

Freshening of the Alaska Coastal Current recorded by coralline algal Ba/Ca ratios

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[1] Arctic Ocean freshening can exert a controlling influence on global climate, triggering strong feedbacks on ocean-atmospheric processes and affecting the global cycling of the world's oceans. Glacier-fed ocean currents such as the Alaska Coastal Current are important sources of freshwater for the Bering Sea shelf, and may also influence the Arctic Ocean freshwater budget. Instrumental data indicate a multiyear freshening episode of the Alaska Coastal Current in the early 21st century. It is uncertain whether this freshening is part of natural multidecadal climate variability or a unique feature of anthropogenically induced warming. In order to answer this, a better understanding of past variations in the Alaska Coastal Current is needed. However, continuous long-term high-resolution observations of the Alaska Coastal Current have only been available for the last 2 decades. In this study, specimens of the long-lived crustose coralline alga *Clathromorphum nereostratum* were collected within the pathway of the Alaska Coastal Current and utilized as archives of past temperature and salinity. Results indicate that coralline algal Mg/Ca ratios provide a 60 year record of sea surface temperatures and track changes of the Pacific Decadal Oscillation, a pattern of decadal-to-multidecadal ocean-atmosphere climate variability centered over the North Pacific. Algal Ba/Ca ratios (used as indicators of coastal freshwater runoff) are inversely correlated to instrumentally measured Alaska Coastal Current salinity and record the period of freshening from 2001 to 2006. Similar multiyear freshening events are not evident in the earlier portion of the 60 year Ba/Ca record. This suggests that the 21st century freshening of the Alaska Coastal Current is a unique feature related to increasing glacial melt and precipitation on mainland Alaska.

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1. Introduction

[2] Freshening of the Arctic Ocean can have considerable impacts on ocean stratification and ventilation [Woodgate *et al.*, 2005], affecting the Arctic sea ice budget [Paquette and Bourke, 1981; Shimada *et al.*, 2006; Mizobata *et al.*, 2010]. Furthermore, Arctic freshening can disrupt the flow of large-scale circulation features such the Atlantic thermohaline circulation [Rahmstorf, 1995; Peterson *et al.*, 2002; Woodgate *et al.*, 2006; Kuhlbrodt *et al.*, 2009]. Recent studies indicate a significant warming and freshening of the Bering Strait throughflow into the Arctic Ocean [Woodgate and Aagaard, 2005; Royer and Grosch, 2006; Woodgate *et al.*, 2006; Ladd

and Stabeno, 2009; Mizobata *et al.*, 2010; Woodgate *et al.*, 2010]. The Bering Strait throughflow accounts for approximately one third of the Arctic Ocean freshwater budget, a quarter of which is determined by freshwater influx from the Alaska Coastal Current, which originates in the Gulf of Alaska and later combines with freshwater from the rivers of western Alaska [Woodgate and Aagaard, 2005; Aagaard *et al.*, 2006; Woodgate *et al.*, 2006]. The Alaska Coastal Current is a narrow coastal jet fed by terrestrial freshwater runoff from British Columbia and mainland Alaska [Weingartner *et al.*, 2005]. It flows westward along the southern coastline of Alaska, through the narrow Unimak Pass and into the Bering Sea (Figure 1a) [Schumacher *et al.*, 1982; Stabeno *et al.*, 2002]. A recent increase in glacial melt in southeast Alaska suggests a growing freshwater contribution of the Alaska Coastal Current to Bering Strait throughflow [Arendt *et al.*, 2002; Royer and Grosch, 2006; Arendt *et al.*, 2009]. While a 20th century runoff record from Gulf of Alaska rivers permits retrospective examination of the Alaska Coastal Current, coastal observations of salinity appear to be better predictors of ACC freshwater variability [Weingartner *et al.*, 2005]. However, long-term high-resolution nearshore oceanographic

