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Do skeletal Mg/Ca ratios of Arctic rhodoliths reflect atmospheric CO_2 concentrations?

Sebastian Teichert[1] · Nora Voigt[1] · Max Wisshak[2]

Abstract

The rhodolith-forming coralline red algal species *Lithothamnion glaciale* is the key ecosystem engineer of rhodolith beds on the coast of Svalbard. Because it significantly increases local biodiversity in this high-Arctic environment, we investigate the potential impact of changing environmental parameters on its calcite skeleton. Using energy-dispersive X-ray spectroscopy and environmental data from the Norwegian government's environmental monitoring, we show that the magnesium concentration within an analysed algal calcite skeleton decreases linearly and significantly over a 40-year time span ($R^2 = 0.267$, $p_{perm} < 0.001$). Mg/Ca ratios show the most significant correlation with atmospheric CO_2 concentrations ($R^2 = 0.614$, $p < 0.001$), and lower correlations to sea ice cover and seawater temperature. This raises the question of whether the Mg/Ca in the rhodolith skeleton is reflecting an increase in aqueous pCO_2 that drives ongoing ocean acidification. Since such a change in geochemistry may alter the stability of the calcite skeleton, our results could imply an impact on the future role of the rhodoliths as ecosystem engineers and consequently on Arctic biodiversity.

Introduction

Coralline algae are a consistently and heavily calcifying group of rhodophytes from the subclass Corallinophycidae Le Gall & Saunders, 2007. Rhodoliths are free-living structures composed mostly (> 50%) of non-geniculate (i.e. lacking uncalcified joints) coralline algae and are abundant from tropical to polar latitudes (Foster 2001). In the Arctic environment of the Svalbard archipelago, they are major carbonate producers (Teichert and Freiwald 2014), producing between 100.9 g $(CaCO_3)$ m^{-2} yr^{-1} in Nordkappbukta (80.5°N) and 200.3 g $(CaCO_3)$ m^{-2} yr^{-1} in Isfjorden (78.3°N). These rhodoliths mainly comprise *Lithothamnion glaciale* Kjellman, 1883 and form beds of nucleated and hollow forms that significantly increase the local biodiversity

(Teichert 2014) by providing ecological niches for a variety of organisms. Therefore, potential changes in the calcification process of the rhodoliths caused by factors associated with ongoing global change—like rising temperatures and anthropogenic CO_2 release—are expected to have effects beyond the rhodoliths themselves.

The calcification process of many coralline algae, including *L. glaciale*, involves the precipitation of high-magnesium calcite within the cell walls, which is spatially controlled by a polysaccharide matrix (Bilan and Usov 2001). Thereby, their cell walls produce an outer zone consisting of thin needle-shaped crystals tangential to the cell wall and an inner zone comprised by radial crystals perpendicular to the cell wall (Bosence 1991). Many coralline algal species also show an annual banding pattern similar to tree rings (Freiwald and Henrich 1994) with distinct summer and winter growth increments, which result from changes in cell size and the composition of the calcite (Foster 2001). The winter growth increments of, e.g. *L. glaciale* have smaller and more intensely calcified cells than the summer growth increments, thus reflecting seasonality (Freiwald and Henrich 1994). Additionally, the winter growth increments are characterized by lower magnesium concentrations compared

✉ Sebastian Teichert
sebastian.teichert@fau.de

1   GeoZentrum Nordbayern, Friedrich-Alexander University
     Erlangen-Nürnberg (FAU), Loewenichstraße 28,
     91054 Erlangen, Germany

2   Marine Research Department, Senckenberg am Meer,
     Südstrand 40, 26382 Wilhelmshaven, Germany

to the summer growth increments (Kamenos et al. 2009). This is thought to be driven by seasonal changes in water temperature, because it is assumed that the substitution of calcium by magnesium in calcite is an endothermic process, so higher Mg/Ca ratios usually correlate with higher temperatures. This dependency has been used to reconstruct past seawater temperatures, not only using coralline algae (Hetzinger et al. 2009) but also other organisms like foraminifera (Lowenstein and Hönisch 2012).

