 690 pp.
- Butler, P.G., Scourse, J.D., Richardson, C.A., Wanamaker Jr., A.D., Bryant, C., Bennell, J.D., 2009. Continuous marine radiocarbon reservoir calibration and the ^{13}C Suess effect in the Irish Sea: results from the first multi-centennial shell-based marine master chronology. *Earth and Planetary Science Letters* 279, 230–241.
- Butler, P.G., Wanamaker Jr., A.D., Scourse, J.D., Richardson, C.A., Reynolds, D.R., 2011. Long-term stability of $\delta^{13}\text{C}$ with respect to biological age in the aragonitic shell of mature specimens of the bivalve mollusk *Arctica islandica*. *Palaeogeography, Palaeoclimatology, Palaeoecology* 302, 21–30 (this issue).
- Deser, C., Blackmon, M.L., 1993. Surface climate variations over the North Atlantic Ocean during winter: 1900–1989. *Journal of Climate* 6, 1743–1753.
- Drinkwater, K.F., 2006. The regime shift of the 1920s and 1930s in the North Atlantic. *Progress in Oceanography* 68, 134–151.
- Druffel, E.M., Benavides, L.M., 1986. Input of excess CO_2 to the surface ocean based on $^{13}\text{C}/^{12}\text{C}$ ratios in a banded Jamaican sclerosponge. *Nature* 321, 58–61.
- Elliot, M., deMenocal, P.B., Linsley, B.K., Howe, S.S., 2003. Environmental controls on the stable isotopic composition of *Mercenaria mercenaria*: potential application to paleoenvironmental studies. *Geochemistry, Geophysics, and Geosystems* 4, 1056. doi:10.1029/2002GC000425.

- Erlenkeuser, H., 1976. ^{14}C and ^{13}C isotope concentration in modern marine mussels from sedimentary habitats. *Naturwissenschaften* 63, 338.
- Foster, L.C., Allison, N., Finch, A.A., Andersson, C., Ninnemann, U.A., 2009. Controls on $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles within the aragonite bivalve *Arctica islandica*. Holocene 19, 549–558.
- Francey, R.J., Allison, C.E., Etheridge, D.M., Trudinger, C.M., Enting, I.G., Leuenberger, M., Langenfelds, R.L., Michel, E., Steele, L.P., 1999. A 1000-year high precision record of $\delta^{13}\text{C}$ in atmospheric CO_2 . *Tellus* 51B, 170–193.
- Friedli, H., Lottschner, H., Oeschger, H., Siegenthaler, U., Stauffer, B., 1986. Ice core record of the $^{13}\text{C}/^{12}\text{C}$ ratio of atmospheric CO_2 in the past two centuries. *Nature* 324, 237–238.
- Gatien, M.G., 1976. A study in the slope water region south of Halifax. *Journal of the Fisheries Research Board of Canada* 33, 2213–2217.
- Gillikin, D.P., De Ridder, F., Ulen, H., Elskens, M., Keppens, E., Baeyens, W., Dehairs, F., 2005. Assessing the reproducibility and reliability of estuarine bivalve shells (*Saxidomus giganteus*) for sea surface temperature reconstruction: implications for paleoclimate studies. *Palaeogeography, Palaeoclimatology, Palaeoecology* 228, 70–85.
- Gillikin, D.P., Lorrain, A., Bouillon, S., Willenz, P., Dehairs, F., 2006. Stable carbon isotopic composition of *Mytilus edulis* shells: relation to metabolism, salinity, $\delta^{13}\text{C}_{\text{DIC}}$ and phytoplankton. *Organic Geochemistry* 37, 1371–1382.
- Goericke, R., Fry, B., 1994. Variations of marine plankton $\delta^{13}\text{C}$ with latitude, temperature, and dissolved CO_2 in the world ocean. *Global Biogeochemical Cycles* 8, 85–90.
- Grinsted, A., Moore, J.C., Jevrejeva, S., 2004. Application of the cross wavelet transform and wavelet coherence to geophysical time series. *Nonlinear Processes in Geophysics* 11, 561–566.
