

# Twentieth century $\delta^{13}\text{C}$ variability in surface water dissolved inorganic carbon recorded by coralline algae in the northern North Pacific Ocean and the Bering Sea

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**Abstract.** The oxygen isotopic composition and Mg/Ca ratios in the skeletons of long-lived coralline algae record ambient seawater temperature over time. Similarly, the carbon isotopic composition in the skeletons record  $\delta^{13}\text{C}$  values of ambient seawater dissolved inorganic carbon. Here, we measured  $\delta^{13}\text{C}$  in the coralline alga *Clathromorphum nereostratum* to test the feasibility of reconstructing the intrusion of anthropogenic  $\text{CO}_2$  into the northern North Pacific Ocean and Bering Sea. The  $\delta^{13}\text{C}$  was measured in the high Mg-calcite skeleton of three *C. nereostratum* specimens from two islands 500 km apart in the Aleutian archipelago. In the records spanning 1887 to 2003, the average decadal rate of decline in  $\delta^{13}\text{C}$  values increased from 0.03‰ yr<sup>-1</sup> in the 1960s to 0.095‰ yr<sup>-1</sup> in the 1990s, which was higher than expected due to solely the  $\delta^{13}\text{C}$ -Suess effect. Deeper water in this region exhibits higher concentrations of  $\text{CO}_2$  and low  $\delta^{13}\text{C}$  values. Transport of deeper water into surface water (i.e., upwelling) increases when the Aleutian Low is intensified. We hypothesized that the acceleration of the  $\delta^{13}\text{C}$  decline may result from increased upwelling from the 1960s to 1990s, which in turn was driven by increased intensity of the Aleutian Low. Detrended  $\delta^{13}\text{C}$  records also varied on

4–7 year and bidecadal timescales supporting an atmospheric teleconnection of tropical climate patterns to the northern North Pacific Ocean and Bering Sea manifested as changes in upwelling.

## 1 Introduction

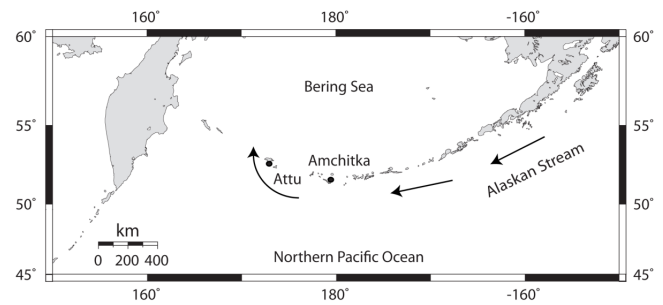
The world's oceans have taken up approximately half of the anthropogenic  $\text{CO}_2$  emitted into the atmosphere (Sabine et al., 2004a). Since anthropogenic emissions of  $\text{CO}_2$  continue to increase, understanding the mechanisms of  $\text{CO}_2$  uptake by the ocean are of considerable importance. The ability of the ocean to take up anthropogenic  $\text{CO}_2$  varies widely depending largely on the local/regional water temperature, ocean circulation, and biological productivity. This is particularly true in the subarctic Pacific Ocean, where estimates of carbon uptake rates from direct measurements and proxy records vary substantially (Newsome et al., 2007; Quay et al., 2003; Tanaka et al., 2003), likely as a result of large seasonal and interannual variability in the physical and biological controls on surface water  $\text{CO}_2$  (Sabine et al., 2004b). Therefore, robust, high-resolution records of seawater  $\text{CO}_2$  in this region are needed to more accurately understand the role of the northern North Pacific Ocean and Bering Sea in absorbing anthropogenic  $\text{CO}_2$ .



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The ratio  $^{13}\text{C}/^{12}\text{C}$  of seawater dissolved inorganic carbon (DIC), expressed as  $\delta^{13}\text{C}_{\text{DIC}}$ , is a useful method to measure the intrusion of anthropogenic  $\text{CO}_2$  into surface waters (Quay et al., 1992). Specifically,  $\delta^{13}\text{C}_{\text{DIC}}$  values record the  $\delta^{13}\text{C}$ -Suess effect (i.e., the burning of isotopically “light” fossil fuels, which decreases the  $\delta^{13}\text{C}$  value of carbon reservoirs). The  $\delta^{13}\text{C}$  values in atmospheric  $\text{CO}_2$  at Pt. Barrow, Alaska decreased  $0.02\text{‰ yr}^{-1}$  from the early 1980s to the early 2000s (Keeling et al., 2001). In contrast, repeated cruises in the subarctic Pacific recorded little to no decrease in  $\delta^{13}\text{C}$  values of surface water DIC between 1970 and 1990 (Quay et al., 2003) while  $\delta^{13}\text{C}_{\text{DIC}}$  values decreased  $0.012\text{‰ yr}^{-1}$  from 1997 to 2001 at the western North Pacific station KNOT (Tanaka et al., 2003). In these studies, the depressed influence of the  $\delta^{13}\text{C}$ -Suess effect in the surface waters of the subarctic Pacific water was attributed to rapid renewal of surface waters which prevents the subpolar gyres from equilibrating with the atmosphere (Quay et al., 2003). This reduces the penetration of atmospheric  $\text{CO}_2$  into the surface waters, and drives the disequilibrium between atmospheric  $\text{CO}_2$  and surface water  $\delta^{13}\text{C}_{\text{DIC}}$  values. However, these instrumental  $\delta^{13}\text{C}_{\text{DIC}}$  measurements are limited both in temporal (i.e., repeat cruise data limited to two data points) and spatial (i.e., one location at station KNOT) distribution. In addition, skeletal  $\delta^{13}\text{C}$  values from available marine proxy records decreased at a rate exceeding that of instrumental records. In a gorgonian soft coral in the Alaskan stream,  $\delta^{13}\text{C}$  values declined at a rate of  $0.015\text{‰ yr}^{-1}$  (Williams et al., 2007). However, this is the only record available from sessile organisms in the northern North Pacific. The  $\delta^{13}\text{C}$  values from subarctic Pacific marine mammals declined at a rate of  $0.02$  to  $0.06\text{‰ yr}^{-1}$  (Newsome et al., 2007; Schell, 2001). These records are also useful, but their source from marine mammals has inherent disadvantages. For example, it is difficult to differentiate changes in the baseline  $\delta^{13}\text{C}_{\text{DIC}}$  relating to anthropogenic causes from temporal shifts in the foraging zones of the marine mammals that have different isotopic values at the base of the food web (Newsome et al., 2007; Hirons et al., 2001). Variability within a marine mammal sample set, i.e., in size, gender, and age, may also obscure baseline changes (Hobson et al., 2004).

