Mg/Ca Ratios in Crustose Coralline Algae as Proxies for Reconstructing Labrador Current Variability

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science

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Abstract

Climate variability in the North Atlantic has been linked in part to the North Atlantic Oscillation (NAO). The NAO influences marine ecosystems in the northwestern Atlantic and the transport variability of the cold Labrador Current (LC). Understanding historic patterns and predicting future changes in LC transport require long-term and high-resolution climate records that are not available from instrumental data sets.

This thesis presents the first century-scale sea surface temperature (SST) reconstructions from the Northwestern Atlantic using Mg/Ca ratios in the long-lived crustose coralline algae Clathromorphum compactum, which is characterized by a high Mg-calcite skeleton exhibiting annual growth increments.

Results indicate strong correlations between interannual variations in Mg/Ca ratios and instrumental SST. The 131-year algal Mg/Ca record reveals NAO-type periodicities and evidence of past cold events and warming periods associated with basin-wide ecosystem shifts. Negative correlations between LC volume transport and algal Mg/Ca reflect the cooling influence of the LC on eastern Canadian shelf ecosystems.
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1. Introduction

Interannual and multidecadal variations of climate in the North Atlantic region have been linked in part to a dominant pattern of atmospheric circulation variability known as the North Atlantic Oscillation (NAO) (Sutton and Hodson, 2003) and a long-term natural climate variability referred to as the Atlantic Multidecadal Oscillation (AMO) (Knight et al., 2006). The NAO is broadly defined as the difference between the atmospheric pressure found at sea level in Iceland and the Azores (Hurrell, 1995). On the other hand, the AMO is a mode of natural climate variability related to sea surface temperature variations in the North Atlantic with 50-70 years cyclicity (Knight et al., 2006). Although atmospheric oscillations in the North Atlantic occur throughout the entire year, they are particularly strong during the boreal winter (Hurrell, 1995). The impacts that these atmospheric oscillations have on the climate in the northern hemisphere include: severe winters over northwest Atlantic regions in contrast to milder winters in Europe (Hurrell, 1995, Polonskii, 2008); changes in the amount of heat transferred from the sea to the air, which results in the alteration of fresh water input to the ocean (Hurrell, 1995); and regional variations in precipitation and snowfall (Appenzeller, et al., 1998; Enfield et al., 2001; Knight et al., 2006). Moreover, either persistent positive or negative NAO conditions influence sea surface temperature (SST) (Hurrell, 1995), seasonal transport variability of the Labrador Current (Mars et al., 1999), and ice cover in the Labrador and Greenland Seas (Deser et al., 2000). Further studies noted that local ecological changes in terrestrial and marine ecosystems in northern regions are driven by the NAO (Ottersen et al., 2001) and AMO fluctuations (Condron et al., 2005).

In recent times, increased attention has been given to the ecological adaptations of species to the constantly changing ecosystems, driven by the changes in the physical
conditions of the Atlantic Ocean (Drinkwater, 2004 and 2006; Condron et al., 2005) because of the role that this area has for fisheries. Drinkwater (2006) suggested that the migration patterns of marine populations to more northern localities (e.g. the northward expansion of cod off West Greenland) and shifts in the dominant species observed during the first half of the 20th century were motivated by a significant warming of sea water, resulting in changes in ocean circulation. The increase in ocean temperatures leads to changes in the ecological conditions, favoring primary production, altering the growing season, and changing fish populations (e.g. shrimp replacing cod) (Drinkwater, 2006). Condron et al., (2005) found evidence that the AMO regulates the abundance of salmon in regions off of Newfoundland. Ultimately, all of these climatic and biological changes will exert economic and social impacts on societies that depend on the fishery industry, particularly in the northwestern Atlantic (Ruitenbeek, 1996; Drinkwater and Mountain, 1997).

Several authors have investigated the relationship between sea surface temperature (SST) and regional climate variability in the North Atlantic (Bjerknes, 1964; Paltridge, and Woodruff, 1981; Deser and Blackmon, 1993; Kushnir, 1994, Sutton and Allen, 1997; Wang et al., 2004). While the above studies have significantly improved our understanding of North Atlantic climate variability through time, common constraints are the quality (accuracy) and availability (temporal and spatial) of the instrumental SST data set that lead to bias and limited results for different reasons. First, changes in techniques for measuring SST after the mid 1940’s have been related to difficulties in interpreting multidecadal climate variations (Deser and Blackmon, 1993; Kushnir, 1994). Second, sparse SST observations before WWII exert a limit on investigating past ocean-climate correlations (Wang et al., 2004). Finally, because instrumental SST data are mainly collected along ship routes, there is no predetermined geographical location to collect data and some areas, especially at high latitudes (e.g. north of latitude 60°N) are poorly sampled or simply lack data (Paltridge and Woodruff, 1981).
In the absence of high-quality century-scale instrumental records, paleoclimatologists turn to natural climate archives for information on past ocean conditions. Reconstructing marine conditions and climate in the Canadian Atlantic back to the 19th century, a time that is generally regarded as delimiting the onset of large scale human-induced impact on natural systems (Lefohn, et al., 1999), is of utmost importance to better understand past climate variations and predict future environmental changes (Kushnir, 1994). Here, I investigate the utility of the crustose coralline alga _Clathromorphum compactum_ as an archive of sea surface temperature variations in the northwestern Atlantic. I present a reconstruction of sea surface temperatures in the Labrador Current (LC) region for the past 131 years using Mg/Ca ratios from _C. compactum_ as a paleotemperature proxy. A century-scale temperature record from the northwestern Atlantic allows a reconstruction of LC dynamics, and will enhance predictability of future changes in LC behavior during ongoing climate change.

### 1.1 Transport variability of the Labrador Current

The Labrador Current (LC), a cold and low-salinity water mass that flows from northern latitudes toward the equator bordering the shelf edge and upper continental slope of Labrador and Newfoundland (Petrie and Anderson, 1983), dominates the ocean circulation in the Canadian Atlantic. The LC originates from an arctic water mass, the Baffin Island Current that makes its way out of the Canadian archipelago and exits through the Davis Strait (Figure 1a) to join the westward branch of the West Greenland Current in the Labrador Sea (Lazier and Wright, 1993). Figure 1b illustrates the two main components that characterize the LC: (1) a surface inshore branch flowing on the continental shelf, whose pathways have been recognized from near surface (upper 20 m) drifter data from several sources, and (2) a deep component, the offshore branch, which travels below 100 m (Petrie and Anderson, 1983). In addition to the atmospheric and water properties that drive the LC, the topographic features on the Canadian continental shelf (e.g. Hamilton Bank, Belle Isle Bank, Bonavista Bank - Figure 1b) have been recognized as major controllers of the water paths of the LC (Petrie and Anderson,
1983; Narayanan et al., 1996). Furthermore, tidal variability linked to meteorological forcing has been suggested as an additional driving mechanism that controls water masses that move out of the Gulf of St. Lawrence crossing the Strait of Belle Isle and eventually form part of the LC (Garret and Petrie, 1981; Han, 2004).

Figure 1. Map showing study area. a) Major oceanic currents in the NW Atlantic. b) Offshore (heavy lines) and inshore (thin lines) branches of the Labrador Current with sampling locations (asterisk). Also shown location of transect NW191 with volume transport data of the LC (After Petrie and Anderson, 1983 and Keigwin et al., 2003). c) Ocean currents crossing the Strait of Belle Isle.

Salinity, temperature, and transport variability of the LC have been reported since the first systematic oceanographic survey in 1913 (Petrie and Anderson, 1983). Beside the distinctive physical properties of the inshore and offshore branches that create horizontal temperature and salinity gradients separating both flows (Colbourne, et al., 1997), an important point of dissimilarity between the two LC branches is their mean
flow velocity. The superficial, cold, and fresh water that makes the inshore branch has a mean flow velocity between 0.05-0.15 m/s, while the mean flow velocities of the warm, saline and deep water in the offshore portion range between 0.3 – 0.5 m/s (Lazier and Wright, 1993; Colbourne et al., 1997).

During its journey to lower latitudes, the LC has an important cooling effect on the Canadian Atlantic provinces affecting ocean productivity by changing the physical and biological properties of the seawater (Petrie and Drinkwater, 1993; Drinkwater and Mountain, 1997). Petrie and Drinkwater (1993) found that cooling and freshening of the LC preceded periods of low water temperature and salinity in the Gulf of St. Lawrence region. Parsons and Colbourne (2000) found that extensive sea ice cover on the Labrador Shelf associated with cold conditions enhance shrimp populations. These variations in the LC have been associated with wind-driven mechanisms (Han et al., 2008) and changes in physical conditions such as sea ice and temperature in the Labrador Sea (Yashayaev and Clarke, 2006).

After passing the Labrador Shelf, the inshore portion of the LC travels along the east coast of Newfoundland and branches out into small flows (Figure 1b). Approximately 15% of the transport heads to the southwest and enters the Gulf of St. Lawrence through the Strait of Belle Isle (Petrie and Anderson, 1983) while the remaining 85% inshore flow maintains its path south over the continental shelf of Newfoundland (Lazier and Wright, 1993).

The detectable loss (~15%) of flow in the inshore branch of the LC caused by the inflow entering the Gulf of St. Lawrence through the Strait of Belle Isle is in some way compensated by a narrow and shallow current (the Strait Current, Figure 1c) moving out from the Gulf of St. Lawrence in the opposite direction (Farquharson and Bailey, 1966; Petrie and Anderson, 1983). Based on moored current measurements, Dawson (1907) was one of the first in finding the narrow surface current exiting from the Gulf of St. Lawrence along the south coast of the Strait of Belle Isle. Following Dawson’s
observations, several studies have found that wind forcing determines interannual variability of this outflow (Farquharson and Bailey, 1966; Garrett and Toulany, 1981; Petrie and Anderson, 1983). Moreover, it has been suggested that the outflow has a tidal control and seasonal variability with its transport being strong in summer and weak in winter (Garrett and Petrie, 1981; Han et al., 1999).

The Strait Current that transports warmer and saltier water than the northern inflow at comparable depths (Petrie et al., 1988), eventually joins the portion of the inshore branch of the LC flowing over the northeastern Newfoundland shelf (Petrie and Anderson, 1983). After flowing around the southeastern portion of the island of Newfoundland, the inshore branch suffers a new division diverting approximately one fifth of its transport westward to enter the Gulf of St. Lawrence through the Cabot Strait and is likely to move northeast along the western coastline of Newfoundland (Petrie and Anderson, 1983). At the same time the remaining inshore flow (aprox. 80% of transport) makes its way eastward to become part of the offshore portion of the LC current (Figure 1b) (Petrie and Anderson, 1983).