However, mesocosm experiments have shown that, beside temperature, the photosynthetic rate, and thus ambient light levels, do also have an impact on the incorporation of magnesium within the calcite tissue (Williams et al. 2018). High light conditions resulted in an increased magnesium uptake, and this effect was even stronger at higher temperatures. However, the study concludes that it is still not clear which is the main driver of magnesium uptake, light or temperature. Regarding the mere production of calcite without accounting for the Mg/Ca ratio, Teichert and Freiwald (2014) have shown that for the calcite production of *L. glaciale*, light intensity is more important than temperature. The influence of light on the calcification of coralline algae was used by Halfar et al. (2013) as a proxy for Arctic sea ice decline. Another variable which has been identified to impact the Mg/Ca ratio in *L. glaciale* is the seawater CO_2 partial pressure, pCO_2 (Ragazzola et al. 2016). This suggests that the rhodolith beds of Svalbard might be susceptible to ongoing ocean acidification, not only in terms of calcite production, which has been shown by Büdenbender et al. (2011), but also in terms of their skeletal composition and integrity.

Given this range of effects, the question arises which parameter has the highest long-term impact. Here, we evaluate the impact of four environmental parameters (atmospheric CO_2, seawater temperature, salinity, and sea ice cover as a proxy for light intensity) on the Mg/Ca ratio of a rhodolith formed by *L. glaciale* in the high-Arctic Mosselbukta at the northern coast of Spitsbergen. This rhodolith grew over a time interval of at least 40 years (1976–2015). We compare data from energy-dispersive X-ray spectroscopy with long-term environmental records. We apply multiple linear regression analysis and stepwise model selection to test our hypothesis that the Mg/Ca ratio within the calcite skeleton of *L. glaciale* negatively correlates with atmospheric CO_2 concentrations.

Methods

Sample collection

Rhodolith samples were obtained during the MSM55 expedition (ARCA) of RV *Maria S. Merian* from 11th to 29th of June 2016 (Wisshak et al. 2017). Rhodolith samples were

collected in Mosselbukta, a bay situated at the north coast of Spitsbergen, Svalbard archipelago (Fig. 1a, b). The site (station MSM55-416-1, 79°54.69′N, 15°48.61′E, referencing to WGS 84) was sampled using the manned submersible JAGO at c. 46 m water depth (Fig. 1c, d). All rhodoliths were dried in cabinet desiccators at 30 °C for 48 h and stored in sealed plastic bags (PE-LD) together with silica gel as a drying agent. One rhodolith (sample number SaM 10352) with preferably long (i.e. old) protuberances was chosen for further analysis.

Mg/Ca analyses

From this rhodolith, one protuberance with a length of 17 mm was cut off, impregnated with epoxy resin (Biresin®) and dried for 72 h at 30°C. To prepare for scanning electron microscopy (SEM), the protuberance was then longitudinally sectioned using a water-cooled low-speed diamond rock saw and the surface was polished with silicon carbide suspensions with grain size P400 on a polishing disc and P800 manually on a glass plate. The surface was then etched with hydrochloric acid (0.2 molL^{-1}) for 30 s, rinsed with demineralised water, and dried in a desiccation cabinet for 48 h at 30°C. The sample was mounted on an aluminium stub using wood glue (Ponal express®) and sputter coated with gold under argon gas for 6 min using 2 min intervals with 30 s breaks at 40 mA and 10,000 V.

The protuberance was analysed semi-quantitatively using a Tescan Vega 2 xmu SEM. SEM images were generated with a detector mix of 70% scatter electrons and 30% backscatter electrons, which resulted in the best recognition of annual growth increments. For energy-dispersive X-ray spectroscopy (EDS), line transects with 10 points per 500 μm (spot size of the probe current was < 200 nm) and c. 400,000 counts per measurement were set automatically in the software package INCA version 19. The line transects were positioned to avoid conceptacles (reproductive structures) wherever possible because conceptacles can have anomalous elemental signatures. Measurements of Mg and Ca in percentage weight (wt%) were conducted with a Peltier-cooled, 50 cm^2 X-Max EDS detector (Oxford Instruments) at 20 kV and 15 mm working distance. The device was calibrated using a copper standard and has a detection limit of c. 0.1 wt%, a standard error of ± 3% and a detection resolution of Mn Kα = 127 eV, F Kα = 64 eV, and C Kα = 56 eV.