Coralline algae are a new climate archive in the subarctic regions (Halfar et al., 2008; Kamenos et al., 2009). In particular, paleo-temperature reconstructions extending to 1887 have been derived from the coralline algae *Clathromorphum nereostratum* (Halfar et al., 2007; Hetzinger et al., 2009), a species which is abundant throughout the Aleutian Islands (Lebednik, 1976). Measurements of skeletal  $\delta^{18}\text{O}$  and  $\text{Mg}/\text{Ca}$  in *C. nereostratum* combined with visible annual growth increments in the skeleton have yielded robust growth chronologies with sub-annual resolution (Halfar et al., 2007; Hetzinger et al., 2009). Therefore, the goal of this paper was to demonstrate the potential of utilizing *C. nereostratum* as recorders of seawater  $\delta^{13}\text{C}_{\text{DIC}}$  and extract robust, high-resolution records of subarctic  $\delta^{13}\text{C}_{\text{DIC}}$ .



**Fig. 1.** Location of sample collection sites offshore of Attu and Amchitka Islands along the Aleutian Arc in the northern North Pacific Ocean and Bering Sea. Black circle indicates sample locations. (Map generated at <http://www.planiglobe.com>.)

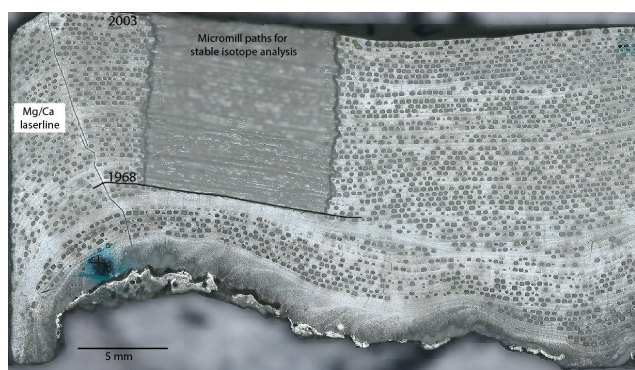
## 2 Methods

### 2.1 Sample collection

Two specimens of the coralline alga *C. nereostratum* (Attu 11-4 and AM4-1) were collected live from 10 m depth during a research cruise in August 2004 from the Aleutian Islands (Fig. 1). Attu 11-4 was collected offshore of the southern side of Attu Island ( $52^{\circ}47.79\text{N}$ ,  $173^{\circ}10.80\text{E}$ ) and was primarily influenced by the Alaskan Stream. The Alaskan Stream originates in the Gulf of Alaska and turns into the Bering Sea through the Aleutian Islands passages where it is the dominant source of relatively warm, fresh and nutrient-rich water (Reed and Stabeno, 1994). AM4-1 was collected offshore of the northern side of Amchitka Island ( $51^{\circ}42.72\text{N}$ ,  $179^{\circ}23.83\text{W}$ ). The US National Herbarium of the Smithsonian Institution in Washington, DC provided a third sample collected live in 1969 from 25 m deep offshore of the northeast side of Amchitka Island (AM-KR-80;  $51^{\circ}41.67\text{N}$ ,  $179^{\circ}28.33\text{W}$ ). Both specimens from offshore Amchitka Island were bathed by the Bering Sea.

### 2.2 Sample preparation and analyses

Untreated algal specimens AM4-1 and Attu 11-4 were sectioned in half and roughly polished onboard the research cruise. A 3-mm thick slice was removed from the museum specimen AM-KR-80 and mounted onto thin-section glass. In the lab, the sections were polished with decreasing grit sizes on a Struers Labopol polishing disk. Polished sections were then photographed using an Olympus reflected light microscope attached to an automated sampling stage-imaging system equipped with geo.TS software (see Hetzinger et al. (2009) for details). Annual increments in the skeleton were clearly visible in the resulting high quality images and were digitally mapped using the geo.TS software. This allowed for the location of each sample milled for stable



**Fig. 2.** Photomosaic of polished section of specimen AM4-1 with laser transect and micromill path. Micromilling path ran parallel to growth increments. Clear annual growth increments from 2003 to 1968 were used in conjunction with Mg/Ca measured by laser ablation inductively coupled plasma mass spectrometry to develop a robust growth chronology for this specimen. Samples for stable isotope analysis were micromilled directly adjacent to the laser transects.

isotope analysis (see below) to be carefully digitized on the photomosaic (Fig. 2). In addition, the widths of each of the growth increments were measured using the geo.TS software.