Several studies have been carried out in order to understand the LC transport variations (Lazier and Wright, 1993; Hand, 2004; Hendry, 2006; Han et al., 2008). These studies have noted that the inshore branch of the LC has noticeable seasonal and spatial transport variability. In fact, the inshore branch has been reported as being strong during the cold seasons (e.g. winter/fall) and weak during warm periods (e.g. spring/summer) (Myers, et al., 1989; Lazier and Wright, 1993; Han et al., 2008). The interannual variations in SST in the North Atlantic caused by the transport variability of the LC have been associated with local atmospheric anomalies driven by surface wind circulation (Petrie and Drinkwater, 1993). But in a larger time scale, interdecadal SST variations have been related with basin scale changes in ocean circulation (Bjerknes, 1964; Kushnir, 1994). Reverdin et al (1997) suggest that changes in temperature and salinity of the LC are the result of interannual and long-term conditions driven by the NAO. Yashayaev and Clarke (2006) found that periods of cooling and freshening of the
Labrador Sea during the 1970’s and 1990’s are correlated to strong positive values of the NAO index. They noted that the interannual variations on the deep Labrador Sea Water contrast with the short-term (seasonal) variability observed in the upper 150 m of the Labrador Sea (Yashayaev and Clarke, 2006). Thus, atmospheric anomalies and ocean circulation patterns combine to drive LC variability.

According to Hendry (2006), in addition to the seasonal variability caused by the increasing heat flux from the ocean to the atmosphere in winter, the superficial waters (0-150m) of the Labrador Sea show a warming trend since 1990. However, an anthropogenic or natural causative relation of this increase in SST still has to be demonstrated (Hendry, 2006). The effects of variations in the Labrador Sea are reflected as changes in the position, strength (velocity), and physical properties (volume, temperature) of the LC (Yashayaev and Clarke, 2006). As mentioned before, the LC has the potential to influence both the water temperature and biological productivity of the Eastern Canadian coast (Wanamaker et al., 2008). However, no major shifts in ecosystem distribution of eastern Canada have been reported during the warming periods in the 1920s and 1930s (Jensen, 1939; Drinkwater, 2006). Hence, understanding the past behavior of climate and ocean currents in the Canadian Atlantic is essential for predicting future changes in LC flow and therefore marine ecosystems. However, this requires the use of long-term (multi-century scale) climate models and high-resolution (intrannual) SST records. At present, those records are either spatiotemporally incomplete or are not available from the short instrumental oceanographic dataset (Hurrell and Trenberth, 1999; Smith and Reynolds, 2003).

1.2 Marine high-resolution climate archives

In an effort to fill gaps in the instrumental SST data set, numerous studies have shown that marine organisms such as corals, bivalves, and crustose coralline algae are faithful recorders of sea water temperatures at annual resolution (Mitsuguchi, 1996; Freitas, et al., 2005; Halfar et al., 2008; Hetzinger et al., 2008). The calcium carbonate skeletons of
the above mentioned organisms show variations in their geochemical composition at different time scales associated with changes in sea water temperature. The relationship between water temperature and the stable oxygen isotopic composition in corals and bivalves has been used to investigate ocean paleotemperatures. Interannual variations in annual δ\(^{18}\)O time series from corals have been interpreted as oceanographic signatures of the El Niño-Southern Oscillation (Evans et al., 2000) and the Atlantic Multidecadal Oscillation (Hetzinger et al., 2008). The variations in annual shell growth of specimens of the long lived bivalve *Arctica islandica* collected at mid to high latitudes were used to reconstruct 245 years of the winter NAO index (Schöne et al., 2003). Furthermore, Schöne et al. (2004 and 2005) presented multidecadal sea surface temperature reconstructions based on oxygen isotope ratios from two *A. islandica* specimens.

Although most seawater temperature reconstructions rely on oxygen isotopes, some studies have investigated the potential of trace elements (e.g. Mg, Sr) as paleotemperature proxies. Klein et al. (1996) found that weekly SSTs can be estimated from the Mg/Ca ratios of the marine mussel *Mytilus trossulus*. Rosenheim et al. (2004) showed that tropical sclerosponges record seasonal variations in ocean temperature as cyclic changes in Sr/Ca ratios. The Mg/Ca and Sr/Ca ratios in calcareous skeletons of corals have been correlated with SST revealing seasonal variability, though diagenesis, growth rate, and differences among species may effect the SST-Trace element correlation (Mitsuguchi, 1996).

Despite the success in reading the paleotemperature signal recorded in the hard parts of marine organisms, there are some limitations in the applicability of these proxies: restricted tropical to subtropical geographical distribution of coral species; halt and decrease in growth rate resulting in loss or low analytical resolution with age in bivalves (Goodwin et al., 2003; Carre et al., 2005); and vital effects, the biological control on the incorporation of trace elements and isotopes during calcification (Dodd and Stanton, 1981; White et al., 1999). On the other hand, the use of biogenic marine
paleoclimate proxies has mainly concentrated on tropical and subtropical latitudes and less work has been done to cover northern oceans (Kaplan and Wolfe, 2006), regardless of the important role of extratropical regions in regulating global climate. The applicability of some suitable biogenic archives at high north latitudes has been hampered by biological restrictions like slow down of growth in *A. islandica* with age, a process known as ontogenetic effect which makes it difficult to read the paleotemperature signal in the more recent years of growth of adult specimens (Schöne et al., 2004). However, high-resolution sampling techniques can improve the data extracted from narrow growth increments (Schöne et al., 2005). Complementing bivalve-based climate reconstructions, crustose coralline algae have emerged as additional marine biological paleotemperature proxies in subarctic regions (Halfar et al., 2000).

1.3 Previous paleoclimate studies using crustose coralline algae

The fact that the incorporation of magnesium, and other trace elements and isotopes, during the formation of calcite skeletons is an endothermic process (Morse et al., 1997) promotes the use of crustose coralline algae as paleothemometers. Among the wide range of trace elements and isotopes integrated through biomineralization in crustose coralline algae (Blunden et al., 1997) Mg, Sr and oxygen isotopes are the most frequently used proxies in paleoclimate reconstructions.

1.3.1 Stable oxygen isotopes

The isotope contents in coralline algae are influenced by not only environmental but also metabolic processes (Borowitzka 1981; Wefer and Berger, 1981). It has been demonstrated that the oxygen isotopes precipitated by some coralline algae are in disequilibrium with their surrounding environment (Wefer and Berger, 1991). Thus, paleoclimate studies based on δ¹⁸O analyses must consider carefully the effects of
photosynthesis, growth rate, and seasonality on oxygen isotope fractionation (Wefer and Berger, 1991).

Lee and Carpenter (2001) found that the δ¹⁸O content in the articulated crustose coralline algae *Amphiroa* *sp.* is lower but relatively constant than the expected equilibrium values. Based on their findings they consider *Amphiroa* *sp.* as a potential environmental proxy. The δ¹⁸O variations in the calcitic skeleton of *Clathromorphum nereostatum* were used to reconstruct paleoclimate from the subarctic North Pacific with annual resolution (Halfar et al., 2007). Halfar et al. (2007) showed that the 117-year long δ¹⁸O-time series from a *C. nereostatum* specimen living in the North Pacific is spatiotemporally correlated with tropical climate patterns such as the El Niño Southern Oscillation. Furthermore, a 12-month field calibration of *Clathromorphum compactum* conducted in the Gulf of Maine, U.S.A., indicated that *C. compactum* records fluctuations in sea surface temperature as changes in stable oxygen isotope content in its calcite skeleton (Halfar et al., 2008). The oxygen isotopes measured at subannual resolution in the monitored specimens represent May to December SST (Halfar et al., 2008). This is generally regarded as the main calcification period in *C. compactum* (Adey, 1965).

1.3.2 Mg/Ca ratios

Algal calcification is a complex biological process in which a living organism behaves and develops according to changes in multiple external factors such as nutrients, and chemical and physical water conditions of their habitats (Ries, 2006). Crustose coralline algae build their calcified skeletons by precipitating calcite crystals directly in the vegetative cell-wall (Cabioch, 1988). While the external factors influencing crustose coralline algae calcification such as temperature, salinity, pH, light, and food availability have been investigated (Adey, 1965; Adey, 1970), the physiological processes are less understood (Chave, 1984; Medakovic et al., 1995; Halfar et al., 2000). Thus, the fact that a vital effect, the biological control that certain organisms exert on the mineralization process and the resulting shift in their climate signal (Weiner and Dove, 2003),
influences calcification in crustose coralline alga is a generally accepted idea (Borowitzka, 1977; Chave, 1984; Halfar et al., 2000).

Several geochemical studies carried out to investigate the mineral composition in calcareous algae show that magnesium calcite is a dominant compound in the algal skeletal structure (Chave, 1954; Borowitzka et al., 1974; Medakovic et al., 1995). After the early notable works by Clarke and Wheeler (1917) and Chave (1954) who showed that the Mg contents in the calcite skeleton of marine organisms increase with increasing water temperature, several studies have confirmed the cyclic variations of Mg content in crustose coralline algae as a response to seasonal changes in ocean temperature (Chave and Wheeler, 1965; Milliman et al., 1971; Henrich et al., 1996; Halfar et al., 2000; Kamenos et al., 2008; Hetzinger et al., 2009).

Chave and Wheeler (1965) carried out X-ray diffraction analyses on Clathromorphum compactum specimens and found that the magnesium content in the algal skeletal calcite is positively correlated to increasing seawater temperature. Instead, Moberly (1968) conducted electron microprobe analyses on the same algal species and found that changes in the Mg content depend mainly on skeletal growth rate variations rather than water temperature. Higher Mg content in the C. compactum skeletons was deposited from June to September (period of rapid growth) than that precipitated between February to March (slow calcification period). However, the same author suggested that growth rate is a function of water temperature, light and physiological cycles.

Variations in Mg content in the subarctic rhodolith (free-living crustose coralline algae) Lithothamnium glaciale indicated a positive Mg-temperature relationship (Halfar et al., 2000). Similarly, Kamenos et al. (2008) showed that sea water temperature is the main factor controlling the incorporation of Mg in the slow growing coralline algae Lithothamion glaciale and Phymatolithon calcareum. Their bi-weekly resolution records of Mg/Ca in L. glaciale and P. calcareum displayed strong Mg-SST correlations (Kamenos
et al., 2008). More recently, Hetzinger et al. (2009) found significant relationships between Mg/Ca ratios in the crustose coralline alga *Clathromorphum nereostratum*, local SST and air temperature in the subarctic Pacific. They concluded that the annual Mg cycles in the continuous 65-year record correspond to seasonal variations in SST (Hetzinger et al., 2009). Kamenos et al. (2009) found that the Mg$^{2+}$ ions take the place of Ca$^{2+}$ in the calcite crystal structure of *Lithothamnion glaciale* and *Phymatolithon calcareu*, and hence are not fixed to organic matter. They concluded that the incorporation of Mg within the calcite lattice is an invariable process during the plant lifetime reinforcing the suitability of these algae as climate proxies.