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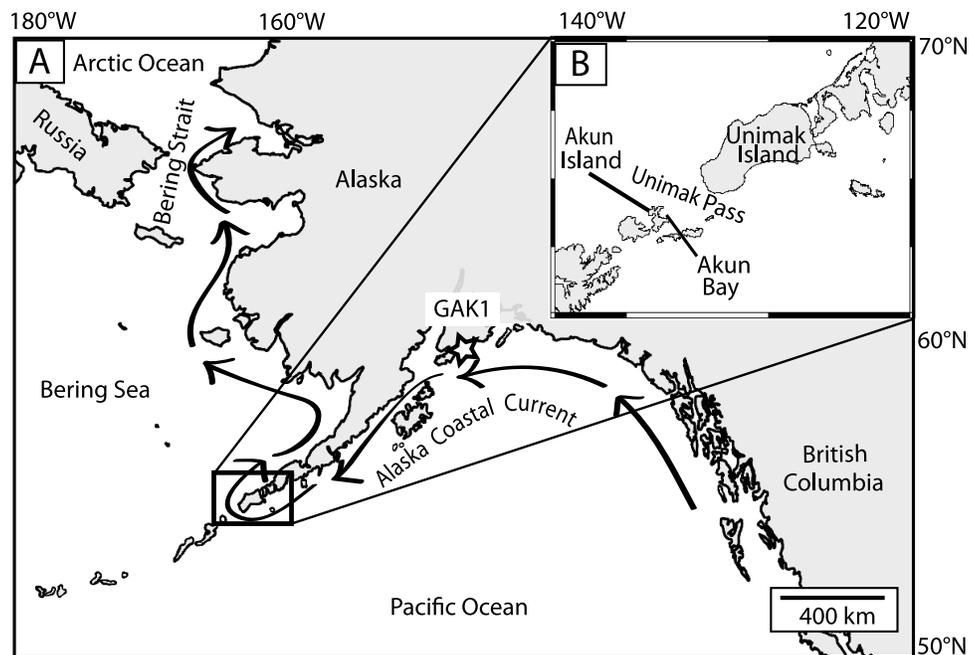


Figure 1. (a) Map of North Pacific/Bering Sea region and Aleutian archipelago. Arrows depict pathway of Alaska Coastal Current based on data from *Schumacher et al.* [1982]. Star represents location of GAK 1 oceanographic station. (b) Sample collection site in Akun Bay, west of Unimak Pass.

observations of Alaska Coastal Current freshwater variability are absent prior to the 1970s.

[3] In this study, we use the nearshore crustose coralline algae *Clathromorphum nereostratum* as a long-term archive for past temperature and salinity variations in the Alaska Coastal Current. High-Mg calcite secreting photosynthetic coralline algae are well-suited for midlatitude to high-latitude century-long oceanographic reconstructions on high-resolution timescales [*Halfar et al.*, 2007; *Kamenos et al.*, 2008; *Hetzinger et al.*, 2009]. Stable oxygen isotopes and Mg/Ca ratios from different species of *Clathromorphum* track in situ sea surface temperatures as well as large-scale climate patterns such as the El Niño Southern Oscillation, North Atlantic Oscillation and Pacific Decadal Oscillation [*Halfar et al.*, 2007; *Gamboa et al.*, 2010].

[4] In contrast, Ba/Ca ratios in *Clathromorphum* display weak correlations with temperature [*Hetzinger et al.*, 2011], but respond to variability in surface ocean Ba content. Upper ocean Ba concentrations are influenced by upwelling of cold Ba-rich deep waters, or by coastal influx of suspended sediments [*Alibert et al.*, 2003]. In open ocean settings, Ba is often depleted in surface waters and enriched in deep waters due to the uptake of Ba as barite (Ba SO_4), associated with the formation of biological particulate matter [*Chan et al.*, 1977; *Dehairs et al.*, 1980; *Collier and Edmond*, 1984; *Dehairs et al.*, 1987; *Bishop*, 1988; *Lea and Boyle*, 1989; *Lea et al.*, 1989; *Lea and Boyle*, 1991; *Falkner et al.*, 1993]. However, corals growing close to shore experience higher levels of Ba compared to those in the open ocean [*Shen and Boyle*, 1988]. Ba is abundant in estuarine environments due to high terrestrial freshwater and sediment influx into coastal waters [*Coffey et al.*, 1997]. Ba previously absorbed by riverine clay minerals is released into the ocean upon encountering more alkaline elements (i.e., Ca, Mg, and Sr) present in the sea-