Polished and photographed sections were cleaned in an ultrasonic bath for three ten-minute intervals with deionized water and dried overnight. Working from the outside edge of the specimen which represented the most recent growth toward the oldest part of the sample, skeletal material for stable isotope analyses was removed by a high-precision, computer-driven micromill attached to an x, y, and z stage using digitized milling path positions. Sampling resolution for stable isotope analysis varied from one to twelve samples per growth increment depending on the width of the growth increment. Removed material was analyzed for  $\delta^{13}\text{C}$  ( $\delta^{13}\text{C} = \text{‰}$  deviation of the ratio of stable carbon isotopes  $^{13}\text{C}:^{12}\text{C}$  relative to Vienna Pee Dee Belemnite Limestone Standard (VPDB) and  $\delta^{18}\text{O}$  ( $\delta^{18}\text{O} = \text{‰}$  deviation of the ratio of stable oxygen isotopes  $^{18}\text{O}:^{16}\text{O}$  relative to Vienna Pee Dee Belemnite Limestone Standard (VPDB)). AM4-1 samples were introduced into a Thermo-Finnigan MAT253 gas source isotope ratio mass spectrometer via a Finnigan Gas Bench in the Geobiology Isotope Laboratory at the University of Toronto. One standard deviation of the mean of duplicate measurements was  $\pm 0.16\text{‰}$  for  $\delta^{13}\text{C}$  and  $\pm 0.08\text{‰}$  for  $\delta^{18}\text{O}$ . At least 10% of all samples were run in duplicate. The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of AM-KR-80 and Attu 11-4 were analyzed at Erlangen University, Germany according to Hetzinger et al. (2009).

## 2.3 Data analyses

The predicted isotopic equilibrium values for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in inorganic high-Mg calcite were estimated from the equations of Romanek et al. (1992) and Kim and O'Neil (1997), respectively. To account for the average 9.9 mol % Mg content in the skeleton (from Hetzinger et al., 2009), 0.24‰ and 1.68‰ were added to the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values, respectively, according to Jiménez-López et al. (2004, 2006). The  $\delta^{13}\text{C}$  value of seawater was calculated from the average of six measurements from less than 15 m depth taken in June and August during two cruises in the northern Pacific during 1992 and 1993 (cruise ID: 31VIC92\_0 and 3250210\_1; data obtained from <http://cdiac.ornl.gov/oceans/home.html>; Key et al. (2004)). The  $\delta^{18}\text{O}$  value of seawater was calculated from the average of 33 measurements from less than 15 m depth taken in June and August in 1990, 1993, and 1995 (data obtained from <http://data.giss.nasa.gov/o18data>; Cooper et al. (1997), Munchow et al. (1999), and Schmidt et al. (1999)).

Chronologies developed in Halfar et al. (2007) and Hetzinger et al. (2009) (also see Sect. 3.1) were applied to the specimens. Isotope data were averaged to annual resolution. T-tests compared average  $\delta^{13}\text{C}$  values from 1937 to 1967 for AM-KR-80 and Attu 11-4 and from 1968 to 2003 for AM4-1 and Attu 11-4. Attu 11-4 was combined with AM4-1 from 1967–2003 and the dataset was smoothed using a 7-year running average from 1937–2003. The line of best fit was calculated using SigmaPlot (Systat Software Inc., San Jose, CA) for this dataset to determine decadal rates of decrease from the 1960s to 2003. The specimen-specific offset for AM-KR-80 (see Sect. 3.3) prevented the inclusion of this sample in this dataset. The Aleutian Low Pressure Index (ALPI), the most important index of climate-ocean dynamics in the North Pacific/Bering Sea (Benson and Trites, 2002; McFarlane et al., 2000). Annually-resolved ALPI data (Beamish et al. (1997); <http://www.pac.dfo-mpo.gc.ca/science/species-especies/climatology-ie/cori-irco/indices/alpi.txt>) was also smoothed with a 7-year running mean. In order to create a robust dataset for time series analysis, each of the original annually-resolved algal  $\delta^{13}\text{C}$  records were normalized by subtracting the mean and dividing by the standard deviation. The resulting records were then combined to form a dataset comprised of Attu 11-4 and AM-KR-80 from 1937 to 1967 and Attu 11-4 and AM4-1 from 1968 to 2003. The line of best fit was calculated using SigmaPlot and the resulting residuals were used to produce a detrended  $\delta^{13}\text{C}$  dataset. Wavelet analysis (Torrence and Compo, 1998) using IDL Wavelet Toolkit (available at: <http://paos.colorado.edu/research/wavelets/>) was applied to the combined and detrended dataset to determine the dominant modes of climate variability.



### 3 Results

#### 3.1 Growth increments and specimen chronologies

In *Clathromorphum* sp., seasonal decreases in temperature and light during winter periods reduce the calcification rate of the algae resulting in growth increment lines in the skeleton (Adey, 1965; Halfar et al., 2007; Hetzinger et al., 2009). In addition, conceptacles, which are annually-formed reproductive structures (Adey, 1965) were also present (Fig. 2). Therefore, the clear growth increments visible here (Fig. 2) were assumed to be annual. The width of the annual growth increments varied from 140 to 680  $\mu\text{m}$  with an average of 381  $\mu\text{m}$  for all three specimens. There was no ontogenetic or overall trend in annual growth increment widths over time in any of the specimens.