Hence the internal morphology and chemical composition of crustose coralline algae make them excellent recorders of extratropical paleoclimate signals (Chave and Wheeler, 1965; Adey, 1970; Halfar et al., 2007; Halfar et al., 2008; and Kamenos et al., 2008). In fact, it has been demonstrated that sea surface temperature can be reconstructed at subannual resolution from crustose coralline algal Mg/Ca ratios (Chave and Wheeler, 1965; Halfar et al., 2000; Hetzinger et al., 2009). All these characteristics along with the absence of a slow down of growth with increasing ontogenetic age, which is common in other marine calcifiers such as bivalves, make crustose coralline algae suitable candidates for reconstructions of SST.

1.4 The biology of the crustose coralline alga *Clathromorphum compactum*

The encrusting crustose coralline alga *Clathromorphum compactum* is a dome-shaped calcified marine plant (Figure 2) that thrives in water depths between 1 to 40 m (Adey, 1965) in mid to high latitude regions with winter water temperatures below 16°C (Adey and Steneck, 2001). *C. compactum* has been found in marine habitats of the Northern Hemisphere, including the North Atlantic, North Pacific, and the Arctic oceans Ocean (Adey and Steneck, 2001). This long-lived crustose coralline alga builds its skeleton by depositing annual layers of high-magnesium calcite (Adey, 1965; Chave and Wheeler, 1965).
Figure 2. *Clathromorphum compactum* benthic habitat. *C. compactum* encrusts on hard substrate forming small mounds up to 3 cm high. Picture courtesy of W. Adey.

Morphologically *C. compactum* displays cell differentiation with small and heavily calcified cells formed during the cold months, separated by large and poorly calcified cells built during the warm periods (Moberly, 1968). This abrupt change is marked by a growth line that indicates the start of the rapid grow season in late spring (Moberly, 1968). The calcification period of some *C. compactum* specimens is evident by the development of cavities (conceptacles) containing the reproductive structures in the fall and early winter (Moberly, 1968). However, the fast development of sporangia, the algal structures that produce and contain the spores, in November-December causes local dissolution of the carbonate material previously deposited, giving the impression that conceptacles are formed in the middle of growth bands (Adey, 1965). Viewed in cross-sectioned specimens, the conceptacles are arranged in a banding pattern perpendicular to the direction of growth where each band represents a year (Figure 3a).
Figure 3. High-resolution geo.TS image of polished *C. compactum*. a) Growth and calcification in *C. compactum* results in annual banding pattern perpendicular to the direction of growth allowing lateral mapping of growth increments, identification of meristem, and discontinuities. b) Detailed view of meristem, which produces vegetative cells for growth. c) Annual cycles of Mg/Ca ratios mimic growth pattern and were used to establish a precise age model. Conceptacles in *C. compactum* contain reproductive cells and are important morphological features.

Although these annual features can potentially be used to date the algae using layer-counting, extreme caution is necessary especially in specimens with very low growth rates since the growth of conceptacles leads to decalcification of underlying tissue (Adey, 1965). In the event of minimal yearly growth a specimen would develop narrow annual bands, hence the decalcification through conceptacle formation can extend to the previous year's band making it difficult to assign single bands to specific calendar years (Moberly, 1968). In addition, growth disturbances by sometimes intensive grazing, poor banding differentiation, and lack of annual conceptacle formation in some specimens of *C. compactum* make simple layer counting problematic in this species.

As stated in the previous section, the main growth season of *C. compactum* spans from May to early December with a mean annual growth rate varying from 330μm for plants living above 6 m to 230μm for plants living below 6 m (Adey, 1965). It has been suggested that growth slows down or even ceases in *C. compactum* during late
December and January, a period of minimum light (W. Adey, pers. comm.). Under normal environmental and nutritional conditions an uninterrupted plant can reach up to 3 cm height (Adey, 1965), which, given the above growth rates relates to a century-scale life span. However, growth disturbances caused by benthic animals such as sea urchins are common and often hard to recognize in cross-sectioned specimens without careful microscopic examination (Adey, 1965).

Another significant issue regarding age determination in crustose coralline algae is the identification of the meristem (Figure 3b). The meristem is the thin outermost layer of the plant that provides new cells for growing (Adey, 1965). The meristem plays an important role in the survival strategies against grazing, internal, and external destruction since the regeneration of crustose coralline algae is based on the recovery of meristematic activities of internal cells and changes in cell functionality (Cabioch, 1988). The healing from the scraping is an important contributor to the irregularity of the surface (Adey, 1965). If the presence of the meristem can be confirmed, one can assure that the plant was alive at the time of collection. Hence, only with known collection date and presence of a meristem, accurate temporal control can be achieved when aging a specimen (Figure 3c).
2. Study Area

The selected study area is located along the eastern coast of Newfoundland and Nova Scotia (Canada) and is largely in the pathway of the inshore branch of the Labrador Current (Figure 1b). Samples of *C. compactum* were collected via SCUBA at an average water depth of 9 m at four locations (Figure 1b) along a latitudinal transect from Quirpon Island, Newfoundland (51° 36.014’ N, 55° 27.445’ W; site descriptor QP) in the north, Cape St. Martin, Newfoundland (50° 1.5’ N, 55° 53’ W; site descriptor CSM), Bread and Cheese Cove, Bay Bulls near St. John’s, Newfoundland (47° 18.496’ N, 52° 47.354’ W; site descriptor SJ in the center, and Ketch Harbor near Halifax, Nova Scotia (44° 28.685’ N, 63° 32.778’ W, site descriptor HA), in the south. This region, excluding Ketch Harbor, is one of the main corridors for icebergs transported by the Labrador Current and has received much attention in the recent oceanographic literature (Miller and Hotzel, 1984; Andrews, 2000; Keigwin, 2003; Han, 2005). The Quirpon, Cape St. Martin, and St. John’s sampling sites experience annual minimum and maximum sea surface temperatures during the months of February and August, respectively. This differs from instrumental SST records obtained for Halifax, which show a SST minimum in March and maximum in August (see Figure 6 in Methods section).

The entire region covered in this study is characterized by marked seasonal changes in the climatic conditions with seasonal sea ice occurring every year off of Labrador and Newfoundland (Hill, 1998) and sporadic coastal sea ice extending as far south as latitude 46°N during extreme cold winters (IPNA, 1989; Hill et al., 2002). The Report of the International Ice Patrol in the North Atlantic (1989) indicates that sea ice conditions on the coast of Labrador start on late December and continue until March. Thus sea ice along the east coast of Newfoundland starts forming in January, reaches its maximum extend in March and starts to retreat in April. The climatology in CSM and QP is characterized by winter conditions suitable to sea ice formation while seasonal sea ice occurrence is sporadic in St. John’s, and absent in Halifax (IPNA, 1989).
2.1 Quirpon Island site (QP)

The Quirpon (QP) sampling site (51° 36.014’ N, 55° 27.445’ W), a sea urchin barren with a flat to moderate slope topography, is located in an archipelago in a wave-protected coastline at the southwest side of the Quirpon Island (Figure 1b). In summer, the depth/temperature curve is typically flat from the surface to 15-20m, at 9-10°C, dropping to 1-7°C at about 20m (W. Adey pers. comm.). However, strong offshore (SW) winds, which are periodically common for many days in late summer, can cause plunges in water temperatures to the 4 – 7°C range for days to a few weeks, especially at 5-20m depth (W. Adey pers. comm.). This sampling site is in close proximity to where the inshore branch of the Labrador Current deviates part of its flow to the west to enter the Gulf of St. Lawrence through the Strait of Belle Isle, while the main branch continues southward bordering the eastern coast of Newfoundland (Figure 1b) (Petrie and Anderson, 1983). A local oceanographic feature that can exert a seasonal influence in the QP site is the Strait Current (Figure 1c), a shallow and warm northeastward outflow from the Gulf of St. Lawrence along the south coast of the Strait of Belle Isle (Garret and Petrie, 1981).

2.2 Cape St. Martin site (CSM)

This site is located west of Cape St. Martin (Figure 1b) at the west side of Hardy Harbor, Newfoundland (50° 1.5’ N, 55° 53’ W). The Cape St. Martin shore is mostly under the influence of the inshore branch of the LC and similar to the QP site, sea ice is present every year and typically most fully developed in March (W. Adey pers. comm.). The Cape St. Martin site is characterized by the presence of heavy coralline cover on ledges with occasional boulders and cobbles.

2.3 St. John’s site (SJ)

The St. John's site (47° 18.496’ N, 52° 47.354’ W) is located at the north side of Bay Bulls in a well-protected area of the Bread and Cheese Cove (Figure 1b) south of St. John's,
Newfoundland. This site exhibits irregular bedrock topography with frequent understory kelp that provides partial shading. Sea ice is sporadic at this site and easterly winds are responsible for wind-driven waves moving westbound into the bay. Among all the sampling sites, St. John’s along with Cape St. Martin represent locations that are well exposed to the LC.

2.4 Halifax site (HA)

The Halifax site (44° 28.685' N, 63° 32.778' W) is situated on the east coast of Nova Scotia (Figure 1b) in a sea urchin barren affected by wind-driven swells. It is characterized by fluctuations in the marine biota driven mainly by changes (warming) in SST that causes massive mortality of sea urchins and consequent abundance of macroalgae (Scheibling, 1986). Hence, periods of low to absence of sea urchins are dominated by substantial growth of kelp forest and development of crustose coralline algae (Scheibling, 1986).

Specimens of *C. compactum* were collected in the outer part of a small bay near Ketch Harbor 30 km south of Halifax, Nova Scotia (Figure 1b). This site is under the influence of the mixture of the LC current and the Scotian Current, a warm outflow coming from the Gulf of St. Lawrence traveling along the south coast of the Cabot Strait (Petrie and Anderson, 1983). It also has been suggested that Gulf Stream eddies might be related with warming of the eastern coast of Nova Scotia affecting ecosystem stability (Scheibling, 1986).
3. Data and Methods

3.1 Sample acquisition

Over 400 live specimens of the long-lived crustose coralline algae *Clathromorphum compactum* were collected via SCUBA at 8-10 m water depth range in August 2008 at three of the four localities described above (Quirpon, St. John’s, and Halifax).

This collection was supplemented with specimens from the same area collected in summer 1961, 1962, and 1964 (courtesy of W. Adey, Smithsonian Institute in Washington, D.C.). One sample from the latter group (sample number 170716) collected at the west side of Cape St. Martin, Newfoundland, at a depth of 10 m, was used in this study.