- Gruber, N., Keeling, C.D., Bacastow, R.B., Guenther, P.R., Lueker, T.J., Wahlen, M., Meijer, H.A.J., Mook, W.G., Stocker, T.F., 1999. Spatiotemporal patterns of carbon-13 in the global surface oceans and the oceanic Suess effect. *Global Biogeochemical Cycles* 13, 307–335.
- Gruber, N., Keeling, C.D., Bates, N.R., 2002. Interannual variability in the North Atlantic Ocean carbon sink. *Science* 298, 2374–2378.
- Hurrell, J.W., van Loon, H., 1997. Decadal variations in climate associated with the North Atlantic Oscillation. *Climatic Change* 36, 301–326.
- Jones, D.S., 1980. Annual cycle of shell growth increment formation in two continental shelf bivalves and its paleoecologic significance. *Paleobiology* 6, 331–340.
- Jones, D.S., Williams, D.F., Arthur, M.A., 1983. Growth history and ecology of the Atlantic surf clam, *Spisula solidissima* (Dillwyn), as revealed by stable isotopes and annual shell increments. *Journal of Experimental Marine Biology and Ecology* 73, 225–242.
- Keeling, C.D., Guenther, P., 1994. Shore based carbon analysis: duplicate carbon measurements made by the Carbon Dioxide Research Group – Scripps Institution of Oceanography, University of California, San Diego. <http://cdiac.esd.ornl.gov/ftp/oceans/keeling/data/>. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee.
- Keeling, C.D., Piper, S.C., Bacastow, R.B., Wahlen, M., Whorf, T.P., Heimann, M., Meijer, H.A., 2005. Atmospheric CO_2 and $^{13}\text{CO}_2$ exchange with the terrestrial biosphere and oceans from 1978 to 2000: observations and carbon cycle implications. *Ecological Studies* 177, 83–113.
- Körtzinger, A., Quay, P.D., Sonnerup, R.E., 2003. Relationship between anthropogenic CO_2 and the ^{13}C Suess effect in the North Atlantic Ocean. *Global Biogeochemical Cycles* 17, 1005. doi:10.1029/2001GB001427.
- Krantz, D.E., Williams, S.F., Jones, D.S., 1987. Ecological and paleoenvironmental information using stable isotope profiles from living and fossil mollusks. *Palaeogeography, Palaeoclimatology, Palaeoecology* 58, 249–266.
- Kröncke, I., Zeiss, B., Rensing, C., 2001. Long-term variability in macrofauna species composition off the island of Norderney (East Frisia, Germany) in relation to changes in climatic and environmental conditions. *Senckenbergiana Maritima* 31, 65–82.
- Lazareth, C.E., Willenz, P., Navez, J., Keppens, E., Dehairs, F., André, L., 2000. Sclerosponges as a new potential recorder of environmental changes: lead in *Ceratoporella nicholsoni*. *Geology* 28, 515–518.
- Lorrain, A., Paulet, Y.-M., Chauvaud, L., Dunbar, R., Mucciarone, D., Fontugne, M., 2004. $\delta^{13}\text{C}$ variation in scallop shells: increasing metabolic carbon contribution with body size? *Geochimica et Cosmochimica Acta* 68, 3509–3519.
- Marchitto, T.A., Jones, G.A., Goodfriend, G.A., Weidman, C.R., 2000. Precise temporal correlation of Holocene mollusk shells using sclerochronology. *Quaternary Research* 53, 236–246.
- McConnaughey, T.A., Gillikin, D.P., 2008. Carbon isotopes in mollusk shell carbonates. *Geo-Marine Letters*. doi:10.1007/s00367-008-0116-4.
- McConnaughey, T.A., Burdett, J., Whelan, J.F., Paull, C.K., 1997. Carbon isotopes in biological carbonates: respiration and photosynthesis. *Geochimica et Cosmochimica Acta* 61, 611–622.
- Meeker, L.D., Mayewski, P.A., 2002. A 1400-year high-resolution record of atmospheric circulation over the North Atlantic and Asia. *Holocene* 12, 257–266.
- Mook, W.G., Tan, F.C., 1991. Stable carbon isotopes in rivers and estuaries. In: Degens, E.T., Kempe, S., Richey, J.E. (Eds.), *SCOPE 42 – Biogeochemistry of Major World Rivers*. Wiley, New York, pp. 245–264.