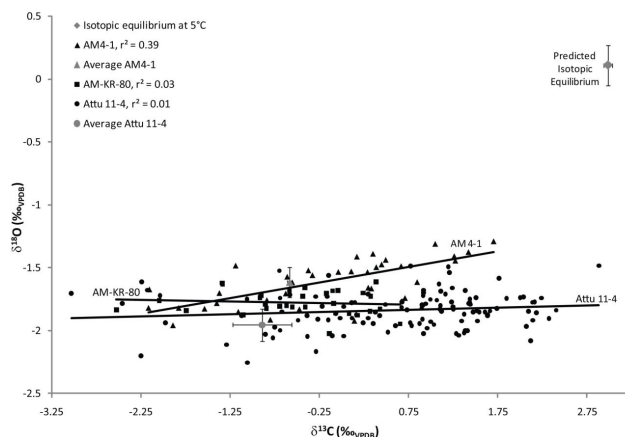
Seasonal variability in Mg/Ca ratios in all of the specimens and  $\delta^{18}\text{O}$  values, as well as absolute dating by U/Th, in Attu 11-4 confirmed the annual periodicity of the growth increments (Halfar et al., 2007; Hetzinger et al., 2009). The outermost growth increment in all of the specimens was formed during the summer of the specimen collection and did not represent a whole year of growth. In specimens AM4-1 and Attu 11-4, the year prior to collection was assigned to the first full skeletal growth increment. In specimen AM-KR-80, the first full year of growth was not sampled and 1967 was assigned to the second full growth increment. Therefore, from Amchitka Island, 35 years were sampled from 1968 to 2003 in specimen AM4-1 and 31 years were sampled from 1937 to 1967 in AM-KR-80. From Attu Island, 116 years were sampled from 1887–2003 in specimen Attu 11-4.

#### 3.2 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotopes

Annually-averaged  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values ranged from  $-3.0$  to  $2.9\text{‰}$  and  $-2.3$  to  $-1.3\text{‰}$ , respectively, for all specimens (Fig. 3). The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values positively correlated in AM4-1 ( $r^2 = 0.51$ ,  $p < 0.0001$ ), but did not correlate in Attu 11-4 and AM-KR-80 (Fig. 3). Average  $\delta^{13}\text{C}$  values for Attu 11-4 and AM4-1 were depleted relative to predicted isotopic equilibrium by 3.9 and 3.6 $\text{‰}$ , respectively, for the period of 1992 and 1993 (Fig. 3). Average  $\delta^{18}\text{O}$  values for the same specimens were depleted relative to predicted isotopic equilibrium by 2.1 and 1.7 $\text{‰}$ , respectively, for the period of 1990, 1993, and 1995 (Fig. 3). Isotope values for AM-KR-80 were not compared to predicted isotopic equilibrium as this specimen was collected prior to the early 1990s and before instrumental measurements of seawater isotopes were obtained close to the Aleutian Islands.

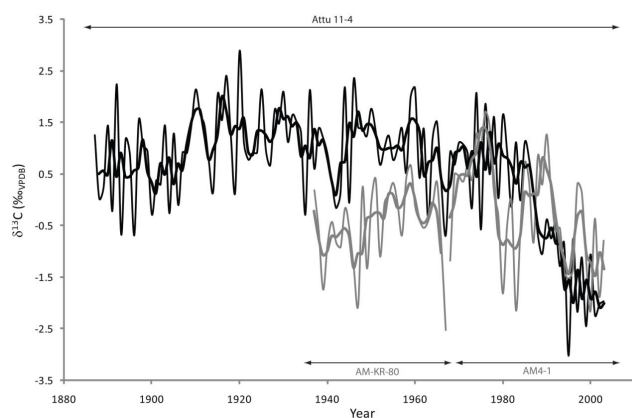
#### 3.3 $\delta^{13}\text{C}$ records

The  $\delta^{13}\text{C}$  values in AM4-1 and Attu 11-4 decreased from the 1970s to 2003. Since AM-KR-80 did not similarly decrease, no ontogenetic trend in  $\delta^{13}\text{C}$  values was present with age. Based on the smoothed 3-year running mean of the annually



**Fig. 3.** The  $\delta^{18}\text{O}$  values plotted against the  $\delta^{13}\text{C}$  values for the skeleton of three specimens of coralline algae with regression lines. Larger grey symbols represent the average  $\delta^{13}\text{C}$  (for 1992–1993) and  $\delta^{18}\text{O}$  (for 1990, 1993, and 1995) for Attu11-4 and AM4-1. Predicted isotopic equilibrium for inorganic calcite is plotted (grey diamond) based on the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for seawater from 1992–1993 and 1990, 1993, and 1995, respectively, and equations from Romanek et al. (1992) and Kim and O’Neil (1997), respectively. In order to account for the fact that coralline algae are High Mg-calcite, the equation for  $\delta^{18}\text{O}$  value incorporated the addition of 0.17 $\text{‰}$  for each mol % Mg according to Jiménez-López et al. (2004). The equation for  $\delta^{13}\text{C}$  value incorporated the addition of 0.024 $\text{‰}$  for each mol % Mg according to Jiménez-López et al. (2006). The value of 9.9 mol % Mg used was the median value from the range given in Hetzinger et al. (2009). Error bars indicate one standard error around the average. Error bars not visible are smaller than symbol. Predicted equilibrium is not plotted for AM-KR-80 as this sample was collected prior to the early 1990s.