All samples, except the one from Cape St. Martin, were labeled according to year of collection and site descriptor followed by a consecutive number. A total of 41 samples were preselected based on the length of record (thickness) and spatial distribution in order to cover the LC path (Table 1). From the 41 samples, a final group of 7 samples were selected for measuring Mg and Ca content using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). The criteria to select the final 7 samples were geographical distribution, vertical thickness (associated with length of record), and growth continuity (absence of disturbances). Thus, 2 samples from each of the sites QP, SJ, and HA, and one from CSM were chosen for Mg/Ca analysis.
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Source</th>
<th>Latitude N</th>
<th>Longitude W</th>
<th>Location</th>
<th>Collection Date (m-y)</th>
<th>Water Depth (m)</th>
<th>Water Temp. (°C)</th>
<th>Age</th>
<th>Continuity</th>
<th>Growth pattern</th>
<th>Length of record</th>
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<td>104-25.1C</td>
<td>Smithsonian Ins.</td>
<td>43°26'</td>
<td>60°28'</td>
<td>Outer Barcaro Pt. Barlington Bay. Nova Scotia</td>
<td>Sep-51</td>
<td>10</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>206-64</td>
<td>Smithsonian Ins.</td>
<td>47°18'</td>
<td>52°47'</td>
<td>Bay Bulls (near St. John's)</td>
<td>Aug-08</td>
<td>8</td>
<td>9</td>
<td>4</td>
<td>4</td>
<td>5</td>
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<tr>
<td>159-22-3</td>
<td>Smithsonian Ins.</td>
<td>50°16'</td>
<td>56°46'</td>
<td>Ke Longue, Queltachi Bay, northern Gulf of St. Lawrence</td>
<td>Jul-64</td>
<td>12.6</td>
<td>8</td>
<td>5</td>
<td>4</td>
<td>4</td>
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<tr>
<td>176-22-4</td>
<td>Smithsonian Ins.</td>
<td>50°16'</td>
<td>62°46'</td>
<td>Ke Longue, Queltachi Bay, northern Gulf of St. Lawrence</td>
<td>Jul-64</td>
<td>10</td>
<td>12</td>
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<td>4</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>189-27-8</td>
<td>Smithsonian Ins.</td>
<td>50°11'</td>
<td>60°08'</td>
<td>Outer Waptaugis Is. northeastern Gulf of St. Lawrence</td>
<td>Jul-64</td>
<td>9.4</td>
<td>12</td>
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<td>5</td>
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<tr>
<td>190-27-6</td>
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<td>60°08'</td>
<td>Outer Waptaugis Is. northeastern Gulf of St. Lawrence</td>
<td>Jul-64</td>
<td>6.4</td>
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<td>5</td>
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<td>55°53'</td>
<td>Cape St. Martin, Newfoundland</td>
<td>Sep-64</td>
<td>9.1</td>
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<td>55°53'</td>
<td>Cape St. Martin, Newfoundland</td>
<td>Sep-64</td>
<td>9.1</td>
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<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
<td>6</td>
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<tr>
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<td>51°15'</td>
<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
<td>3</td>
<td>4</td>
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<td>4</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>258-64-4</td>
<td>Smithsonian Ins.</td>
<td>51°15'</td>
<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
<td>9</td>
<td>4</td>
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<td>5</td>
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<tr>
<td>269-64-4</td>
<td>Smithsonian Ins.</td>
<td>51°15'</td>
<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
<td>5</td>
<td>4</td>
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<td>4</td>
<td>5</td>
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</tr>
<tr>
<td>280-64-4</td>
<td>Smithsonian Ins.</td>
<td>51°15'</td>
<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
<td>5</td>
<td>4</td>
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<tr>
<td>306-64-2</td>
<td>Smithsonian Ins.</td>
<td>51°36'</td>
<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
<td>5</td>
<td>4</td>
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<tr>
<td>317-64-2</td>
<td>Smithsonian Ins.</td>
<td>51°36'</td>
<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
<td>5</td>
<td>4</td>
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<td>5</td>
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<tr>
<td>328-64-2</td>
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<td>51°36'</td>
<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
<td>5</td>
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<tr>
<td>339-64-2</td>
<td>Smithsonian Ins.</td>
<td>51°36'</td>
<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
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<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
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<td>51°36'</td>
<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
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<td>51°36'</td>
<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
<td>5</td>
<td>4</td>
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</tr>
<tr>
<td>383-64-2</td>
<td>Smithsonian Ins.</td>
<td>51°36'</td>
<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
<td>5</td>
<td>4</td>
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<tr>
<td>394-64-2</td>
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<td>51°36'</td>
<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
<td>5</td>
<td>4</td>
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<td>4</td>
<td>5</td>
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<tr>
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<td>51°36'</td>
<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
<td>5</td>
<td>4</td>
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<tr>
<td>416-64-2</td>
<td>Smithsonian Ins.</td>
<td>51°36'</td>
<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
<td>5</td>
<td>4</td>
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<td>4</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>427-64-2</td>
<td>Smithsonian Ins.</td>
<td>51°36'</td>
<td>55°23'</td>
<td>Grignon Island</td>
<td>Aug-08</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Summary of information for preselected 41 samples (Good=5 and Poor=1).
3.2 Sample preparation

The initial subset of 41 samples was cleaned and washed with regular soap and left in an oven set at 50°C for a week. Subsequently, they were cut parallel to the direction of growth using a fine diamond blade. Then, a 7 mm-thick slab from each sample was glued onto standard petrographic glass slides using epoxy resin. The mounted samples were then sanded with 150 μm and 120 μm grit sized sand paper using a Logitech CL50 polishing machine to obtain even and parallel surfaces and eliminate major scratches before starting the automatic polishing process. After each sanding process the samples were brushed and washed thoroughly with soap and placed in a sonicator for about 10 to 15 minutes to clean any residual material and to avoid contamination during the next polishing step. Next, the samples were placed to dry at 50°C. At this point, a visual examination of the samples in order to determine discontinuities or overgrowths was made. After this initial assessment 38 samples were selected for the final polishing process (Figure 4). Next, the 38 samples were machine polished at 80 – 100 rpm using diamond solutions of varying grit sizes: 9μm, 3μm, and 1μm for 30, 90, and 90 minutes, respectively. The diamond solution was applied to a polishing cloth previously lubricated with water-based lubricant that served as coolant for the rotational disc. After each automatic polishing step, samples were carefully washed with soap, sonicated, and placed into the oven to dry.
Figure 4. Latitudinal spatial distribution of samples and ages estimated from counting layers and measuring thickness vs. growth rate ratio. An asterisk indicates samples analyzed in this study.
Once the machine-operated polishing was complete, the samples were scanned using a fully automated Olympus BX51 high resolution microscope using geo.TS software. This software was coupled with an automated stage that enabled high-resolution images to be mapped and stitched at 50x magnification. These high-resolution photomosaics were used to ensure that surfaces were smooth (free of scratches), identify major discontinuities not seen in the first evaluation, and check for the presence of the meristem as an indication that the specimen was alive at the time of collection (Figure 3). Growth increments were mapped (Figure 3a) on the high-quality images of the samples and the specimens were assigned a preliminary approximate age (Figure 4) based on either growth increment counts or thickness/growth rate ratio with 300µm as the annual growth average for *C. compactum* (Adey, 1965). The final age of the specimens reported in the results section was calculated by counting the annual Mg/Ca cycles after the age model was complete on the basis that each Mg/Ca cycle represents a calendar year (Figure 3c). Based on this microscopic visual examination, samples lacking the meristem or exhibiting pronounced growth disturbances were excluded from this study. This led to a final group of 7 samples (highlighted on Table 1) selected for geochemical analysis.

On the basis of the annual-growth increment patterns, two overlapping transects perpendicular to the growth bands were positioned on each sample (Figure 5a) for subsequent LA-ICP-MS analysis (see below). The two transects per sample help to evaluate the reproducibility of the Mg and Ca measurements and allow the assessment of the robustness of the proxy data. The transects were digitized on the image using geo.TS software avoiding conceptacles, disturbed areas, and regions of uneven growth. In order to import the digital transects from geo.TS into the LA-ICP-MS system, two reference points were digitized at the opposite corners of the sample image (Figure 5a). The digital x and y positions of the reference points and transects were uploaded into the laser system assuring accurate positioning of the laser line scans along the predetermined paths.
3.3 Laser Ablation Inductively Coupled Plasma Mass Spectrometry analyses

The elemental measurements were carried out at the LA-ICP-MS Laboratory at the Department of Geosciences, Johannes Gutenberg-Universität, Mainz, Germany using an Agilent 7500ce quadrupole ICP-MS coupled to a New Wave Research UP-213 laser ablation system (213 nm wavelength, Nd:YAG Laser). Individual transects of 6000 µm in length or less were measured with laser energy densities of 6 J/cm² and Helium as carrier gas at a scanspeed of 10µm/second, spot size of 65µm, 10Hz pulse rate (54% output energy), and cycling time of 0.3 sec. The detection limit for Mg was 0.016 ppm. The internal standard was ⁴³C with calcium concentrations measured by Electron Probe Microanalyser (EPMA). The use of the external standard SRM NIST 610 (Jochum and Stoll, 2008) made it possible to verify that drift by instrumentation was insignificant. The commercial software GLITTER 4.4.2 was used for data processing and data reduction (filtering). 1-sigma error for Mg measurements varies between 3.38% and 8.40% (Table 2).
Table 2. Analytical error for Mg measurements.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Transect 1</th>
<th>Transect 2</th>
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<td>3.49</td>
</tr>
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<td>08-SJ-28</td>
<td>3.62</td>
<td>3.82</td>
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<td>08-QP4-3</td>
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<td>08-QP4-4</td>
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<td>3.38</td>
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<td>08-HA-70</td>
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</tr>
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<td>08-HA-80</td>
<td>3.66</td>
<td>3.69</td>
</tr>
<tr>
<td>170716</td>
<td>5.86</td>
<td>8.40</td>
</tr>
</tbody>
</table>

The LA-ICP-MS procedure requires that the sample measurements be bracketed between standard measurements. In other words, the standard is measured before and after a given sample is run. In order to detect potential drifts of the ICP-MS over the course of the test, each transect was split into two or three segments, all bracketed by standard measurements. Thus, an overlap between sections covering two to four bands (years) was set up in order to later compile and accurate and continuous record. The continuous laser profiles revealed the cyclic pattern of annual Mg/Ca variations in *C. compactum*. The two Mg/Ca transects in each sample were compared in order to test the quality and reliability of the geochemical signal and help to increase the robustness of the final results.

A set of trace elements (Li, B, Na, Mg, Al, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Rb, Ser, Cd, Ba, Pb, and U) were measured in 08-QP4-3, 08-QP4-4, 08-SJ-21; for samples 08-HA-70, 08-HA-80, 170716, and 08-SJ-28 the elements Ti, Rb, Fe, Ni were not included. However, this study only discusses measurements of Mg and Ca. In order to eliminate ICP-MS interferences the isotopes $^{24}$Mg and $^{44}$Ca were selected.

### 3.4 Establishing of age model

Continuous Mg/Ca LA-ICP-MS profiles were obtained at an equidistant sampling resolution of 3.044 microns/measurement. This relates to ~100 individual Mg/Ca measurements/year, depending on variable annual growth increment widths. In order
to downsample this data set to a sampling resolution of 12 samples/year and compare the proxy data to instrumental data a reliable age model had to be established. This was achieved by visually delimiting annual cycles in a comparison between image mosaics and Mg/Ca cycles (Figure 5b).