water [*Hanor and Chan*, 1977; *Li and Chan*, 1979; *Shen and Boyle*, 1988; *Guay and Falkner*, 1998; *Falkner et al.*, 1994; *Sinclair and McCulloch*, 2004]. Thereafter, Ba commonly behaves as a conservative dissolved tracer, and is incorporated into the carbonate skeleton of calcifying organisms in proportion to ambient seawater concentrations [*Lea et al.*, 1989]. Skeletal Ba/Ca ratios have proven to be a valuable proxy for seawater Ba/Ca, providing information on coastal sediment transport, freshwater discharge, salinity, as well as nutrient and alkalinity distributions [*Lea and Boyle*, 1989, 1991; *Sinclair et al.*, 1998; *McCulloch et al.*, 2003; *Sinclair and McCulloch*, 2004; *Fleitmann et al.*, 2007; *Grove et al.*, 2010]. However, these Ba/Ca-based proxy studies have typically been conducted in tropical, low-latitude regions. In the North Pacific where historical records are sparse, a proxy for long-term changes in freshwater variability of the Alaska Coastal Current would be highly valuable. Here we employ coralline algal Ba/Ca and Mg/Ca ratios to reconstruct temperature and salinity variability of the Alaska Coastal Current in order to demonstrate that a recent freshening episode of the Alaska Coastal Current is unprecedented during the last 60 years.

2. Methods

[5] In June 2008, living specimens of the coralline alga *Clathromorphum nereostratum* were collected at 10 m water depth using SCUBA from Akun Bay (54.2°N , 165.5°W) on the western shore of Unimak Pass, the main conduit for flow of the Alaska Coastal Current from the North Pacific into the Bering Sea (Figure 1b) [*Stabeno et al.*, 2002]. Samples were sectioned vertically and polished to $1\ \mu\text{m}$. High-resolution digital photomosaics of the polished specimens were scanned using an automated sampling stage-imaging

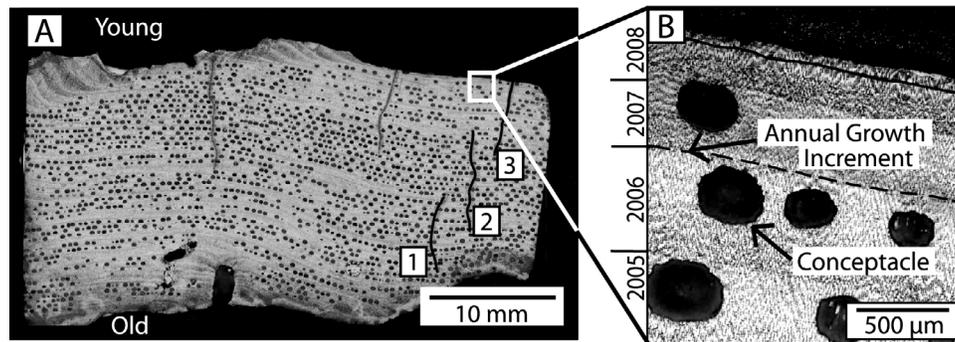


Figure 2. (a) Overview image of polished *C. nereostratum* thick section with overlapping laser transects (lines 1, 2, and 3). Element ratios obtained from overlapping sections were averaged. (b) Magnified view of alga depicting annual growth increments and conceptacle cavities.

system equipped with Geo.TS (Olympus Soft Imaging Systems) software (for details, see *Hetzinger et al.* [2009]). The resulting photomosaics enabled the identification of annual growth increments which are identified by the occurrence of rows of annually forming conceptacles (cavities containing reproductive structures) (Figures 2a and 2b). Laser-line transects were digitized along the growth axis of each sample using Geo.TS (Figures 2a and 3), carefully avoiding conceptacle cavities and areas of discontinuous growth. The resulting x,y coordinates were used for positioning line transects for Laser Ablation Inductively Coupled Plasma Mass Spectrometer (LA-ICP-MS) analysis.

[6] LA-ICP-MS analysis of Mg/Ca and Ba/Ca elemental ratios were conducted at the Earth System Science Research Centre at the University of Mainz Germany, using an Agilent 7500 ce Quadrupole ICP-MS attached to a New Wave Research UP-213 laser ablation system equipped with a large format cell. Laser measurements were performed using laser energy densities of 6 J/cm^2 , and helium as a carrier gas. Transect lengths were limited to $6000 \mu\text{m}$ in order to minimize the effect of ICP-MS drift and were analyzed at a scan speed of $10 \mu\text{m/second}$, with a $65 \mu\text{m}$ spot size and 10 Hz pulse rate. NIST SRM 610 (U.S. National Institute of Standard and Technology Standard Reference Material) glass reference material was used as an external standard. Data for NIST SRM 610 were extracted from the GeoReM database available from (http://georem.mpch-mainz.gwdg.de/sample_query_pref.asp). Detection limits were: Mg = 0.02 ppm, Ca = 5.47 ppm, Ba = 0.01 ppm. Additional details on the analytical setup used can be found in the works of *Jacob* [2006] and *Hetzinger et al.* [2011].

