

**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  $\text{CO}_2$ . 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  $-2.7 \pm 0.2\text{‰}$  corresponding to a 6.2 to  $10.8 \pm 0.8\%$  contribution of respiratory  $\text{CO}_2$  ( $-25\text{‰}$ ). 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  $\text{CO}_2$ . 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.

## Keywords

sclerochronology, stable carbon isotope ratio, carbon dioxide, dissolved inorganic carbon, oceanic Suess effect

## 1. Introduction

Approximately  $118 \pm 19$  Pg C (1Pg C =  $10^{15}$  g C = 1Gt 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 ( $\text{CO}_2$ ) resulting from the combustion of fossil energy sources, deforestation and changes in land use is depleted in  $^{13}\text{C}$  (Tans, 1981). During the last 200 years the stable carbon isotope ratio of atmospheric  $\text{CO}_2$  ( $\delta^{13}\text{C}_{\text{atm}}$ ) 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  $\text{CO}_2$  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 & Benavides, 1986; Böhm et al., 1996, 2002; Swart et al., 1998; Lazareth et al., 2000; Moore et al., 2000), 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  $\text{CO}_2$  (Gruber et al., 2002; Quay et al., 2003, 2007). This uptake rate, however, underlies significant spatiotemporal variations which are poorly 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  $\text{CO}_2$  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 & Benavides, 1986; Böhm et al., 1996, 2002; Swart et al., 1998; Lazareth et al., 2000; Moore et al., 2000), 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 life-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., 1999), 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  $\text{CO}_2$  (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  $\text{CO}_2$  and to evaluating the potential consequences for future climate change and ecosystems.

## 2. Material and Methods

Four shells of the ocean quahog, *Arctica islandica*, were collected alive by dredging from surface waters (ca. 30m 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 0.4mm thick low concentration-diamond wafering blade (LC15). The shell slabs were subsequently mounted on glass slides, ground with 800 and 1200 SiC grit powder and polished with 1 $\mu$ m Al<sub>2</sub>O<sub>3</sub> 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, 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 3,532 powder samples were obtained from the shells. Following the shape of the microgrowth increments,  $\text{CaCO}_3$  powder was milled from the outer shell layer (Fig. 2) under a stereomicroscope at 10 to 20X magnification (Schöne et al., 2005a). The cylindrical diamond drill bit measured 1mm in diameter and was firmly mounted on a Rexim Minimo drill. The widths of the milling steps ranged between 20 and 300 $\mu\text{m}$  in the direction of shell growth and represented ca. 1 to 45 weeks of growth. The shells from the Gulf of Maine and Flatey were sampled from age one onward, whereas sampling in specimens Langanes 5 and 9 started at ontogenetic age 18 and 28, respectively. Each milling yielded approximately 40 to 120  $\mu\text{g}$  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 ( $1\sigma$ ) was better than  $\pm 0.03\%$ . Annually averaged data are given in the Appendix.

### 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 prewhitened with first-order autoregressive (AR-1) modeling (Box & Jenkins, 1976). This approach removed lag-1 autocorrelation from the time-series. AR-1 coefficients ( $\alpha$ ) 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 & 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  $\theta$  given in degree) are indicated by arrows and permit to 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  $179^\circ$  and  $\theta=-1$  to  $-179^\circ$ ) (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  $90^\circ$  equals a lead of  $270^\circ$ .

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 (3-12m) of  $45^\circ$ - $59^\circ\text{N}$  and  $0^\circ$ - $59^\circ\text{W}$  (Keeling & 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 (5p.m.) in Distillfjörður SW þórshöfn, southwestern tip of Langanes peninsula (N66°11'22.26", W15°21'9.54) in ca. 15m water depth. This  $\delta^{13}\text{C}_{\text{DIC}}$  value (+0.36‰) was not depicted in Figure 3.