Based on the monthly HadISST1 data set (Rayner et al., 2003); provided by the Hadley Centre for Climate Prediction and Research, Met Office, Bracknell, UK.; for each site, August and February were defined as the warmest and coldest months respectively at Quirpon, Cape San Martin, and St. John's. In the same way, the climatologic data for the Halifax site showed August as the warmest month and March as the coldest (Figure 6).

![Figure 6. Monthly sea surface temperatures at individual collection sites. Data compiled from HadISST1 (Rayner et al., 2003); averaged over 130 years to determine warmest and coldest months.](image)

In a second step, highs and lows of Mg/Ca cycles for each annual cycle were identified and related to the coldest and warmest months (Figure 7) respectively for each sampling site. This approach follows Moberly’s (1968) observations regarding growth rate and calcification in *C. compactum*. After identifying the warmest and coldest months, they were manually tied to maximum and minimum Mg/Ca values respectively.
in each annual cycle. During the process of assigning the warmest and coldest month to extreme Mg/Ca measurements, both laser transects of the same sample were visually compared between each other in order to match cycles and identify possibly missing years.

Figure 7. Annual Mg/Ca cycles. High Mg/Ca values represent summer and low values winter months. Count number refers to specific position of measurements within sample.

Figure 8 shows the analytical steps required to transform raw Mg/Ca cycles to an annual resolution age model using the software Analyseries 2.0.4.2 available at http://ngdc.noaa.gov/paleo/softlib/softlib.html (Paillard et al., 1996). The preparation of the geochemical dataset involves definition of 4 columns (Figure 8a) as follow: column 'no.', contains consecutive numbers starting from 1; column 'HL' show manually position High (H) and Low (L) identifiers for each cycle; column 'Mg/Ca', contains raw data of Mg/Ca ratios; and column 'Marker' shows the temporal component (the first four digits represent the year and the last three digits the month). Highs (H) were tied to the warmest month, Lows (L) to the coldest months. The first Mg/Ca maximum is the year before collection; so for samples collected in August 2008, the first Mg/Ca maximum represented August 2007. After all the cycles were manually labeled, plots of
the two transects from the same sample were compared to identify possible missing years. Once the correlations between cycles and images were satisfactory a simple cycle-counting was done in order to determine the age of each specimen. Because of the high resolution and quality obtained from LA-ICP-MS analyses, the risk of miscounting years is negligible when the dating is based on the Mg/Ca ratios compared with visual recognition of annual bands on scanned images. Subsequently, the column ‘H/L’ is deleted and a new column, called ‘new no.’ is inserted to renumber the Mg/Ca values; the gaps in the ‘Marker’ column are filled by running a simple interpolation using Analyseries in order to assign calendar date to each measurement (Figure 8b). Next, the columns ‘Mg/Ca’ and ‘Marker’ were switched and data were sorted descending based on the ‘new no.’ column (Figure 8c). In the final step, the high-resolution LA-ICP-MS results are resampled using the Analyseries software with a step of 0.083333 in order to obtain 12 Mg/Ca values per calendar year (0.041666 for 24 samples/year resolution). By following this procedure, the high resolution LA-ICP-MS results are converted from data related to a depth scale (thickness o sample) into data related to a time (age) scale (Figure 8d). If any discrepancy was found between transects of the same sample, the age model of that given sample was refined in an iterative procedure.
Figure 8. Calculations completed to establish age model with 12-samples/year resolution. See text for detailed explanation.

The validation of the age model was possible by comparing Mg/Ca cycles in the time series with mapped growth increment patterns where visible. This method significantly improves age control and therefore the robustness of the data set. However, an error of 1 – 2 years in any given time series has to be considered.
The visual analyses of image mosaics reveal the non-annual character of conceptacles formation in C. compactum specimens from the Canadian North Atlantic region. This results in difficulties aging the specimens based on layer counting. Thus, specimen aging was achieved by counting of pronounced annual Mg/Ca cycles. This cyclic pattern was also used to calculate average growth rates from the raw data once the seasonal time markers were set. In general, the annual cycles from the Mg/Ca profiles for the QP, CSM, and SJ samples were easily recognizable in contrast to HA samples that presented sporadic short cycles misrepresenting annual bands.

In addition to the set of Mg/Ca time series obtained for each site, a 131-year long Mg/Ca master chronology was created. This master chronology is composed of four transects from site SJ and three transects from site CSM. The selection of transects included in the master chronology was based on the results of correlations of Mg/Ca time series against HadISST1 and length of records.

3.5 Comparison of Mg/Ca ratio time series with instrumental data

The 12 sample/year resolution Mg/Ca time series was annually averaged and compared to spatially averaged instrumental SST data at each location. The SST records in this report correspond to the monthly-resolution HadISST1 data set (Rayner et al., 2003). HadISST1 uses two SST data sets to cover more than a century and a half of observations. From 1850 to 1997 it utilizes data from the International Comprehensive Ocean-Atmosphere Data Set (ICOADS), and from 1998 to present it uses data collected from the Global Telecommunication System by the National Centers for Environmental Prediction (NCEP-GTS). Although the HadISST1 contains an over 150-year record, the comparisons of Mg/Ca with SST presented here were done using post-WWII data only. The reasons are that the quality and consistency of techniques for measuring the sea surface temperature prior to the 1950’s have been controversial (Kushnir, 1994); and the number of observations used for calculating HadISST1 in the studied area is low prior to WWII (Figure 9).
In order to investigate the climate dynamics recorded as decadal and multidecadal variations in the crustose coralline algal geochemical signal, the Mg/Ca master chronology was compared to the NAO and AMO indexes. The annual mean NAO index used in this study was calculated from the NAO station based monthly index available at the Climate Analysis Section (http://www.cgd.ucar.edu/cas/jhurrell/indices.html). The AMO index used in this report was computed with the KMNI Climate Explorer (http://climexp.knmi.nl/getindices.cgi) using the averaged HadSST2 dataset over the region between 25° to 60° N and 7° to 75° W, minus regression on global mean temperature (Rayner et al., 2006).

The Mg/Ca master chronology was analyzed using the multitaper spectral method (MTM – calculated with K-spectra Toolkit version 2.21). Power spectrum analysis, like MTM, allows the identification of dominant periodicities in noisy time series (Mann and Lees, 1996) resulting in interannual and interdecadal variabilities that can be associated with natural climatic oscillations (e.g. NAO, AMO). Before running the power spectrum analysis, the long-term change in the mean of the time series was removed by mathematically subtracting the linear trend from the annual Mg/Ca data.
Additional verification of the multidecadal variability in the climatic signal recorded by crustose coralline algae was possible from a wavelet power spectrum (Torence and Compo, 1998) of the Mg/Ca master chronology. The wavelet analysis was carried out to separate recurrent oscillations occurring in the short term (few years) from those observed only at decadal scales (Yiou et al., 1996). The wavelet tool is intended to analyze time series and detect variances at different timescales (Torence and Compo, 1998). The wavelet application used in this study was accessed at http://paos.colorado.edu/research/wavelets.

A map showing the spatial variability of correlation between the proxy Mg/Ca master chronology and the instrumental HadISST1 covering the North Atlantic region between 40° to 60° N and 40° to 70° W for the comparison period (1950 – 2007) was computed in Climate Explorer (http://climexp.knmi.nl/corfield.cgi). The purpose of this map is to investigate the regions from where SSTs have an influence on the sampling sites.

In addition to the correlations with climate parameters, the Mg/Ca time series were also compared with volume transport of the LC measured in Sverdrup (1 Sv=10^6 m^3/s.). The LC volume transport data were obtained from http://www.meds-sdmm.dfo-mpo.gc.ca where surface volume transport (positive equatorward) is provided between the 200-3000 m isobaths from 1993 onwards. Figure 1b shows the location of the track along which LC volume transport data were measured.
4. Results

This section presents the results of the LA-ICP-MS analyses for each site, individual and composite Mg/Ca time series, correlated with climate observations and indices, such as sea surface temperature, Multidecadal Atlantic Oscillation (AMO), North Atlantic Oscillation (NAO), and Labrador Current volume transport. For the purpose of this study, a composite time series is defined as the combination (average) of different transects within the same sample, whereas the master time series is composed of data from multiple specimens. The annual SST time series used in the correlations corresponds to the 8-month average (May to December) since this is regarded as the main growth period in *C. compactum* (Halfar et al., 2008).

Both, growth rates and ages of crustose coralline algae reported here were calculated using Mg/Ca ratios. Growth rates of *C. compactum* were established on the basis of number of values (measurements) per cycle (year) once the lows and highs were tied to the coldest and warmest months (see Establishing of age model section). Ages of individual specimens of *C. compactum* were determined by counting cycles after comparing the two transects from the same sample to validate the respective age models. Because in each sample two LA-ICP-MS transects with slightly different lengths were measured, the final age represents the number of years between the youngest and the oldest years recorded by either of the two transects. Table 3 presents a summary of the statistical correlations between Mg/Ca time series and instrumental SST (Annual average HadISST1<sub>May-Dec</sub>).
Table 3. Significance of correlations between 3-year mean Mg/Ca time series from QP, SJ, and HA with 3-year mean instrumental SST (HadISST1 averaged from May to December for each collection site, see text for exact location). QP time series compared with SST from Gulf of St. Lawrence.

4.1 Quirpon Island Mg/Ca time series (QP)

The two *C. compactum* specimens from Quirpon Island, 08-QP4-3 and 08-QP4-4, grew at an average rate of 345 µm/yr with estimated ages of 76 and 68 years, respectively. Although the raw Mg/Ca data displayed good annual cyclicity, the comparison of the composite Mg/Ca time series of both samples shows poor similarity (Figure 10 c and f). The QP site is located in a zone of confluence of at least two contrasting surface currents flowing in and out of the Gulf of St. Lawrence through the Strait of Belle Isle (Garret and Petrie, 1981); namely the inflow of a portion of the inshore Labrador Current and the outflow of the Strait Current (Fig. 1c). Therefore, two SST data sets, representing temperatures of water masses off of Labrador (spatially averaged HadISST1 data from 52° to 54° N and 53° to 55° W) and the Gulf of St. Lawrence (GSL) (spatially averaged...
HadISST1 data from 50° to 51° N and 57.5° to 58.5° W) were compared to the QP Mg/Ca times series.