Environmental data

Environmental data were obtained from MOSJ (Environmental Monitoring of Svalbard and Jan Mayen, https://www.mosj.no), which is an environmental monitoring system of the Norwegian government. Data on the annual mean
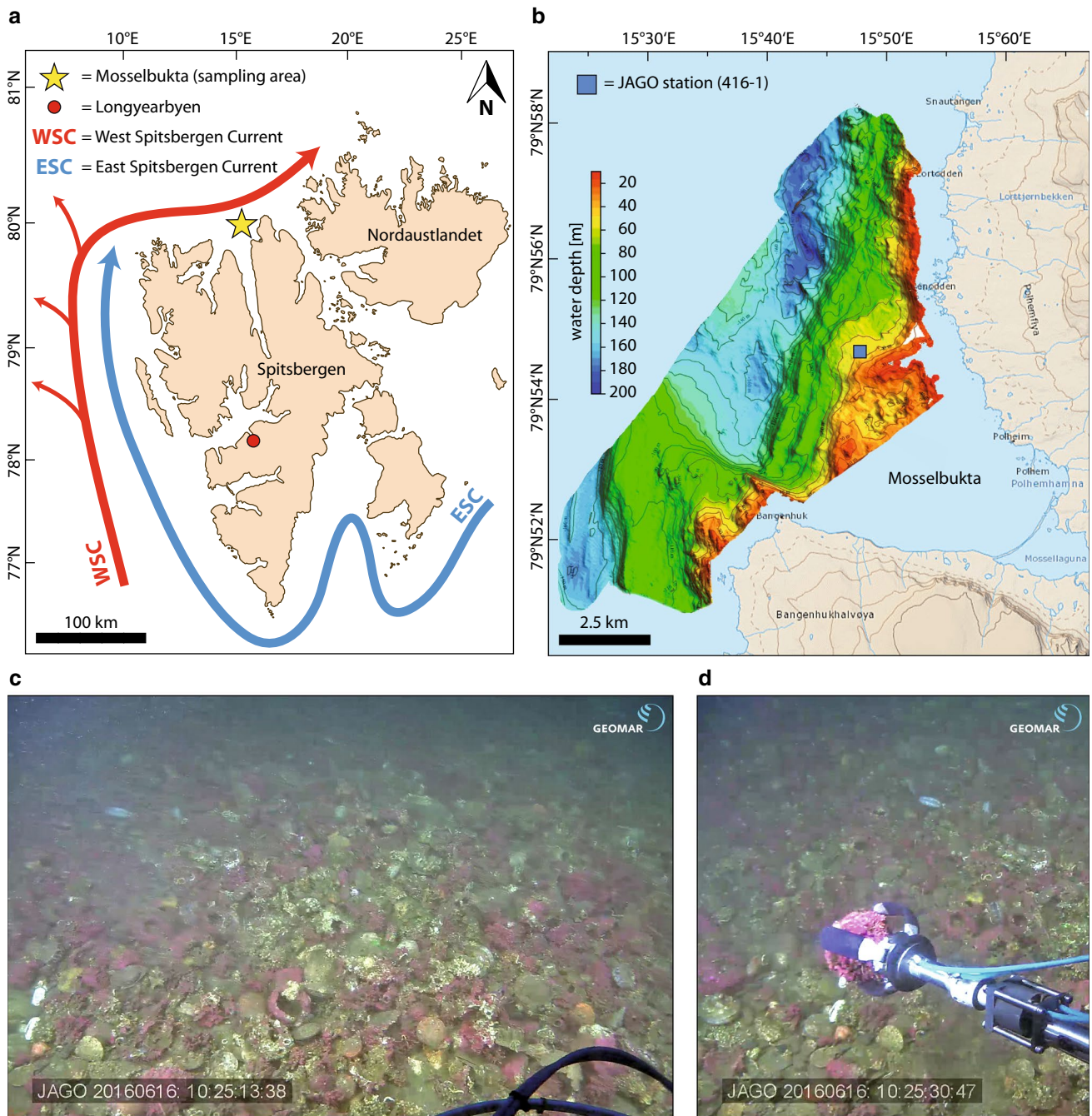
Fig. 1 Rhodolith sampling. **a** Location of the sampling area in Mosselbukta, north Spitsbergen, Svalbard archipelago. **b** Multibeam map of Mosselbukta indicating sampling station MSM55-416-1 (79°54.69′N, 15°48.61′E) in c. 46 m water depth. **c** Sampled rhodolith bed in Mosselbukta. **d** Manipulator arm of the JAGO submersible collecting the analysed rhodolith (sample number SaM 10352)