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### 3. Results

The four uninterrupted, annually resolved  $\delta^{13}\text{C}_{\text{shell}}$  chronologies of *Arctica 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 Langanes and Gulf of Maine shells, the specimen from Flatey showed a strong enrichment in  $^{13}\text{C}$ . 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‰; Langanes 5 = 1.95‰). Conversely, the average isotope records of the specimens from Langanes and the Gulf of Maine deviated only by 0.2‰ from each other. According to high-pass filtered data (Fig. 3B), however, even isotope records from specimens living in close distance (few tens of meters) from each other (Langanes shells) did not perfectly match (see also Tab. 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, Tab. 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 Langanes 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.  $-0.003\text{‰ yr}^{-1}$  ( $-0.42\text{‰}$  and  $-0.35\text{‰}$ , respectively) between 1790 and 1920 (Fig. 3, Tab. 1). However, between ca. 1920 and 1986,  $\delta^{13}\text{C}_{\text{shell}}$  values of all studied bivalves changed, on average, by about  $-0.010\text{‰ yr}^{-1}$  or  $-0.73\text{‰}$  (Tab. 1). During the same time interval,  $\delta^{13}\text{C}_{\text{atm}}$  values exhibited a more pronounced shift of  $-0.014\text{‰ yr}^{-1}$  ( $-0.95\text{‰}$ ), whereas sclerosponges reflected a lower negative change of only  $-0.008\text{‰ yr}^{-1}$  ( $-0.53\text{‰}$ ; Fig. 3B, Tab. 1).

Notably, shell and atmospheric stable carbon isotope values often decoupled from each other. For example, between 1920 and 1955, the  $\delta^{13}\text{C}_{\text{shell}}$  values of the specimen from Flatey dropped by  $-0.43\text{‰}$  ( $-0.012\text{‰ yr}^{-1}$ ), i.e. nearly three times as fast as atmospheric values ( $-0.16\text{‰}$  or  $-0.004\text{‰ yr}^{-1}$ ) or tropical sclerosponge records ( $-0.15\text{‰}$  or  $-0.004\text{‰ yr}^{-1}$ ; Fig. 3B, Tab. 1). During the same time interval, shells from Langanes and the Gulf of Maine decreased, on average, by  $-0.010\text{‰ yr}^{-1}$  or  $-0.36\text{‰}$  (Fig. 3B, Tab. 1). Conversely, atmospheric and sclerosponge  $\delta^{13}\text{C}$  values shifted by ca.  $-0.88\text{‰}$  and  $-0.41\text{‰}$  ( $-0.028\text{‰ yr}^{-1}$  and  $-0.013\text{‰ yr}^{-1}$ ), respectively, between 1960 and 1990, whereas only a  $-0.27\text{‰}$  ( $-0.009\text{‰ yr}^{-1}$ ) change was observed in the Iceland shells. In the Gulf of Maine, these changes were even smaller:  $-0.12\text{‰}$  or  $-0.004\text{‰ yr}^{-1}$  (Fig. 3B, Tab. 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 (Fig. 3A) (Keeling & Guenther, 1994). During this time interval, the carbon isotope chemistry shifted by about -

0.032‰ yr<sup>-1</sup>. 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; Tab. 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 & Guenther (1994) was observed in the case of sclerosponges (Fig. 3B, Tab. 1).

A water sample taken in Distillfjörður, Langanes pensinsula 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 & 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, Tab. 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, 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  $90^\circ$  (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  $\text{CO}_2$  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 & Mackensen (1987) 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  $\delta^{13}\text{C}_{\text{shell}}$  shift<sup>1</sup> within the last nine years of a 21-year-old *Arctica 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 & 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.

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<sup>1</sup> 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).

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 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 Figure 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  $\text{CO}_2$  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 (Tab. 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., this issue).