Figure 10. Correlation between Mg/Ca time series from site QP and instrumental SST from Gulf of St. Lawrence (spatially averaged HadISST1 data from 50° to 51° N and 57.5° to 58.5° W). (a) and (b) Transects 1 and 2 of sample 08-QP4-3 respectively. (c) Composite Mg/Ca time series for 08-QP4-3. (d) and (e) Transects 1 and 2 of sample 08-QP4-4 respectively. (f) Composite Mg/Ca time series for sample 08-QP4-4. (g) Combination of the 4 transects from QP. SST corresponds to the 8-month (May to December) average. Dashed line indicates SST prior to 1950; r-values represent comparison between 1950-2007 only.
A 3-year running mean was applied to proxy and SST data; hence all the $r$ values presented here are adjusted to take into account the loss of degrees of freedom. The individual transects of the 08-QP4-3 specimen (Figure 10a and b) show distinct correlation coefficients ($r=0.11$, $p=0.05$, $n=56$ for Transect 1 and $r=0.52$, $p=0.01$, $n=56$ for Transect 2) when compared with SST from the GSL. When both transects were averaged to obtain the composite time series (Figure 10c), the correlation is significantly improved ($r=0.55$, $p=0.01$, $n=56$) suggesting that an averaged proxy record revealed higher correlation with SST than either of the individual records. For 08-QP4-3 the highest correlations are found from 1959 onwards. In contrast, the individual and composite 08-QP4-4 time series display insignificant (negative) correlations with SST from the GSL (Figure 10d, e, and f).

A similar situation was seen when the Mg/Ca time series are correlated with HadISST1 off Labrador, an area mainly influenced by the Labrador Current. Correlation for the 08-QP4-3 composite are positive ($r=0.31$, $p=0.05$, $n=56$) but lower compared to those observed for the SST data set from the GSL (Figure 11a to g). The 08-QP4-4 time series (individual transects and composite) show negative correlation with SST off of Labrador.

The lack of similarity in the geochemical signal between the two QP samples can possibly be associated with unconformities by grazing events. These disruptions, if present, are in fact unrevealed in the scanned images and may also lead to a disagreement between SST and Mg/Ca for some periods especially before 1959 (Figure 10c) for sample 08-QP4-3. Based on these results the samples 08-QP4-4 and QP-4-3 were considered inadequate to be included in further calculations of composite time series (e.g. Mg/Ca Master Chronology).

The low frequency interannual oscillations observed in the entire Mg/Ca time series of 08-QP4-3 follow the general trend of the SST variations (Figure 10c). The decrease in Mg/Ca for the first 10 years of growth (1930–1940) is followed by a relatively rapid increase that reaches its maximum in 1946. Thereafter, a longer (1946-1963) decline in the Mg/Ca values is followed by a rebound until 1985.
Figure 11. Correlation between Mg/Ca time series from site QP and instrumental SST off Labrador (spatially averaged HadISST1 data from 52° to 54° N and 53° to 55° W). (a) and (b) Transects 1 and 2 of sample 08-QP4-3, respectively. (c) Composite Mg/Ca time series for 08-QP4-3. (d) and (e) Transects 1 and 2 of sample 08-QP4-4 respectively. (f) Composite Mg/Ca time series for sample 08-QP4-4. (g) Combination of the 4 transects from QP. SST corresponds to the 8-month (May to December) average. Dashed line indicates SST prior to 1950; r-values represent comparison between 1950-2007 only.
4.2 Cape St. Martin Mg/Ca time series (CSM)

A sample collected at Cape St. Martin in September 1964 extends back to 1875 and therefore spans 87 years (this sample was obtained from the Smithsonian Institution collection in Washington D.C.; Alg. Coll. #-00170716 provided by A.W. Adey). The calculated mean annual growth rate of this specimen is 297 µm/yr.

Figure 12 shows the individual and composite Mg/Ca time series for sample 170716 correlated with instrumental SST data (HadISST1 data from 50°N 55°W). Because the comparison period of this sample with reliable SST is rather short spanning only 12 years (1950 to 1961) no r-values are shown. However, Figures 12a and b illustrate that the Transect 2 presents better correlation with SST than Transect 1. The composite time series for 170716 (Figure 12c) also includes a third transect that represents the 12 oldest years (1875-1887) of growth and overlaps 2 years with Transect 2.

Figure 12. Correlation between Mg/Ca time series from site CSM and instrumental SST (HadISST1 data from 50°N 55°W). (a) and (b) Transects 1 and 2 of sample170716 respectively. (c) Composite Mg/Ca time series for 170716 by combining the 2 transects. SST corresponds to the 8-month (May to December) average.
4.3 St. John's (SJ) Mg/Ca time series

In general, the Mg/Ca profiles at SJ display clear annual resolution with average vertical growth rates between 215 µm/yr and 220 µm/yr. Specimen lifespan ranges from 1908 to 2007 (08-SJ-21) and 1918 to 2007 (08-SJ-28).

Figure 13 shows the Mg/Ca time series for the individual transects as well as the composite (four transects averaged) correlated with instrumental SST (HadISST1 from 47°N 52°W). The correlations between individual Mg/Ca transects and SST for the comparison period (1950-2007) are always positive and with variable $r$ values ranging from $r=0.23$ ($p=0.05$, n=57 for 08-SJ-21 Transect 1) to $r=0.53$ ($p=0.01$, n=57 for 08-SJ-21 Transect 2) (Table 3).

Comparing the results of the two SJ samples, 08-SJ-21 displays better correlations with HadISST1 (47°N 52°W) than 08-SJ-28 not only for the individual transects but also for the composite time series (Figure 13). When comparing the four stacked transects with local HadISST1 (Figure 13g), the correlation improves drastically ($r=0.82$, $p=0.005$, n=57). Significant correlations observed between the stacked Mg/Ca transects and SST indicates that the combination of several transects provides a more robust paleoclimate signal and confirms that *C. compactum* accurately records variations in SST as changes in Mg/Ca in its calcite skeleton.
Figure 13. Correlation between Mg/Ca time series from site SJ and instrumental SST off St. John's (HadISST1 data from 47°N 52°W). (a) and (b) transects 1 and 2 of sample 08-SJ-21 respectively. (c) Composite Mg/Ca time series for 08-SJ-21. (d) and (e) Transects 1 and 2 of sample 08-SJ-28 respectively. (f) Composite Mg/Ca time series for sample 08-SJ-28. (g) Combination of 4 transects from SJ. SST corresponds to the 8-month (May to December) average. Dashed line indicates SST prior to 1950; r-values represent comparison between 1950-2007 only.

4.4 Halifax Mg/Ca time series (HA)

Mg/Ca ratios obtained from samples collected near Halifax show poor annual cyclic patterns. Correlations of raw data between two transects in the same samples are insignificant (Figure 14 a and b), leading to a poorly constrained age model. Figure 14
shows a comparison of raw Mg/Ca profiles between samples from sites HA (Figure 14a and b) and SJ (Figure 14c) and illustrates the quality of cyclic pattern in the geochemical record. Growth irregularities in the HA samples, mainly caused by intensive grazing (Figure 15), include either narrow or broad annual cycles; small cycles misrepresenting annual growth; and cycles without an evident peak in the Mg/Ca raw data (Figure 14a and b).

Figure 14. Raw Mg/Ca data for site HA. Transect 1 (a) and Transect 2 (b) show lack of consistency in cyclicity. High-quality Mg/Ca cycles at site SJ shown for comparison. Arrows indicate periods where algae exhibit irregular growth rates. The following irregularities are identified: Narrow cycles (A), lack of distinctive maximum (B), or misrepresented annual growth increments (C). Left side on X axis represents the top (youngest) part of the sample.
Figure 15. Intensive grazing on living surface of crustose coralline algae (arrows on left panel) lead to disturbances in thallus (right panel). (R) Missing row of conceptacles due to grazing damage and (U) U-shaped outline and removal of conceptacle (U). (Image from Samaroo, 2009).

Despite the large interannual growth variations observed in the Halifax C. compactum specimens, the calculated average annual growth rates vary between 230 µm/yr and 270 µm/yr for individual transects, and are therefore similar to growth rates calculated at the other study sites. However, longevity of Halifax specimens is low as samples only reached 33 (08-HA-70) to 48 years (08-HA-80).

Figure 16 shows the annual Mg/Ca time series for individual transects and the composite time series compared to instrumental SST (spatially averaged HadISST1 data from 42° N to 44° N and 63° W to 65° W). Comparison between the proxy data and instrumental SST resulted in poor to no correlation for the HA samples (Table 3). However, from Figures 16 (a) and (b) it is evident that 1987 separates two very distinct trends in the Mg/Ca values for 08-HA-70. The first 14 years, from 1973 to 1987, are marked by Mg/Ca values lower than 0.085 µg/g. After 1987 Mg/Ca increases from 0.073 µg/g to 0.089 µg/g and remain high between 0.094 µg/g and 0.084 µg/g (except for 2002) until 2004 when Mg/Ca plunges again to 0.07 µg/g. A similar trend is also observed in the annual mean SST data (Figure 16 a and b) with a sudden increase from 14.6° C to 15.2° C around 1987. In addition to the high Mg/Ca ratios observed after 1987, the record is dominated by large year-year variations in contrast to the low frequency variations observed in the earlier 14-year period of low Mg/Ca ratios similar
to the SST trend (Figure 16d). Based on these results, it is reasonable to say that although individual years do not correlate with SST, the long-term trend observed in the SST is reflected in this sample.

Figure 16. Correlation between Mg/Ca time series from site HA and instrumental SST off Halifax (spatially averaged HadISST1 data from 42° to 44° N and 63° to 65° W). (a) and (b) Transects 1 and 2 of sample 08-HA-70 respectively. (c) Composite Mg/Ca time series for 08-HA-70. (d) and (e) Transects 1 and 2 of sample 08-HA-80 respectively. (f) Composite Mg/Ca time series for sample 08-HA-80. (g) Combination of the 4 transects from HA. SST corresponds to the 8-month (May to December) average.
Unlike 08-HA-70, 08-HA-80 displays negative correlations with SST (Figures 16d, e, and f). In addition to correlating the HA samples with SST, correlations were done with local instrumental SST data measured at 44.63° N, 63.58° W available at the Integrated Science Data Management webpage (ISDM - http://www.meds-sdmm.dfo-mpo.gc.ca/isdm-gdsi/azmp-pmza/climat/index-eng.htm). Similarly no significant correlation was found.

4.5 Inter-site comparison

The inter-comparison among the 4 correlations of the composite Mg/Ca time series (QP, CSM, SJ, and HA) against instrumental SST shown in Figure 17 illustrates the spatial and temporal behavior of SST recorded in crustose coralline algae. The low number of transects that cover the earliest years (e.g. before 1920) can explain the weak correlations during that period. The period of overlap starts with an increasing trend from the early 1920’s to early 1940’s with a strong signal at CSM (Figure 17b) and SJ (Figure 17c). This period is followed by a decreasing phase that lasted over 20 years and reaches its lowest point at the mid 1970’s at SJ (Figure 17c) and early 1960’s at QP (Figure 17a) and HA (Figure 17d). The decrease in SST is recorded as a step-like decline in Mg/Ca content at QP and SJ. For CSM, the Mg/Ca record shows the decline (Figure 17b) until the end of the age model finished in 1962.