[7] Subannually resolved age models were constructed using annual variations in algal Mg/Ca. Calendar years were assigned to annual growth increments starting from 2008 (year of collection) and extending back in time. The Mg/Ca cycles were then graphically superimposed on a photomosaic of the sample surface depicting the laser transects where maxima in Mg/Ca were aligned with the center of each growth increment, and minima with growth increment transitions (Figure 3). Using the compiled information from the Mg/Ca cycles and photomosaics, subannual markers were assigned to the maxima (representing the warmest month of the year) and minima (representing the coldest month of the year) of each annual Mg/Ca cycle. Based on monthly sea surface temperature averages from bias-corrected satellite

measurements obtained from Reynolds Optimum Interpolation sea surface temperature analysis (1982–2008), the month exhibiting the warmest (coldest) temperature at Akun Bay was August (March) [*Reynolds et al.*, 2002]. Markers were assigned beginning at the first minimum (i.e., March 2007), followed by the first maximum (i.e., August 2006), and continuing back in time. The algal time series was linearly

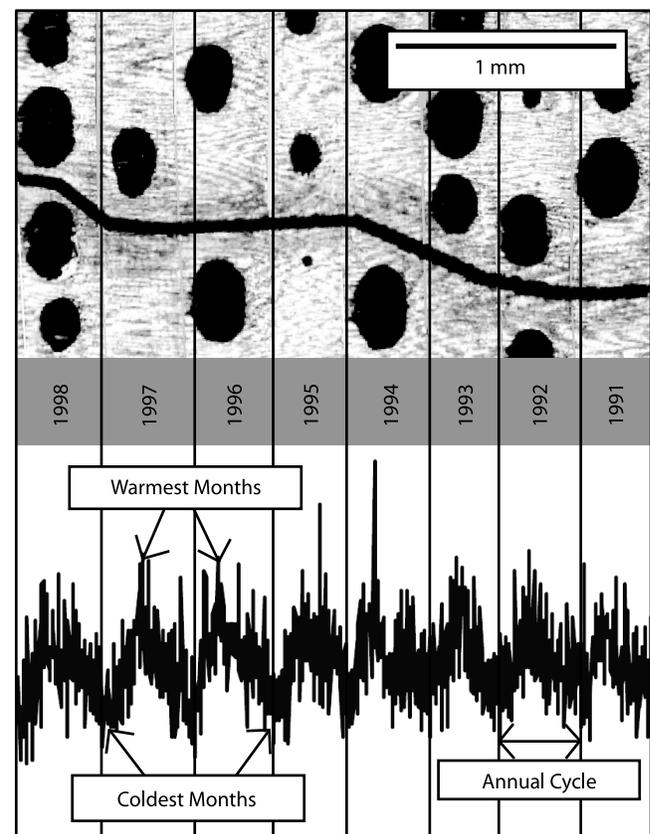


Figure 3. Algal Mg/Ca cycles obtained from LA-ICP-MS superimposed on photomosaic of sample cross section with laser transect. Mg/Ca measurements display distinct seasonal cycles. Areas with high (low) Mg/Ca ratios are interpreted to be summer (winter) periods of algal growth, with one full cycle representing 1 calendar year. Calendar years were assigned by counting annual growth increments.