interpolated data,  $\delta^{13}\text{C}$  values in the longest dated record, Attu 11-4, increased from 0.6 $\text{‰}$  in 1887 to a maximum of 2.0 $\text{‰}$  in 1916 before decreasing to  $-2.0\text{‰}$  in 2003 (Fig. 4). There was an overall trend toward positive  $\delta^{13}\text{C}$  values in AM-KR-80 (1937–1967), although  $\delta^{13}\text{C}$  values were higher at the start of the record than at the end ( $-0.2\text{‰}$  and  $-1.0\text{‰}$ , respectively) (Fig. 4). AM-KR-80 was collected prior to the beginning of growth of AM4-1, so direct comparisons between the two records are difficult, however  $\delta^{13}\text{C}$  values at the end of the AM-KR-80 record in 1967 were 0.6 $\text{‰}$  lower than at the start of the AM4-1 record in 1968 (Fig. 4). In addition, the  $\delta^{13}\text{C}$  values for AM-KR-80 (average  $\delta^{13}\text{C} = -0.5\text{‰}$ ) were significantly lower than for Attu 11-4 (average  $\delta^{13}\text{C} = 1.0\text{‰}$ ) from 1937–1967 (t-test,  $p < 0.0001$ ) while  $\delta^{13}\text{C}$  values in AM4-1 were the same as Attu 11-4 (average  $\delta^{13}\text{C} = -0.2$  for both) from 1968–2003. The  $\delta^{13}\text{C}$  values from the best-fit line were relatively constant from the 1940s to the 1960s and then decreased 2.5 $\text{‰}$  from the 1960s to 2000 (Fig. 5). Decadal rates of decrease were 0.3 $\text{‰}$  for the 1960s, 0.5 $\text{‰}$  for the 1970s, 0.7 $\text{‰}$  for the 1980s and 0.95 $\text{‰}$  for the 1990s (Fig. 5). Wavelet analysis of the detrended and



**Fig. 4.** Annually-resolved  $\delta^{13}\text{C}$  values for three *Clathromorphum nereostratum* specimens collected offshore of the Aleutian Islands with 3-year running mean in bold.

combined  $\delta^{13}\text{C}$  dataset documents significant spectral power at 4–7 years during the 1970s and at  $\sim 16$  years throughout the record (Fig. 6).

## 4 Discussion

### 4.1 Carbon and oxygen isotopes

*C. nereostratum* forms high-Mg calcite depleted in both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  relative to predicted isotopic equilibrium (Fig. 3). However, since  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  co-varied in only one specimen (AM4-1), and the range in  $\delta^{18}\text{O}$  values was small, we hypothesized that the correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values in this specimen largely reflected anthropogenically-driven changes in the isotopes resulting from decreasing  $\delta^{13}\text{C}_{\text{DIC}}$  ( $\delta^{13}\text{C}$ -Suess effect; see below) and increasing temperature/decreasing salinity (warmer/less saline; see Halfar et al. (2007)), rather than a kinetic effect common to all *C. nereostratum*. Depleted  $\delta^{18}\text{O}$  values relative to predicted equilibrium are consistent with previous studies. This offset is expected to be species-specific and constant over time, thus facilitating the use of coralline algal-derived oxygen isotope archives for paleoceanographic reconstructions (e.g., Halfar et al. (2000); Halfar et al. (2007); Halfar et al. (2008); Lee and Carpenter (2001); Wefer and Berger (1991)). Similar to  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$  values in *C. nereostratum* were also depleted relative to predicted isotopic equilibrium (Fig. 3). In addition, the range in  $\delta^{13}\text{C}$  values from  $-3.0\text{‰}$  to  $2.9\text{‰}$  measured here compared well to previous studies that reported values ranging from  $-3.6\text{‰}$  to  $2.2\text{‰}$  (Milliman, (1974); Rahimpour-Bonab (1997); Wefer and Berger (1991)). Metabolic processes such as respiration and photosynthesis may alter  $\delta^{13}\text{C}$  values resulting in observations that deviate from predictions based on isotopic equilibrium (Swart, 1983). Respiration in the calcifying microenvironment may cause  $^{13}\text{C}$ -

depletion in  $\text{CO}_2$ . On the other hand, photosynthesis may cause  $^{13}\text{C}$ -enrichment in the same  $\text{CO}_2$  microenvironment within the skeleton (i.e., photosynthesis removes  $^{12}\text{C}$ ). The algal  $\delta^{13}\text{C}$  values measured were depleted relative to equilibrium predictions. This result indicates that respiratory  $\text{CO}_2$  contributed a significant amount of the carbon in the skeleton (Borowitzka, 1977).