Although no age-related  $\delta^{13}\text{C}_{shell}$  trends were observed, shells of the ocean quahog were most likely precipitated with a constant offset 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  $\delta^{13}\text{C}_{shell}$  values (Langanes and Gulf of Maine) were nearly identical to the  $\delta^{13}\text{C}_{\text{DIC}}$  values (1.52‰; Tab. 1). Taking the fractionation factor  $\epsilon$  between aragonite and  $\text{HCO}_3^-$  of  $2.7 \pm 0.2\text{‰}$  into account (Romanek et al., 1992), *A. islandica* formed its shell  $-2.7 \pm 0.2\text{‰}$  away from isotopic equilibrium with the ambient DIC pool. Assuming a  $\delta^{13}\text{C}$  value of  $-25\text{‰}$ , 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 & Fry, 1994), this offset translates into a contribution of respiratory  $\text{CO}_2$  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 & 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  $1.2\text{‰}$  more negative than the basin-wide average. If the local Langanes  $\delta^{13}\text{C}_{\text{DIC}}$  value of  $0.36\text{‰}$  is used, the (Icelandic) shells would only have formed  $-1.54 \pm 0.2\text{‰}$  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, Tab. 1). It appears unlikely that these differences were caused by individual differences in the (ontogenetically unchanged) metabolic  $\text{CO}_2$  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  $^{13}\text{C}$ ), 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  $^{13}\text{C}$  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  $-25\text{‰}$  for soft tissue and POM given above is only an average value and can change by as much as  $5\text{‰}$  (Goericke & Fry,

1994). Further studies are, however, required to confirm our interpretation that individual differences in respiratory CO<sub>2</sub> incorporation into the shell carbonate of the ocean quahog are negligibly small.

#### 4.3. Inter-annual variability of the $\delta^{13}\text{C}_{shell}$ 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  $\delta^{13}\text{C}_{shell}$  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  $\delta^{13}\text{C}_{DIC}$  data are snapshot measurements and in fact, the seasonal variability of  $\delta^{13}\text{C}_{DIC}$  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 & van Loon, 1997) and large-scale lower-frequency fluctuations (e.g., 12-16 years) of sea surface temperature in the North Atlantic (Deser & 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  $\text{CO}_2$ .

However, the observed periodic variations were not always phase-locked among the studied shells (Figs. 5, 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 & 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  $\pm 0.14\text{‰}$ ) 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 ( $-0.71\text{‰}$ ) was slightly lower than the decline of atmospheric stable carbon isotope values ( $-0.95\text{‰}$ ), but slightly higher than  $\delta^{13}\text{C}_{\text{sponge}}$  values from the tropics ( $-0.53\text{‰}$ ) 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 & 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  $\text{CO}_2$  almost contemporaneously (Körtzinger et al., 2003) with the starting of the industrialization during the late 18<sup>th</sup> 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 & 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<sup>2</sup>. 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. $\delta^{13}\text{C}_{shell}$ values as a measure for oceanic uptake rate of anthropogenic $\text{CO}_2$ ?

Although long-term trends and decadal variability in the carbon chemistry of the ocean can be recognized in the  $\delta^{13}\text{C}_{shell}$  data, it appears unlikely that the studied shells are

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



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  $\text{CO}_2$  absorption by the surface ocean. Whereas the equilibration time of  $\text{CO}_2$  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  $\text{CO}_2$ . 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  $\text{CO}_2$  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, *Arctica 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  $\text{CO}_2$  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  $\text{CO}_2$ . 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  $\text{CO}_2$ . 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.

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## Figure Captions

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.

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.

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 & 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  $^{12}\text{C}$ . Shells of *Arctica islandica* are precipitated with a constant offset of ca.  $-1.54$  to  $-2.7 \pm 0.2\%$  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 from the late 18<sup>th</sup> 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 ‘Langanes’ is from specimen “Langanes 9”, longer record from specimen “Langanes 5”.

Fig. 4: Continuous wavelet power spectra of the pre-whitened and standardized  $\delta^{13}\text{C}_{\text{shell}}$  time-series (A = Flatey; B = Langanes 9; C = Langanes 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.

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.

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).

Table 1: Comparison of stable carbon isotope ( $\delta^{13}\text{C}$ ) data from instrumental records [atmospheric  $\text{CO}_2$  (Friedli et al., 1986; Francey et al., 1999; Keeling et al., 2005), oceanic dissolved inorganic carbon, DIC (Keeling & Guenther, 1994)] and biogenic hard parts [sclerosponges (Böhm et al., 1996, 2002); bivalves]. For original values see supplementary information.