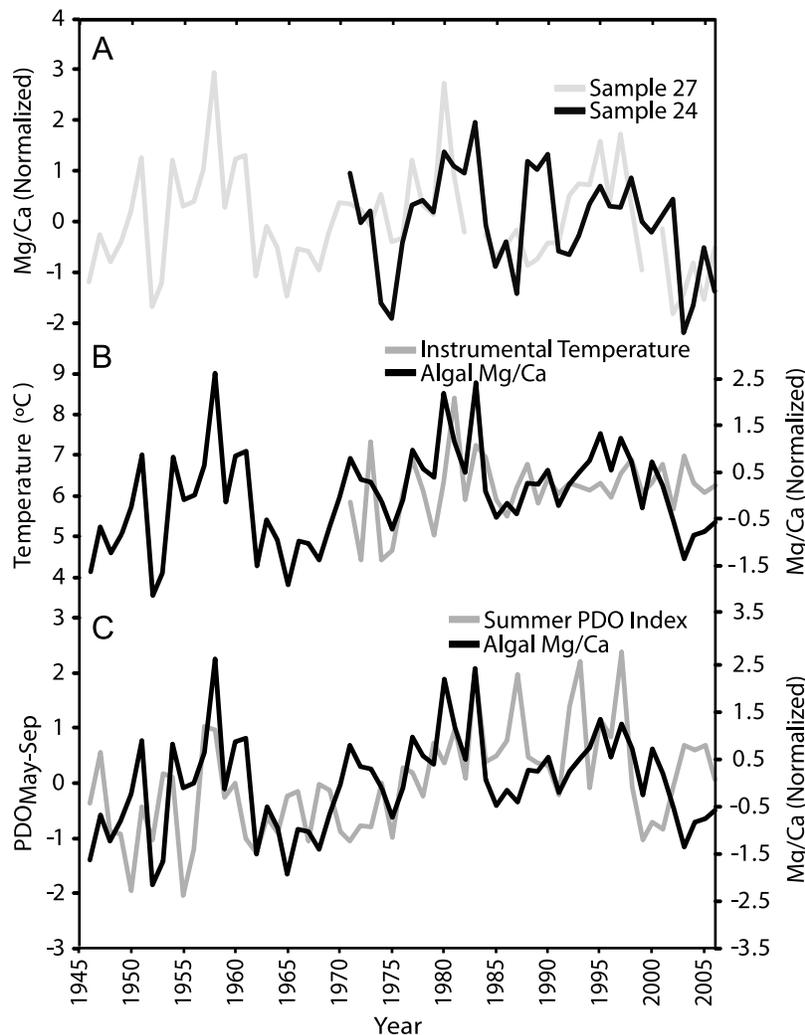


Figure 4. (a) *C. nereostratum* Mg/Ca time series from samples 24 and 27. Overlapping regions in laser transects were averaged to create the final Mg/Ca time series. (b) Annual algal Mg/Ca time series (averaged) compared to annual mean instrumental temperature from oceanographic station GAK 1 (1971–2006; $n = 35$, $r = 0.32$, $p = 0.06$). (c) Annual algal Mg/Ca correlated to Pacific Decadal Oscillation (May–September) index ($n = 60$, $r = 0.41$, $p = 0.001$).

interpolated between these anchor points using AnalySeries software [Paillard *et al.*, 1996] to obtain a proxy time series with monthly resolution. Since algal Ba/Ca ratios do not exhibit annual cyclicity, the anchor points derived from the Mg/Ca age model were adapted to the Ba/Ca data. In addition, given that coralline growth rates vary throughout the year (e.g., highest rates in summer, lowest in winter, insignificant or no growth between January and April) the 12 equidistant data points were assigned to growing season months according to a growth model established by Halfar *et al.* [2008].

[8] The final algal record was constructed from the average of two samples: sample 24 from 1971 to 2006; and sample 27 from 1946 to 2006 (Figure 4a). The resulting algal Mg/Ca and Ba/Ca time series were correlated to instrumental temperature and salinity observations. Since long-term, high-resolution in situ oceanographic data are nonexistent from Unimak Pass, sea surface temperature and salinity observations from oceanographic station GAK 1 (located within the

flow of the narrow Alaska Coastal Current at the mouth of Resurrection Bay, Alaska; 59.8°N, 149.5°W; Figure 1a), were used for correlations with algal elemental ratios (GAK 1 data are available from <http://www.ims.uaf.edu/gak1/>). GAK 1 observations from the early 1970s and 1980s are sparse and irregular [Janout *et al.*, 2010]. However, since 1991 more frequent quasi-monthly measurements of temperature and salinity have been made available using conductivity, temperature, depth recorder casts with accuracies of $\pm 0.1^\circ\text{C}$ and ± 0.2 psu for temperature and salinity, respectively [Royer and Grosch, 2006].