- Moore, M.D., Charles, C.D., Rubenstone, J.L., Fairbanks, R.G., 2000. U/Th-dated sclerosponges from the Indonesian Seaway record subsurface adjustments to west Pacific winds. *Paleoceanography* 15, 404–416.
- Nicol, D., 1951. Recent species of the veneroid pelecypod *Arctica*. *Journal of the Washington Academy of Sciences* 41, 102–106.
- Nozaki, Y., Rye, D.M., Turekian, K.K., Dodge, R.E., 1978. A 200 year record of carbon-13 and carbon-14 variations in a Bermuda coral. *Geophysical Research Letters* 5, 826–828.
- Olsen, A., Omar, A.M., Bellerby, R.G.J., Johannessen, T., Ninnemann, U., Brown, K.R., Olsson, K.A., Olafsson, J., Nondal, G., Kivimäe, C., Kringstad, S., Neill, C., Olafsdottir, S., 2006. Magnitude and origin of the anthropogenic CO_2 increase and ^{13}C Suess effect in the Nordic seas since 1981. *Global Biogeochemical Cycles* 20, GB3027. doi:10.1029/2005GB002669.
- Quay, P.D., Sonnerup, R.E., Westby, T., Stutsman, J., McNichol, A.P., 2003. Changes in the $^{13}\text{C}/^{12}\text{C}$ of dissolved inorganic carbon in the ocean as a tracer of anthropogenic CO_2 uptake. *Global Biogeochemical Cycles* 17, 1004. doi:10.1029/2001GB001817.
- Quay, P., Sonnerup, R., Stutsman, J., Maurer, J., Körtzinger, A., Padin, X.A., Robinson, C., 2007. Anthropogenic CO_2 accumulation rates in the North Atlantic Ocean from changes in the $^{13}\text{C}/^{12}\text{C}$ of dissolved inorganic carbon. *Global Biochemical Cycles* 21, GB1009. doi:10.1029/2006GB002761.
- Rogers, J.C., 1985. Atmospheric circulation changes associated with the warming over the northern North Atlantic in the 1920s. *Journal of Climate and Applied Meteorology* 24, 1303–1310.
- Romanek, C.S., Grossman, E.L., Morse, J.W., 1992. Carbon isotopic fractionation in synthetic aragonite and calcite: effects of temperature and precipitation rate. *Geochimica et Cosmochimica Acta* 56, 419–430.
- Ropes, J.W., Jones, D.S., Murawski, S.A., Serchuk, F.M., Jearld Jr., A., 1984. Documentation of annual growth lines in ocean quahogs, *Arctica islandica* Linné. *Fisheries Bulletin* 82, 1–19.
- Rowell, T.W., Chaisson, D.R., McLane, J.T., 1990. Size and age of sexual maturity and annual gametogenic cycle in the ocean quahog, *Arctica islandica* (Linnaeus, 1767), from coastal waters in Nova Scotia, Canada. *Journal of Shellfish Research* 9, 195–203.
- Sabine, C.L., Feely, R.A., Gruber, N., Key, R.M., Lee, K., Bullister, J.L., Wanninkhof, R., Wong, C.S., Wallace, D.W.R., Tilbrook, B., Millero, F.J., Peng, T.-H., Kozyr, A., Ono, R., Rios, A.F., 2004. The oceanic sink for anthropogenic CO_2 . *Science* 305, 367–371.
- Schöne, B.R., 2008. The curse of physiology – challenges and opportunities in the interpretation of geochemical data from mollusk shells. *Geo-Marine Letters* 28, 269–285.
- Schöne, B.R., Freyre Castro, A.D., Fiebig, J., Houk, S.D., Oschmann, W., Kröncke, I., 2004. Sea surface water temperatures over the period 1884–1983 reconstructed from oxygen isotope ratios of a bivalve mollusk shell (*Arctica islandica*, southern North Sea). *Palaeogeography, Palaeoclimatology, Palaeoecology* 212, 215–232.