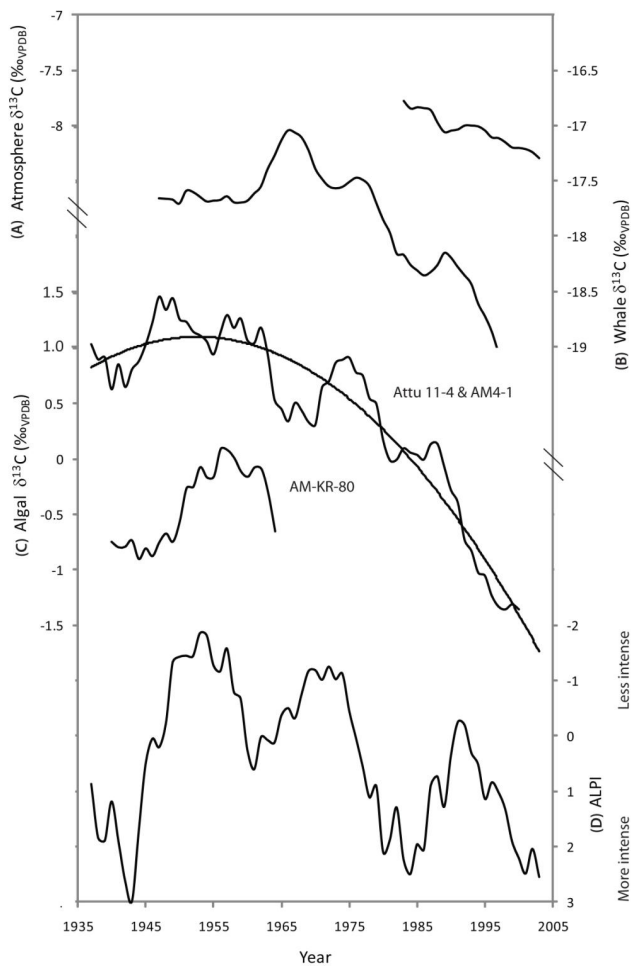
### 4.2 $\delta^{13}\text{C}$ records

Average  $\delta^{13}\text{C}$  values in AM-KR-80 were significantly lower than in Attu 11-4. Although a specimen-specific effect cannot be ruled out, we hypothesized that the lower  $\delta^{13}\text{C}$  values more likely resulted from the lower light levels to which the deeper AM-KR-80 (25 m) plant was exposed to during growth resulting in decreased photosynthesis relative to Attu 11-4 and AM4-1 (10 m) plants. Light levels are known to influence growth rates in coralline algae (Adey, 1970) and presumably photosynthesis as well. Decreased photosynthesis from lower light levels would have reduced discrimination against  $\delta^{13}\text{C}$  during growth, resulting in decreased  $\delta^{13}\text{C}$  values in the skeleton. Therefore, the collection depth of an algal specimen (or more specifically, differences in ambient light regimes) needs to be considered before comparing  $\delta^{13}\text{C}$  values among different specimens. In addition, since light levels may vary widely over very small spatial scales, for example as a result of local shading by macroalgae, averaging of more than one sample is recommended to reduce any influence of light on  $\delta^{13}\text{C}$  values.

The  $\delta^{13}\text{C}$  values in marine calcium carbonate organisms are driven by changes in the  $\delta^{13}\text{C}_{\text{DIC}}$ , as well as any metabolic and kinetic effects that were present during growth (McConnaughey, 1989). We hypothesized that kinetic effects were not a significant factor here (see Sect. 4.1), and assuming that offsets resulting from metabolic effects were constant over time and/or were accounted for by averaging multiple specimens, then  $\delta^{13}\text{C}$  values largely reflect  $\delta^{13}\text{C}_{\text{DIC}}$ . Thus, the skeletal  $\delta^{13}\text{C}$  records can reconstruct the primary factors influencing oceanic  $\delta^{13}\text{C}_{\text{DIC}}$ : anthropogenic  $\delta^{13}\text{C}$ -Suess effect (Andreasson and Schmitz, 1998), surface-ocean primary production (Krantz et al., 1987), upwelling events (Killingley and Berger, 1979), and water column stratification (Arthur et al., 1983).

### 4.3 Long-term decrease in $\delta^{13}\text{C}$ values

The decline in  $\delta^{13}\text{C}$  values recorded by the coralline algal specimens examined in this study clearly exceeds what can be attributed to the  $\delta^{13}\text{C}$ -Suess effect alone (Fig. 5). The  $\delta^{13}\text{C}$  values in bowhead whale baleen and steller sea lions bone collagen (Schell, 2000, 2001; Hirons et al., 2001) also declined at an enhanced rate; therefore, an algal-specific effect or site-specific variability were unlikely to be the primary cause of the decline observed in our study. It would appear more likely that changes in the  $\delta^{13}\text{C}_{\text{DIC}}$  pool to which



**Fig. 5.** (A) Annual atmospheric  $\delta^{13}\text{C}$  values from Pt. Barrow, Alaska (data from Keeling et al. (2001); [http://scrippsco2.ucsd.edu/data/flask\\_co2\\_and\\_isotopic/monthly\\_iso/monthly\\_ptb\\_c13.csv](http://scrippsco2.ucsd.edu/data/flask_co2_and_isotopic/monthly_iso/monthly_ptb_c13.csv)), (B) the  $\delta^{13}\text{C}$  values from the baleen of bowhead whales (data from Schell et al. (2001)), (C) the  $\delta^{13}\text{C}$  values from algal specimen AM-KR-80 and combined  $\delta^{13}\text{C}$  values from specimens Attu 11-4 (1937–1967) and AM4-1 and Attu 11-4 (1968–2003) with line of best fit calculated using SigmaPlot (Systat Software Inc., San Jose, CA), and (D) ALPI values (data from Beamish et al. (1997); <http://www.pac.dfo-mpo.gc.ca/science/species-especes/climatology-ie/cori-irco/indices/alpi.txt>). Whale, algal and ALPI datasets were smoothed with a 7-year running mean. Algal and whale  $\delta^{13}\text{C}$  values decreased at a rate exceeding that expected due solely to the  $\delta^{13}\text{C}$ -Suess effect and likely reflects the combined influence of the  $\delta^{13}\text{C}$ -Suess effect and an intensifying ALPI. Note that the y-axis for the ALPI is reversed.

both coralline algae and phytoplankton were exposed (the latter subsequently transmitted via the food web to whales and sea lions) drove the strongly decreasing  $\delta^{13}\text{C}$  values. Decreases in skeletal  $\delta^{13}\text{C}$  values greater than that observed in atmospheric  $\text{CO}_2$  have also been found in corals from restricted environments, and in these cases, the increased rate of decline was attributed to enhanced input of organic mate-

rial that oxidized to release isotopically depleted  $\text{CO}_2$  (Swart et al., 2010). Our field site in the central Aleutian Islands is exposed to the open ocean, and thus an alternative explanation is needed to explain the rate of decline measured here.