3. Results and Discussion

3.1. Mg/Ca–Temperature Relationship

[9] Linear regression analysis reveals that annually averaged algal Mg/Ca ratios are weakly correlated to annual mean sea surface temperatures at GAK 1, 1400 km to the east of the coralline algal collection site at Unimak Pass (Figure 4b;

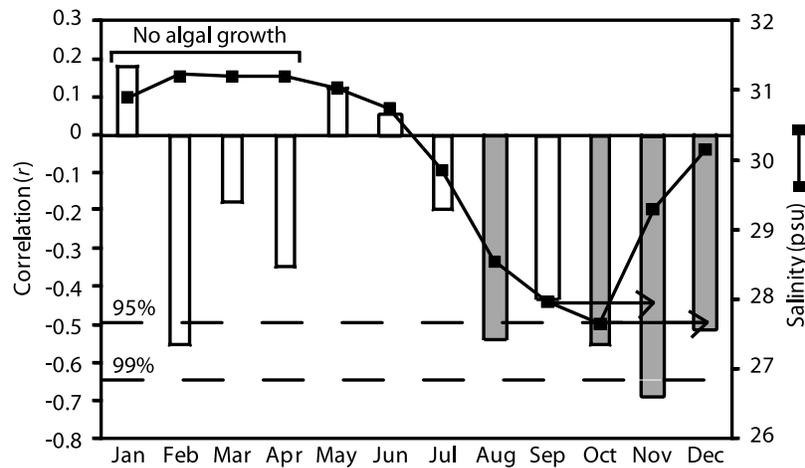


Figure 5. Correlation of annually averaged Ba/Ca values of *C. nereostratum* with monthly GAK 1 salinity (1991–2006). Black line indicates monthly salinity average at GAK 1 for the same time period. Arrows depict recording lag of algae due to transport time between GAK 1 and Unimak Pass. Note that algal growth is insignificant from January through April.

$n = 35$, $r = 0.32$, $p = 0.06$). In the absence of longer nearby multidecadal instrumental temperature time series, the algal Mg/Ca–temperature relationship was also compared with the large-scale pattern of the summer Pacific Decadal Oscillation (May–September) (Figure 4c; $n = 60$, $r = 0.41$, $p = 0.001$). Algal Mg/Ca ratios closely track the decadal-to-multidecadal variability of the Pacific Decadal Oscillation, the dominant pattern influencing North Pacific climate on 20–30 year periodicities [Mantua *et al.*, 1997]. While the expression of the Pacific Decadal Oscillation is strongest in the Gulf of Alaska, the Pacific Decadal Oscillation signal is likely advected from the Gulf of Alaska to Unimak Pass via the Alaska Coastal Current [Weingartner *et al.*, 2005]. This is consistent with a 117 yearlong *C. nereostratum* oxygen isotope record from the western Aleutian Islands located within the pathway of the Alaskan Stream, which also exhibited positive Pacific Decadal Oscillation correlations [Halfar *et al.*, 2007]. Here, algal Mg/Ca ratios closely track sea surface temperature patterns, although correlations with both instrumental temperatures and the Pacific Decadal Oscillation are significantly diminished after 2002. This divergence could reflect a salinity effect on the incorporation of Mg into the algal skeleton caused by strong freshening of the Alaska Coastal Current beginning in 2001. In fact, recent studies of high-Mg calcite in echinoderm skeletons and foraminiferal tests field-collected or cultured in different salinities have demonstrated a clear negative effect on Mg/Ca ratios [Ferguson *et al.*, 2008; Kisakürek *et al.*, 2008; Borremans *et al.*, 2009].

3.2. Timing of Alaska Coastal Current Freshwater Signal at Unimak Pass

[10] Annually averaged Ba/Ca ratios were compared to monthly instrumental GAK 1 salinities for the period of quasi-monthly instrumental observations (1991–2006) in order to determine the seasonal timing of the Alaska Coastal Current freshening at Unimak Pass. The annual cycle of sea surface salinity observed at GAK 1 is characterized by high values spanning from winter to spring (December–July), declining to the lowest values in the fall (August–November)

associated with the period of maximum discharge due to fall storm activity [Royer, 1982] and enhanced glacial melt (Figure 5, black line). Satellite-tracked drifter measurements have revealed an average transport time of ~ 2.5 months from the head of the Gulf of Alaska (approximate location of GAK 1) to Unimak Pass, located 1400 km to the west [Stabeno *et al.*, 2002]. Therefore, the significant negative correlations between annual Ba/Ca and monthly GAK 1 salinity from mid to late fall demonstrates the propagation of the September–November freshening signal at GAK 1 to the algal collection site, resulting in an increase in algal Ba/Ca values from October–December (Figure 5, gray bars). Significant Ba/Ca–GAK 1 salinity correlations during August are attributed to late spring snowmelt [Royer, 2005] in mainland Alaska. Correlations in late winter and early spring were not included in the analyses, as the algae do not exhibit significant growth during these months [Halfar *et al.*, 2008]. In the following we focus on comparing the fall maximum discharge (September–November) recorded by GAK 1 salinities with the lagged October–December algal Ba/Ca ratios.