Data set	Inter-annual ( $\% \text{ yr}^{-1}$ ) and long-term $\delta^{13}\text{C}$ change ( $\%$ )				Average inter-annual $\delta^{13}\text{C}$ variability ( $\%$ )*	Average $\delta^{13}\text{C}$ ( $\%$ )	
	1790-1920	1920-1955	1920-1986	1960-1990		1979-1986	1979-1999
Atmospheric $\text{CO}_2$	-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
<u>Bivalves</u>							
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

\*Errors given in standard deviations ( $1\sigma$ ). 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.

**Appendix.** Summary of instrumental and proxy stable carbon isotope data ( $\text{‰}_{\text{VPDB}}$ ). Data were annually averaged, weighted averages in the case of bivalves. Atmospheric data were assembled from air inclusions in firn ice and measured  $\text{CO}_2$  at Hawaii (Friedli et al., 1986; Francey et al., 1999; Keeling et al., 2005). DIC values came from the temperate North Atlantic (Keeling & 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	Langes 9	Langes 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
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
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	2.01	1.76
1946			2.55	2.24	2.15	1.74
1947		4.47	2.50	2.18	1.95	1.80
1948	-6.9	4.51	2.49	2.10	1.82	1.78
1949			2.39	1.98	1.74	1.61
1950			2.58	1.99	1.89	1.60
1951		4.49	2.36	1.86	1.92	1.67
1952		4.48	2.54	1.97	1.74	1.43
1953	-6.87	4.45	2.51	1.96	1.87	1.49
1954		4.49	2.51	1.97	1.77	1.64
1955			2.51	1.94	2.07	1.58
1956		4.41	2.76	2.05	2.16	1.62
1957			2.91	1.91	1.68	1.56
1958			2.93	2.07	1.76	1.62
1959		4.46	2.43	1.95	1.46	1.54
1960		4.41	2.62	1.82	1.52	1.60
1961		4.36	2.89	1.80	1.52	1.72
1962	-6.96		2.64	1.74	1.54	1.69
1963			2.44	1.92	1.53	1.68
1964		4.43	2.54	1.94	1.51	1.66
1965	-7.02	4.44	2.22	1.85	1.65	1.37
1966			2.53	1.91	1.63	1.52
1967		4.38	2.76	1.86	1.63	1.47
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	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