The  $\delta^{13}\text{C}_{\text{DIC}}$  in the northern North Pacific Ocean and Bering Sea regions is largely controlled by biological activity and upwelling/deep-water mixing (Tanaka et al., 2003). Decreases in primary productivity would increase the amount of  $\text{CO}_2$  in surface waters, thus reducing carbon fractionation during the calcification process and leading to lower  $\delta^{13}\text{C}$  values in the resulting skeleton. In fact, a decline in phytoplankton cell growth rates, and hence primary productivity, has been hypothesized to drive the declining trends in the whale baleen and sea lion bone collagen  $\delta^{13}\text{C}$  (Schell, 2000, 2001; Hirons et al., 2001). However, available evidence does not support a decrease in new primary production (Hunt Jr et al., 2002). In addition, there is no multi-year trend of decrease in growth-increment widths in the three *C. nereostreatum* specimens over the past 50 years.

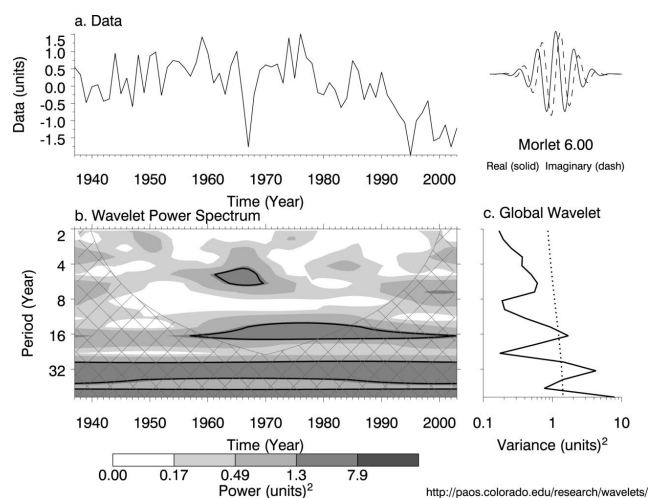
An increase in upwelling and/or deepening of the mixed layer would also change  $\text{CO}_2$  concentrations in the surface waters of northern North Pacific Ocean and Bering Sea (Patra et al., 2005), and thus  $\delta^{13}\text{C}_{\text{DIC}}$  values and  $\delta^{13}\text{C}$  values of the algal skeleton. Authors of previous studies have suggested that upwelling and deep mixing may reduce the influence of the Suess effect in the subarctic Pacific as a consequence of dilution by deep water that has not been influenced by anthropogenic carbon emissions and the limited amount of time for  $\text{CO}_2$  equilibration to take place (Gruber et al., 1999; Quay et al., 1992; Schell, 2001; Sonnerup et al., 1999). However,  $\text{CO}_2$  concentrations increase and  $\delta^{13}\text{C}_{\text{DIC}}$  decreases with depth (e.g., Koopnick et al. (1972);  $\delta^{13}\text{C}_{\text{DIC}}$  decrease by up to  $\sim 2\%$  within the top 200 m of the water column in measurements from WOCE.P13N, <http://cdiac3.ornl.gov/waves/discrete>), and the ability of upwelling and/or mixing of deep water to drive surface water  $\delta^{13}\text{C}_{\text{DIC}}$  values has previously been reported by Bacastow et al. (1996). Increased  $\text{CO}_2$  concentrations resulting from more upwelling and/or deepening of the mixed layer theoretically decreases fractionation during calcification resulting in lower  $\delta^{13}\text{C}$  values of the skeleton. In addition, the deeper water brought up to the surface will have low  $\delta^{13}\text{C}_{\text{DIC}}$  values due to the remineralization of organic matter with depth, thus contributing to decreased  $\delta^{13}\text{C}_{\text{DIC}}$  in surface waters. The mixed layer depth in the subarctic North Pacific has shoaled in recent decades, which has been attributed to warming and freshening that in turn has produced enhanced stratification of the surface waters (Freeland et al., 1997); therefore, upwelling is likely the driving factor of the enhanced rate of decline in the  $\delta^{13}\text{C}$  proxy records. Changes in the Aleutian Low pressure system could explain the increase in upwelling. When the low pressure system was intense, oceanic upwelling under the centre of the Aleutian Low was increased (Reid, 1962; Thomson, 1981), bringing higher concentrations of  $\text{CO}_2$  with low  $\delta^{13}\text{C}$  values to the surface. This upwelled  $\text{CO}_2$  was

moved to the edges of the Alaska gyre via horizontal divergence (similar to other nutrients and biomass; Brodeur and Ware, 1992; Reid, 1962) and was incorporated into the Alaskan Stream. Once incorporated into the Alaskan Stream, the  $\text{CO}_2$ -rich water flowed southwestward along the continental slope of the Alaska Peninsula and entered the Bering Sea through the Aleutian Island Archipelago. By this mechanism,  $\text{CO}_2$ -rich water was transported to the environment in which the algal specimens grew. In contrast, when the Aleutian Low weakened, oceanic upwelling was reduced and water with less  $\text{CO}_2$  and lower  $\delta^{13}\text{C}$  values was brought to the surface. The ALPI, which is a measure of the intensity of the Aleutian Low (Beamish et al., 1997), indicates that the Aleutian Low has generally been increasing in strength since the late-1940s (Fig. 5). In addition, the large scale variability in the ALPI was mirrored with an approximately three-year lag in the algal  $\delta^{13}\text{C}$  records from 1937 to 1989, which corresponded to the 1989 regime shift evident in the ALPI and in biological records (Beamish et al., 1999; Hare and Mantua, 2000). The lag likely represents the interval of time between the change in the pressure system, increase or decrease in upwelling, and transport of the water to the central Aleutian Islands where the  $\delta^{13}\text{C}$  ultimately was taken up by the algae. The cause of the decoupling between the Aleutian Low and the algal  $\delta^{13}\text{C}$  records after the 1989 regime shift is unknown.