3.3. Ba/Ca–Freshwater Relationship

[11] An algal Ba/Ca time series was constructed from the average of samples 24 and 27 (Figure 6a). Algal Ba/Ca (October–December) ratios are significantly correlated with GAK 1 (September–November) salinities (0–20 m) from 1971 to 2006 (Figure 6b; $n = 35$, $r = -0.65$, $p < 0.0001$). Furthermore, a brief freshening event recorded by GAK 1 in 1990 is recorded by both algal samples, with sample 27 showing a strong increase in Ba/Ca. This demonstrates that algal Ba/Ca ratios at Unimak Pass provide a continuous and reliable record of the Alaska Coastal Current freshwater signature. Algal Ba/Ca ratios can therefore be used to reconstruct Alaska Coastal Current freshwater transport prior to 1970 when instrumental observations are nonexistent.

[12] A recent freshening episode of the Alaska Coastal Current is represented by a decrease in GAK 1 salinities and an increase in algal Ba/Ca from 2001 to 2006 (Figure 6b, gray box). The multiyear episode of 21st century freshening

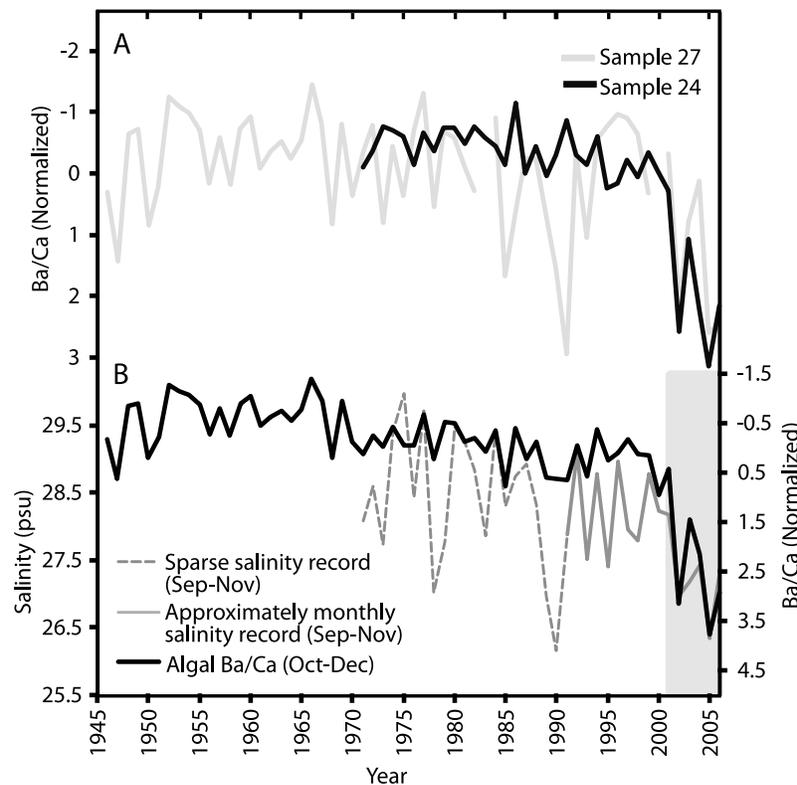


Figure 6. (a) *C. nereostratum* Ba/Ca time series from samples 24 and 27. Overlapping regions in laser transects were averaged to create the final Ba/Ca time series (shown in Figure 6b). (b) Subannual GAK 1 (September–November) highly correlates to (October–December) algal Ba/Ca (1971–2006) ($n = 35$, $r = -0.65$, $p < 0.0001$). The period of scarce oceanographic measurements (prior to 1991, where observations in 5 or more months of the year are missing) is indicated by dashed gray line. Period of quasi-monthly instrumental measurements (post 1991) is indicated by solid line. Grey bar highlights the significant multiyear freshening of the Alaska Coastal Current from 2001 to 2006 recorded by both instrumental and algal records.