Fig. 1



Fig. 2

ACQ

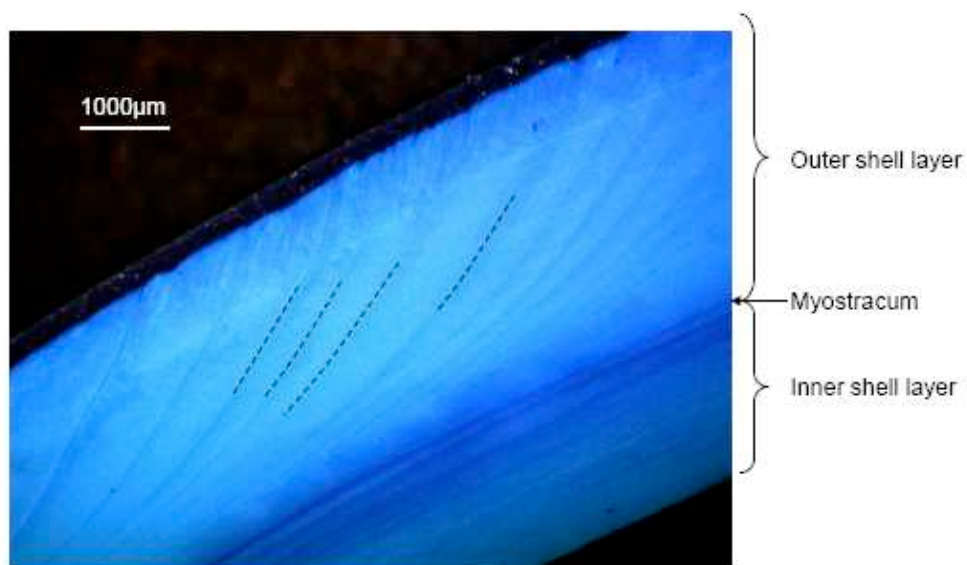


Fig. 3

ACCEPTED MANUSCRIPT

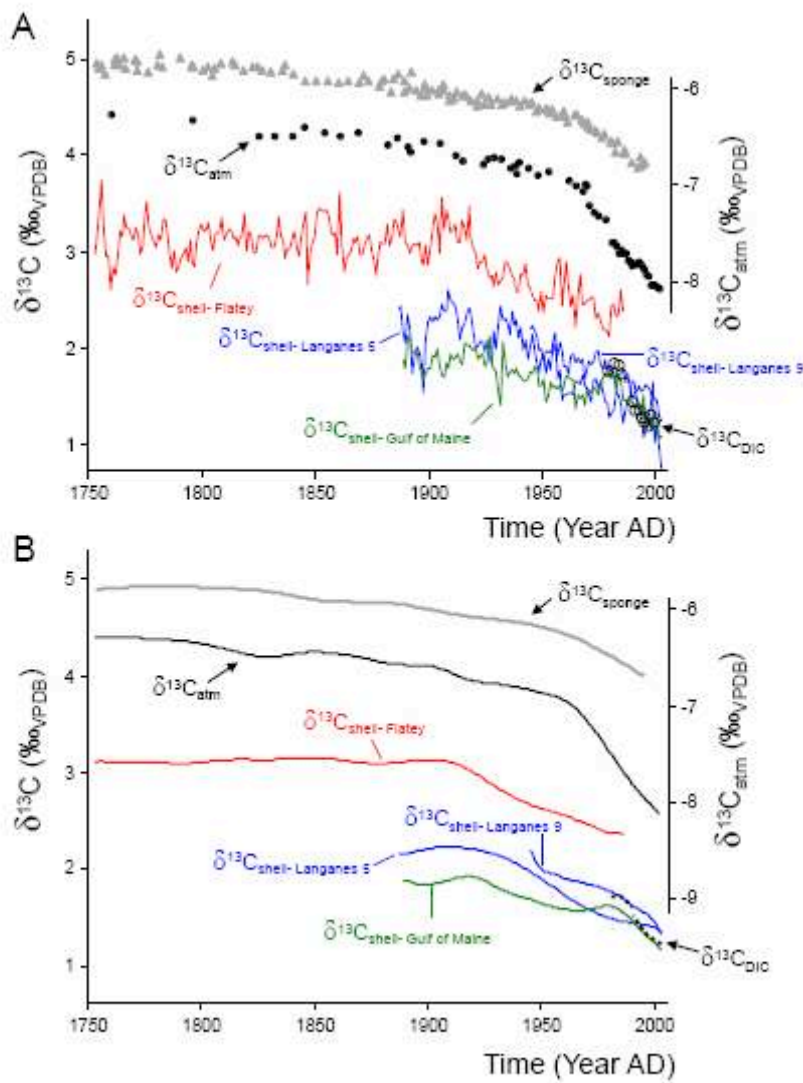