From the early 1970’s a renewed increase in SST is reflected by increasing values of Mg/Ca at QP and SJ. Fluctuations in the Mg/Ca ratios are highly associated with SST variations, though the upward trend suggests a general warming event. The relative short proxy record at site HA is characterized by the sudden increase in Mg/Ca values around the mid 1980’s that represents the increase in SST at that time. This abrupt rise in SST is preceded by a cold episode, which is not present in the northern sites (QP and SJ). After the early 1990’s the increase in Mg/Ca ratios is evidence for the recent warming trend illustrated in the SST record (Figure 17).
A 131-year long Mg/Ca master chronology was constructed by averaging the annual Mg/Ca values of the three transects of sample 170716 with the four transects of the samples collected in 2008 at site SJ. The criteria to choose the 3 samples to build the
Master Chronology were: 1) length of record, 2) absence of grazing or other growth disturbances, 3) significance of their correlations with instrumental SST dataset, and 4) exposure to the LC current. Hence, the HA samples were omitted because of abundance signs of grazing (=frequent disturbances), influence of Nova Scotia Current, and short record; and the QP samples were not used as the proxy signal shows a mixed influence of Gulf of St. Lawrence water masses (the Strait Current) and the Labrador Current obscuring a strong LC signature.

The Master Chronology therefore combines 7 different transects from 3 samples from two sites exposed to the LC. Each transects spans between 75 years and 99 years in length. Transects were combined based on ages assigned for each individual sample and the averaged values for the overlapping periods were calculated.

When the Mg/Ca master chronology is compared to HadISST1 for the period 1950-2007 (spatially averaged data from 46°N to 52°N and 55°W to 50°W), correlations are high \((r=0.57, p=0.005, n=57; \text{Figure 18b})\). It is worth noting that the correlation of the master chronology against instrumental SST is similar to that obtained for the composite time series at SJ as sample 170716 only covers 12 years (1950-1961) of the comparison period.
Figure 18. 131-year Mg/Ca master chronology generated by averaging 7 transects from 3 different samples. (a) Individual transects as well as the averaged (heavy line) Mg/Ca. (b) Mg/Ca master chronology compared to instrumental SST (HadISST1 spatially averaged data from 46°N to 52°N and 55°W to 50°W) between 1950 to 2007. SST corresponds to the 8-month (May to December) average.

4.7 Mg/Ca master chronology compared to AMO

Despite departures in the early 1880’s and 1950’s, the correlation between the normalized Mg/Ca master chronology and the Atlantic Multidecadal Oscillacion index (AMO) is highly significant ($r=0.36$, $p=0.001$, $n=131$). The positive anomalies in the Mg/Ca master chronology correspond with the positive multidecadal fluctuations in the AMO (Figure 19). Both, the proxy and instrumental climate records show positive anomalies during 1875 to 1905, 1925 to 1940, and 1970 to 2000 and negative anomalies during 1905 to 1925 and 1940 to 1970.
Figure 19. Normalized Mg/Ca master chronology compared to AMO index (annual resolution upper panel). Lower panel shows the 10-year moving average of proxy and instrumental data.

4.8 NAO index in the Mg/Ca master chronology

The normalized Mg/Ca master chronology was also compared to the NAO index (Figure 20). Despite a weak, but significant correlation between NAO and Mg/Ca ($r=0.22$, $p=0.05$, $n=127$), the long-term trend of the NAO is well represented by the algal Mg/Ca content. Low algal Mg/Ca content records the extreme negative states of the NAO in the late 1870's and 1960's.

Interestingly, the historical minimum in SST around the 1880's that has been associated
with an extreme negative NAO phase (Marsh, et al., 1999) is well represented by the lowest Mg/Ca values in the proxy record. In the same way, the increasingly positive NAO during the 1920’s that extended to the 1940’s and the negative NAO anomaly from the 1950’s to the mid 1960’s is well reflected in the Mg/Ca time series. The increasing Mg/Ca values since the early 1970’s match the return of the NAO index to a positive phase.

Figure 20. Normalized Mg/Ca master chronology compared to NAO index. Positive (negative) phases of NAO correspond to high (low) Mg/Ca content in crustose coralline algae.
4.9 Spectral analysis of proxy climate data

A multitaper spectral analysis of the Master Chronology reveals significant periodicities at 2 to 4, 9 and 25 to 40 years (Figure 21). Similarly, a wavelet analysis reveals two significant periodicities centered at 45 to 50 and 4 to 5 years (Figure 22). These frequencies are comparable to periodicities observed in the AMO and NAO, respectively. As can be seen by the cone of influence, the region in which edge effects become important and limits the certainty of the power spectrum, the relatively ‘short’ (131-year) record of the Master Chronology is a constraint for identifying low-frequency multidecadal oscillations such as the AMO (Figure 22).

Figure 21. Multitaper power spectrum of the Mg/Ca master chronology displaying significant peaks at 2 to 4 and 9 years representing NAO periodicity. A broad peak between 20 to 45 years might represent AMO periodicity.
Figure 22. (a) Wavelet power spectrum of master chronology; dark contours indicate frequency of the dominant periodicities centered at ~ 50 years associated with multidecadal variations of the AMO. (b) Global wavelet spectrum of master chronology indicating significant power around 45 years.

4.10 Labrador Current transport variability and Mg/Ca

The Mg/Ca time series was further compared to a seasonal resolution time series of LC volume transport (Figure 23). Results show a significant inverse relationship ($r=-0.51$, $p=0.001$, n=59) over the entire length of instrumental measurements, implying that a strong flow of the LC relates to reduced Mg/Ca values, which in turn represent decreased temperatures. As shown in Figure 23, the decreasing trend in the volume transport of the LC from 1993 to 1997 is comparable with the increase in Mg/Ca content in crustose coralline algae. A continuing decrease in Mg/Ca values since 1999 is associated with a gradual increase of water mass transported by the LC delivering cold water to the Newfoundland shelf. The relationship between Mg/Ca – LC volume transport can help to understand the influence that the cold water masses moving from the Arctic to the equator along the eastern Canadian coast exert on marine ecosystems in the NW Atlantic (Scheibling and Hennigar, 1997; Drinkwater, 2006).
Figure 23. Comparison between composite Mg/Ca time series of SJ and volume transport of Labrador Current indicating a negative relationship (quarterly resolution Track SW191–See Figure 1b for position of transect; Sverdrup, Sv=10^6 m^3/s). Volume transport data from http://www.meds-sdmm.dfo-mpo.gc.ca.
5. Discussion

5.1 Quality and suitability of *C. compactum* as a paleoclimate proxy

The results presented here demonstrate that the crustose coralline alga *Clathromorphum compactum* records fluctuations in SST as variations in the Mg/Ca ratio in its high Mg-calcite skeletons. Changes in the Mg/Ca ratios of *C. compactum* are positively correlated with annually averaged instrumental HadISST1May-Dec data. Moreover, spectral analyses of the proxy time series reveal interannual and multidecadal signals that reflect NAO and AMO periodicities. Hence, this study confirms the value of this alga as a proxy for reconstructing marine climate in the Northwestern Atlantic.

Differences in the local environmental and ecological conditions in the marine ecosystems along the east coast of Canada result in a shorter or longer growing season affecting calcification rate in *C. compactum* specimens. Extreme cold and persistent seasonal sea ice conditions off Labrador (Hill, 1998; Hill et al., 2002) contrast with the free sea ice and warm climate off Nova Scotia (IPNA, 1989). The best correlations of Mg/Ca time series against SST for the 56-year comparison period were observed at the site SJ followed by sites QP and HA (CSM is not considered here given the short period of overlap with comparison period from 1950 onwards). The high correlations observed at the SJ site might be attributed to oceanographic and biological factors. First, the SJ site is mainly exposed to the inshore branch of the LC; and second, in contrast to sites QP and HA, SJ is covered by understory macroalgae that provide shading and abundant food for sea urchins.

The inter-site comparison of results indicates that changes in local oceanographic and ecosystem conditions influence the final quality of paleoclimate signal in crustose coralline algae. Habitats where specimens are exposed to intensive grazing (e.g. site HA) and water mixing (e.g. site QP) led to low correlation values, while specimens from
areas mainly influenced by the inshore Labrador Current (e.g. SJ) exhibited significance correlation with SST.

5.2 Mixing ocean currents and the quality of the proxy record

The fact that Mg/Ca variations in *C. compactum* from QP are better correlated with SST data from the Gulf of St. Lawrence than SST off of Labrador suggests that this site does not exclusively record changes in SST associated with the LC. In fact, water masses are exported by the Strait Current flowing northeast from the GSL along the southeast side of the Strait of Belle Isle (Garret and Petrie, 1981) (Figure 1c).

At site QP mixing takes place between the cold water masses associated with the inshore branch of the LC and the warm outflow of the Strait Current at the Strait of Belle Isle (Garret and Petrie, 1981; Petrie and Anderson, 1983). The dominant inflow entering the Gulf of St. Lawrence through the Strait of Belle Isle in late fall and winter (Garret and Petrie, 1981) is in agreement with a strong LC during the cold months (Lazier and Wright, 1993; Han et al., 2008). In contrast, a weak LC during the summer months results in an increased outflow from the Gulf of St. Lawrence (Garret and Petrie, 1981). These seasonal oceanographic conditions lead to the strong Mg/Ca signal in crustose coralline algae correlated with SST from the Gulf of St. Lawrence at QP. The time of strong Strait Current (e.g. summer) coincides with the main period of calcification (=growth) in crustose coralline algae, which has been identified as taking place during warm seasons (Halfar et al. 2008).

An additional source for water masses influencing QP is an incoming cross-shelf flow north of the Belle Island Bank (Figure 1b) that brings warmer and more saline waters from the offshore branch of the LC (Narayanan, et al., 1996). This eastward cross-shelf flow compensates the westward outflow through the Strait of Belle Isle. The potential exposure of the QP site to the warm cross-shelf flow pulses of the offshore branch of the LC (Narayanan, et al., 1996) may contribute to a disturbed climate signal recorded by *C. compactum* at this location.
A similar situation can be occurring at HA site, but here the fresh and warm water of the Nova Scotia Current (Figure 1b) coming out from the Gulf of St. Lawrence through the southern side of Cabot Strait (Drinkwater et al., 1979) can potentially mix with the LC (Houghton and Fairbanks, 2001). In fact, the entire eastern coastline of Nova Scotia is mainly affected by the Nova Scotia Current. Moreover, increases in SST off Halifax have been linked to warm water masses transported to the east coast of Nova Scotia by Gulf Stream eddies (Scheibling and Hennigar, 1997). This mixing of ocean currents with different physical properties (e.g. salinity and temperature) occurring along the east coast of Nova Scotia potentially obscures the climatic signal recorded by crustose coralline algae collected at site HA. In contrast, Mg/Ca ratios derived from samples from the SJ site that is well exposed to the inshore branch of the LC are highly correlated with instrumental SST data.