There is large spatial and temporal variability in upwelling and ocean currents, and consequently  $\text{CO}_2$  concentrations, throughout the subarctic North Pacific (Stabeno et al., 2004; Murphy et al., 2001). Therefore, the location of a specific  $\delta^{13}\text{C}_{\text{DIC}}$  record relative to upwelling and/or currents transporting the upwelled water explains the large variability in  $\delta^{13}\text{C}$  instrumental and/or proxy records. The variable rate of decline recorded by the different instrumental and proxy records likely reflects local changes in  $\delta^{13}\text{C}_{\text{DIC}}$  instead of basin-wide changes. As a consequence, extrapolation of a single record from one location to the entire basin provides an incomplete picture of carbon dynamics in the northern North Pacific Ocean and Bering Sea. Additional records are urgently needed to further understand changes occurring and to calculate the role of subarctic oceans in taking up anthropogenic  $\text{CO}_2$ .

#### 4.4 Detrended $\delta^{13}\text{C}$ variability

The significant spectral power on interannual timescales (4–7 years; Fig. 6) in the detrended and combined  $\delta^{13}\text{C}$  record corresponds to fluctuations of the El Niño Southern Oscillation (ENSO). Niebauer (1988) and Emery and Hamilton (1985) suggested an atmospheric link between the tropical ENSO events and the northern Pacific/Bering Sea related to the winter position of the Aleutian Low such that it is intense and shifts eastward during El Niño conditions, driving warm, moist air northward along the northeast Pacific coast towards Alaska and into the Bering Sea. The increase in intensity of the Aleutian Low associated with El Niño



**Fig. 6.** The wavelet power spectrum for  $\delta^{13}\text{C}$  values from detrended and combined dataset from 1937 to 2003. The contour levels are chosen so that 75%, 50%, 25%, and 5% of the wavelet power is above each level, respectively. The cross-hatched region is the cone of influence, where zero padding has reduced the variance. Black contour is the 10% significance level, using a white-noise (autoregressive lag1) background spectrum. Analyses made using IDL Wavelet Toolkit (Torrence and Compo (1998); available at: <http://paos.colorado.edu/research/wavelets/>).

conditions increased upwelling, bringing more  $\text{CO}_2$ -rich water with low  $\delta^{13}\text{C}$  values into the surface waters. In contrast, a weakened Aleutian Low corresponded to cold events in the tropics (Emery and Hamilton, 1985). This supports a link between the tropical Pacific ENSO, and the subarctic Aleutian Low and algal  $\delta^{13}\text{C}$  records drove the 4–7 year variability. The significant spectral power on approximately 16-year timescales (Fig. 6) was generally consistent with the bidecadal (15–25 year) variations in the North Pacific Index (NPI) (Minobe, 1999). The NPI is another time series index representing the Aleutian Low, and is inversely correlated to the ALPI. Thus similar patterns between the NPI and the algal  $\delta^{13}\text{C}$  values was expected. These relationships support the influence of shifts in climate regimes (i.e., ENSO, PDO) on the surface water  $\delta^{13}\text{C}_{\text{DIC}}$  values, in addition to the anthropogenic  $\delta^{13}\text{C}$ -Suess effect.

## 5 Summary

The  $\delta^{13}\text{C}$  values from coralline algae clearly demonstrated a decrease in  $\delta^{13}\text{C}$  values over the past 30 years exceeding that resulting solely to the anthropogenic  $\delta^{13}\text{C}$ -Suess effect. The enhanced rate of decline was consistent with records from some marine mammals. This indicates that the  $\delta^{13}\text{C}_{\text{DIC}}$  which was taken up by primary producers, i.e., phytoplankton at the bottom of the marine food web and benthic coralline algae, was the cause of the enhanced rate of decline.

We hypothesized that a combination of the  $\delta^{13}\text{C}$ -Suess effect and an increasingly intense Aleutian Low drove the strongly decreasing  $\delta^{13}\text{C}$  values. An intense Aleutian Low increased upwelling of  $\text{CO}_2$ -rich water to the surface with a low  $\delta^{13}\text{C}$  signature. The higher concentrations of  $\text{CO}_2$  in the surface water will decrease fractionation by the algae during photosynthesis, lowering  $\delta^{13}\text{C}$  values of the skeleton. The combined and detrended dataset varied on ENSO and bidecadal scales supporting an atmospheric teleconnection between the tropics and the subarctic Pacific. This study demonstrates the utility of coralline algal  $\delta^{13}\text{C}$  records in understanding the factors influencing  $\delta^{13}\text{C}_{\text{DIC}}$ , and cautions that spatially-limited records should not be extrapolated to describe carbon dynamics for the entire northern Pacific Ocean and Bering Sea.

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