Fig. 4

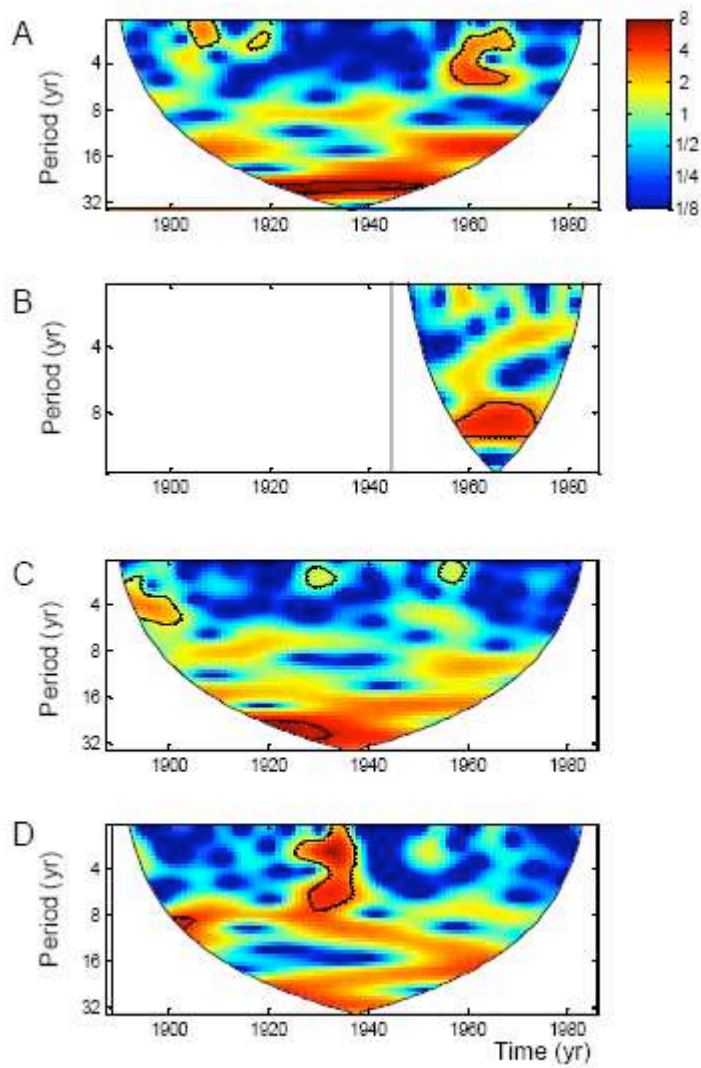


Fig. 5

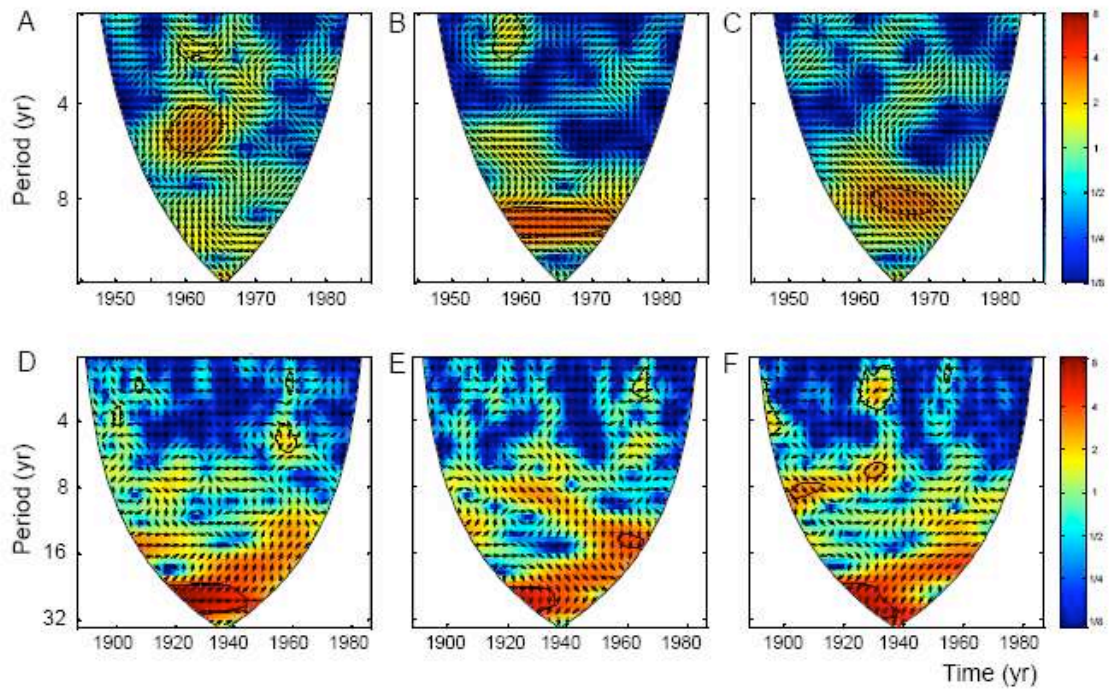


Fig. 6