of the Alaska Coastal Current recorded by algal Ba/Ca ratios and GAK 1 observations was also detected in mooring-based studies of Bering Strait throughflow, which shows an incremental freshening of water masses with a combined Alaska Coastal Current and western Alaska river outflow signature along the eastern Strait from 2002 to 2004 [Woodgate *et al.*, 2006]. In addition, a long-term decrease in salinity of about 0.06 psu in the upper 100 m at GAK 1 since 1970 is consistent with increasing algal Ba/Ca ratios and an increase in freshwater runoff off mainland Alaska over the same time period [Royer, 2005]. The observed freshening of the Alaska Coastal Current is likely due to an increase in annual mean air temperatures, generating a longer warm season and a shorter ice season [Stroeve *et al.*, 2005; Woodgate *et al.*, 2006], resulting in an increased rate of glacial thinning in southeast Alaska since the mid-1990s [Arendt *et al.*, 2002, 2009]. In addition, warmer air temperatures lead to enhanced moisture transport and coastal precipitation along the Gulf of Alaska [Weingartner *et al.*, 2005; Janout *et al.*, 2009]. In mountainous coastal regions such as the Gulf of Alaska where there is a steep weathering terrain, high suspended sediment loads in seasonal runoff likely deliver large volumes of barium-enriched freshwater to coastal regions [Coffey *et al.*, 1997; Guay and Falkner, 1997]. In fact, extremely high Ba concentrations were de-

tected on the eastern side of the Bering Strait associated with the Alaska Coastal Current [Guay and Falkner, 1997]. Although upwelling could potentially be a significant source of barium in surface water masses, it is unlikely to occur during the fall when the coastal environment in the Gulf of Alaska is dominated by freshwater discharge and downwelling-favorable winds. The resulting freshwater cap enhances vertical stratification, thus preventing mixing of deep nutrient-rich water with the surface [Weingartner, 2007]. Both the instrumentally measured elevated barium concentrations of the Alaska Coastal Current and the subsequent depletion of barium by biological scavenging after passage of the Alaska Coastal Current into the Arctic Chukchi Sea [Guay and Falkner, 1997] likely point to a largely conservative behavior of Ba in the lower reaches of the Alaska Coastal Current. This, however, does not preclude that at least some of the barium signal recorded by the Unimak Pass algae is influenced by nonconservative behavior of barium. Nonconservative behavior of barium would result in the coralline algal Ba/Ca signal to be dampened with respect to the amount of barium introduced into the Gulf of Alaska.

[13] In contrast to the Unimak Pass algal Mg/Ca time series, multidecadal variability (e.g., Pacific Decadal Oscillation) is not evident in the 60 year Ba/Ca record. This is similar to

instrumental observations at GAK 1, where interannual temperature variability follows the Pacific Decadal Oscillation but salinity anomalies show no relationship to the Pacific Decadal Oscillation [Royer, 2005]. Hence, 21st century freshening of the Alaska Coastal Current as indicated by algal Ba/Ca ratios and instrumental observations is not part of multidecadal North Pacific climate variability and is not observed in the earlier portion of the 60 yearlong algal Ba/Ca time series. This suggests that recent freshening of the Alaska Coastal Current is unprecedented in the past 60 years.

4. Conclusions

[14] We use Mg/Ca and Ba/Ca ratios of the long-lived coralline alga *Clathromorphum nereostratum* collected from within the flow path of the Alaska Coastal Current to provide a 60 year record of temperature and freshwater variability. While Mg/Ca ratios track temperature variability associated with the Pacific Decadal Oscillation, Ba/Ca ratios exhibit no multidecadal variability, but closely relate to instrumental salinity observations for the period of overlap between the time series. Based on this relationship, algal Ba/Ca ratios are used as a tracer of coastal freshwater runoff into the Gulf of Alaska for the past 60 years. While it remains to be tested if this relationship has been robust over longer time frames, both instrumental data and algal Ba/Ca ratios indicate a period of enhanced freshening in the 21st century superimposed on a long-term trend of decreasing salinities of the Alaska Coastal Current since the 1970s. Recent freshening of the Alaska Coastal Current, which plays an important role in delivering freshwater into the Bering Sea and possibly even the Arctic Ocean, is attributed to enhanced coastal freshwater and sediment discharge. Enhanced coastal discharge in turn is a likely result of warming air temperatures resulting in an increase in coastal precipitation in the Gulf of Alaska, as well as an increase in the rate of glacial thinning in southeast Alaska. Episodes similar to the 21st century freshening are not observed in the earlier portion of the 60 yearlong algal Ba/Ca time series, indicating that the recent Alaska Coastal Current freshening is unique in the last 60 years.

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