5.3 Ecosystem conditions and the quality of the proxy record

An additional factor that contributes to the weak correlation observed in 08-QP4-4 and both HA samples could be the result of stressed biological conditions. QP and HA samples were collected on sea urchin barrens with no shading but potential grazing pressure, in contrast, the SJ site had significant understory kelp and its samples displayed good records. SJ is described as having understory kelp from where a somehow controlled sea urchin community could get their food supply instead of eating the coralline algae (Steneck, 1982). However the presence of macroalgae at any of the sites might have been very different in the recent past since its spatial extend is not stable but changes overtime (Scheibling, 1999). While fleshy macroalgae are a primary food source of sea urchins, the latter tend to graze on coralline algae in the absence of their main food source (Steneck, 1982; Scheibling, 1999).

The temporally alternating sea urchin barren and kelp bed communities observed in marine ecosystems along the east coast of Nova Scotia (Scheibling, 1986) may explain why SST and Mg/Ca in samples from the HA site do not show significant relationships with annual SST. Habitats can change from barrens to kelp in relatively short time
scales (e.g. decades or less Scheibling et al., 1986) promoting the consumption of crustose coralline algae by sea urchins. After complete grazing of kelp bed sea urchins use crustose coralline algae as an alternate food source (Steneck, 1982; Scheibling et al., 1999; Maneveldt et al., 2006). External and internal signs of sea urchin grazing on coralline algae (Figure 15) are abundant at sites HA (Samaroo, 2009) and QP resulting in local disturbances or the partial removal of individual growth increments affecting Mg/Ca cycles. The partial removal of growth increments may also contribute to low growth rates observed in the HA samples. In the absence of grazing one would expect higher growth rate associated with warmer waters at this site compared to all other sites studied here.

In addition, it has been found that calcification rates on crustose coralline algae can be reduced above an optimum temperature range of 5 - 10 °C for boreal subarctic regions (Adey, 1970). This can be the case for HA where local summer sea temperatures can reach 16° C (Scheibling, 1986) a value considered at the limit of the species distribution (Adey and Steneck, 2001). Hence, a number of external factors contribute to the varying quality of the records observed in C. compactum from different sites.

5.4 The eastern Newfoundland shelf and large scale climate patterns in the North Atlantic

The NAO, as defined previously, is a periodic pattern of atmospheric circulation variability with decadal recurrence calculated from the pressure difference between Azores and Iceland (Bjerknes, 1964). The anomalous atmospheric circulation patterns associated with NAO eventually affect ocean circulation in the North Atlantic (Hurrell, 1995), which in turn causes variations in the ocean temperature (Flatau et al., 2003). The interdecadal fluctuations in SST associated with the NAO oscillations follow broadly the trend observed in the Mg/Ca master chronology.

Analyses of hydrographic data have demonstrated that a high (positive) NAO index leads to strong westerly winds in winter, which in turn weakens the volume transport in the Labrador Sea the following summer (Han and Tang, 2001; Myers, et al., 1989).
This seasonal variability of LC transport can explain the positive correlation between the NAO index and the Mg/Ca time series presented here. Variations in temperature and volume transport of the baroclinic, buoyancy-driven inshore branch of the Labrador Current have been found significantly correlated with the NAO variability (Lazier and Wright, 1983) and are in agreement with instrumental observations (Flatau et al., 2003; Han and Tang, 2001; Petrie and Drinkwater, 1993). This can be explained by the decreased interchange (ocean-atmosphere) of heat in winter associated with weakened westerlies over the Labrador Sea and North Atlantic during persistent NAO negative mode along with the improved movement of arctic water masses to the south (Dickson et al., 1996). The cyclic long-term oscillations between positive and negative phases of the NAO are recorded as high and low trends in the Mg/Ca master chronology.

Similarly, the strong correlation between the 131-year Mg/Ca master chronology and the AMO index suggests that the interdecadal variability in the AMO influences the SST along the Eastern Canadian coast. The evidence presented here, confirms that decreasing water temperatures associated with negative modes of the NAO and AMO are linked to strong Labrador Current volume transport (Petrie and Drinkwater, 1993). The influence of AMO variability on the volume transport of the Labrador Current has been associated to large-scale ocean circulation in the North Atlantic (Dima and Lohmann, 2007). Freshening of the Atlantic Ocean driven by sea ice/fresh water export from the Arctic weakens the Thermohaline Circulation, which in turn increases southward buoyancy transport (Dima and Lonmann, 2007) resulting in the anomalous cold SSTs in the Northwestern Atlantic (Petrie and Drinkwater, 1993). The decreasing ocean temperatures in the eastern coast of Canada control the incorporation of Mg in the calcite skeleton of crustose coralline algae.

5.5 Mg/Ca ratios as recorders of regional oceanography

The cooling effect of cold Arctic water transported by the LC is reflected by low Mg/Ca ratios in C. compactum. The strong negative correlation between LC volume transport and the Mg/Ca time series helps to explain the link between significant changes in
ocean circulation and SST observed in the Canadian Atlantic. The relation LC volume transport-SST is illustrated by several studies like the devastating extreme cold episode in the early 1880’s that eventually caused the mass mortality of tilefish in 1882 in the shelf waters off the north-eastern United States (Marsh, et al., 1999). This natural ecological disaster is represented by extreme low Mg/Ca values around the 1880’s in the master chronology and corresponds with a minimum in the NAO.

Similar but less devastating oceanographic and atmospheric conditions were observed during the mid 19th century when a significant cooling from the early 1950’s to the mid 1960’s is followed by an increasing trend in SST since 1970 (Petrie and Drinkwater, 1993); these variations in SST follows NAO oscillations and are well represented in the Mg/Ca master chronology.

5.6 Evolution of Mg/Ca based temperatures through time

The spatial correlation of the proxy time series against instrumental SST (HadISST1) reveals a strong regional signal (Figure 24) in the Northwest Atlantic associated with the inshore branch of the Labrador Current flowing along the Labrador coastline and the eastern coast of Newfoundland. This supports the idea that the observed temperature variations along the Northwestern Atlantic are linked to fluctuations in the volume transport of the LC (Petrie and Drinkwater, 1993, Loder et al., 2001).

The 131-year long master chronology offers an overview of the evolution of SST in the Northwestern Atlantic since the late 1880’s (Figure 25) with two distinct long-term patterns. From 1890 to 1950 the Mg/Ca master chronology indicates a relatively weak LC represented by high (average > 0.08 µg/g) Mg/Ca ratios. After 1950 lower Mg/Ca ratios suggest that a stronger LC causes cooling of the Canadian Atlantic until the early 1990’s when a rebound in SST is marked by increase in Mg/Ca ratios.

The beginning of the proxy record is marked by minimum Mg/Ca values around 1880. This all-time Mg/Ca low is correlated with the extreme cold event in 1882 characterized
by historical minimum SST that resulted in the massive mortality of tilefish in shelf waters off the north-eastern U.S.A. (Marsh et al., 1999). The physical conditions of the dead fish suggested that a sudden incursion of cold water might be the cause of such biological disaster (Marsh et al., 1999). The crustose coralline algae shows minimum incorporation of Mg in their calcite around the 1880's providing strong evidence that low SST prevailed at that time off of Newfoundland. This cooling episode is followed by an increasing trend in the Mg/Ca values during the end of the 19th century that extends until the early 1900's when a new cooling phase is observed. The gradual decrease in Mg/Ca at the beginning of the 20th century brought values back close to normal average until the early 1920's when Mg/Ca experienced a new recovery resembling the warming in the North Atlantic at the beginning of the last century (Bengtsson, et al., 2004).

Figure 24. Spatial correlation of Mg/Ca master chronology with instrumental HadISST1_May-Dec from 1950 to 2007 indicating that crustose coralline algae record temperature patterns associated with the Labrador Current. Asterisks indicate location of samples. Analysis conducted at http://climexp.knmi.nl/.
The well-documented Arctic warming during 1920-1940 (Bengtsson, et al., 2004) has been linked to ecosystem shifts in marine species in the North Atlantic (Drinkwater, 2006). But the presence of this warming in the Northwestern Atlantic has been questioned because of the lack of evidence with changes in SST (Drinkwater, 2006). However, the increasing Mg/Ca content in the crustose coralline algae during the 1920’s and 1940’s presented here indicates that warming of the ocean along the eastern Canadian coast during this period occurred (Figure 25).

The second half of the 20th century shows a distinctive pattern with interdecadal fluctuations of Mg/Ca very similar to changes in SST. The 1950’s and 1960’s are characterized by a cooling trend represented in the master chronology as decreasing Mg/Ca values. The decrease in SSTs in the mid-20th century has been associated with a four-fold intensification of LC volume transport (Petrie and Drinkwater, 1993). Possible mechanisms associated with the low SST observed in the early 1950’s and mid 1960’s are the incursion of cold slope waters (offshore branch of the Labrador Current) onto the shelf and vertical mixing (Petrie and Drinkwater, 1993). From 1970 to the present, the Mg/Ca ratios display relatively regular interannual variations with no indication of major changes in the climate and oceanographic conditions.

Figure 25. Significance of the algal proxy record showing some important paleoclimate events.
6. Conclusions

1. This is the first study using LA-ICP-MS determined Mg/Ca ratios of the crustose coralline algae *C. compactum* as recorders of subarctic SSTs in the Northwest Atlantic.

2. Annually-resolved Mg/Ca time series in the crustose coralline algae *C. compactum* are strongly correlated with local and regional instrumental SST after 1950. Instrumental SST observations before 1950 are scarce in the subarctic NW Atlantic. Multiple averaged Mg/Ca records from spatially distant *C. compactum* specimens result in a more robust SST reconstruction than individual records alone. A combination of annual resolved Mg/Ca data from modern and museum-collected specimens yielded a 131-year long master chronology that reveals low-frequency oscillations related to the Atlantic Multidecadal Oscillation. Higher-frequency periodicities centered at 2.5 and 9 years are similar to oscillations exhibited by the North Atlantic Oscillation.

3. Negative correlation of Mg/Ca ratios with Labrador Current volume transport demonstrates the cooling effect of the LC on eastern Newfoundland near-shore habitats. Hence, using *C. compactum* from the NW Atlantic volume transport of the LC inshore branch can be reconstructed for the past 131-years. The results indicate weakening of the LC after 1880 with minimum volume around 1890 represented by high Mg/Ca ratios. After that, there is a recovery in the volume transport of the LC until the mid 1920’s when a new increasing trend in the Mg/Ca values, which lasts for almost 2 decades, suggests a weak LC.

4. Careful site and specimen selection is of utmost importance when using crustose coralline algae as climate recorders. Growth irregularities, caused by grazing activity (e.g. sea urchins) and other physical disturbances, can significantly affect the climate signal contained in individual specimens. Furthermore, longevity of plants appears to be reduced when grown under environmental stress, such as high-temperature stress.
near their limits of biogeographic distribution.

5. Future work should apply cross-dating techniques commonly used in dendrochronology to construct time series from numerous modern and submodern specimens. Furthermore, multiproxy studies combining crustose coralline algae with other marine and terrestrial archives can improve century-scale subarctic climate reconstructions.
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