- Schöne, B.R., Fiebig, J., Pfeiffer, M., Gleß, R., Hickson, J., Johnson, A.L.A., Dreyer, W., Oschmann, W., 2005a. Climate records from a bivalved *Methuselah* (*Arctica islandica*, Mollusca; Iceland). *Palaeogeography, Palaeoclimatology, Palaeoecology* 228, 130–148.
- Schöne, B.R., Houk, S.D., Freyre Castro, A.D., Fiebig, J., Kröncke, I., Dreyer, W., Oschmann, W., 2005b. Daily growth rates in shells of *Arctica islandica*: assessing subseasonal environmental controls on a long-lived bivalve mollusk. *Palaos* 20, 78–92.
- Schöne, B.R., Dunca, E., Fiebig, J., Pfeiffer, M., 2005c. Mutvei's solution: an ideal agent for resolving microgrowth structures of biogenic carbonates. *Palaeogeography, Palaeoclimatology, Palaeoecology* 228, 149–166.
- Schöne, B.R., Zhang, Z., Jacob, D., Gillikin, D.P., Tütken, T., Garbe-Schönberg, D., McConnaughey, T., Soldati, A., 2010. Effect of organic matrices on the determination of the trace element chemistry (Mg, Sr, Mg/Ca, Sr/Ca) of aragonitic bivalve shells (*Arctica islandica*) – comparison of ICP-OES and LA-ICP-MS data. *Geochimical Journal* 44, 23–37.
- Sicre, M.-A., Jacob, J., Ezat, U., Rousse, S., Kissel, C., Yiou, P., Eiriksson, J., Knudsen, K.L., Jansen, E., Turon, J.-L., 2008. Decadal variability of sea surface temperatures off North Iceland over the last 2000 years. *Earth and Planetary Science Letters* 268, 137–142.
- Sutton, R.T., Allen, M.R., 1997. Decadal predictability of North Atlantic sea surface temperature and climate. *Nature* 388, 563–567.
- Swart, P.K., Moore, M., Charles, C., Böhm, F., 1998. Sclerosponges may hold new keys to marine paleoclimate. *EOS Transactions AGU* 79, 636–638.
- Tanaka, N., Monaghan, M.C., Rye, D.M., 1986. Contribution of metabolic carbon to mollusc and barnacle shell carbonate. *Nature* 320, 520–523.
- Tanaka, T., Watanabe, Y.W., Watanabe, S., Noriki, S., Tsurushima, Y., Nohji, Y., 2003. Oceanic Suess effect of $\delta^{13}\text{C}$ in subpolar region: the North Pacific. *Geophysical Research Letters* 30, 2159. doi:10.1029/2003GL018503.
- Tans, P., 1981. $^{13}\text{C}/^{12}\text{C}$ of industrial carbon dioxide. In: Bolin, B. (Ed.), *SCOPE 16 – Carbon Cycle Modelling*. Wiley, New York, pp. 127–130.
- Thompson, I., Jones, D.S., Ropes, J.W., 1980a. Advanced age for sexual maturity in the ocean quahog *Arctica islandica* (Mollusca: Bivalvia). *Marine Biology* 57, 35–39.
- Thompson, I., Jones, D.S., Dreibelbis, D., 1980b. Annual internal growth banding and life history of the ocean quahog *Arctica islandica* (Mollusca: Bivalvia). *Marine Biology* 57, 25–34.
- Torrence, C., Compo, G., 1998. A practical guide to wavelet analysis. *Bulletin of the American Meteorological Society* 79, 61–78.
- Wanamaker Jr., A.D., Heinemeier, J., Scourse, J.D., Richardson, C.A., Butler, P.G., Eiriksson, J., Knudsen, K.L., 2008a. Very long-lived mollusks confirm 17th century AD tephra-based radiocarbon reservoir ages for North Icelandic shelf waters. *Radiocarbon* 50, 399–412.
- Wanamaker Jr., A.D., Kreutz, K., Schöne, B.R., Pettigrew, N., Borns, H.W., Introne, D.S., Belknap, D., Maasch, K.A., Feindel, S., 2008b. Coupled North Atlantic slope water forcing on Gulf of Maine temperatures over the past millennium. *Climate Dynamics* 31, 183–194.