atmospheric concentration of CO_2 were recorded at the Zeppelin Observatory in Ny-Ålesund, northwest Spitsbergen, by the Stockholm University from 1988 to 2013 using a continuous infrared CO_2 instrument and by the Norwegian Institute for Air Research (NILU) from 2013 to present using a cavity-ring-down spectrometer. Decadal running average temperatures and salinities of the West Spitsbergen Current

(WSC) between 20 and 200 m water depth were recorded by the Norwegian Polar Institute using repeated hydrographic profiles penetrating the narrow (~ 10 km) WSC core. Sea ice extent in Fram Strait in April was calculated using data from the National Snow and Ice Data Center (NSIDC). Fram Strait was demarcated by latitudes 70°N and 82°N and longitudes 20°W and 15°E and grid cells of 25 × 25 km were

defined as ice covered if 15% or more of the area was covered by ice. According to MOSJ, this is a global standard for the definition of ice cover in relation to sea ice extent. All environmental data are compiled in Table 1.

Statistical analyses

Mean Mg/Ca values including standard errors were calculated for every annual growth increment and evaluated in terms of a linear trend. For a better visualization of a potential linear trend, Mg/Ca data were smoothed by a weighted moving average using a Gaussian kernel with standard deviation set to 1/5 of the window size (of n points). Additionally, increment widths were measured using Fiji (Schindelin et al. 2012) and evaluated in terms of a linear trend.

Our hypothesis that the Mg/Ca ratios within the skeleton of *L. glaciale* decline with rising atmospheric CO_2 concentrations was assessed quantitatively using Spearman's rank-order correlation between the unsmoothed annual mean Mg/Ca ratios and the annual mean concentrations of atmospheric CO_2 and regression residuals were tested for autocorrelation. The differential influences of annual mean atmospheric CO_2 concentration [ppm], decadal average core temperature of the West Spitsbergen Current [°C], decadal average salinity (PSU), and sea ice extent in Fram Strait in April [10^3 km^2] were then assessed via multiple linear regression analysis with an adjusted coefficient of determination. Additionally, influences were estimated using stepwise model selection based on the Akaike Information Criterion (AIC) for linear regression models. Statistical analyses were performed in R version 3.6.0 (R Core Team 2019) and PAST version 3.25 (Hammer et al. 2001).

Results

The raw and smoothed annual mean Mg/Ca ratios and increments widths are compiled in Table 1. The annual mean Mg/Ca ratios (wt%) fluctuated between 0.049 and 0.100 and showed a significantly decreasing trend through time (raw data $R^2 = 0.267$, $p_{perm} < 0.001$, see Figs. 2 and 3a; smoothed data $R^2 = 0.353$, $p_{perm} < 0.001$, see Fig. 3b). Regarding the annual growth increment widths, there was no significant temporal trend ($R^2 = 0.006$, $p_{perm} = 0.623$, see Fig. 3c).

Spearman's rank correlation showed a negative correlation between the Mg/Ca ratios within the skeleton of *L. glaciale* and atmospheric CO_2 concentrations (Fig. 4a) and regression residuals were not autocorrelated (Fig. 4b). The multiple linear regression analysis identified atmospheric CO_2 concentration to be more important than temperature for the Mg/Ca ratio, while salinity and sea ice extent did not show significant relationships (Table 2). Stepwise model selection in the linear model selected the variables

atmospheric CO_2 concentration, sea ice extent, and temperature for the final model, with only the relationship to atmospheric CO_2 concentration being significant (Table 3). Residuals were not autocorrelated (Fig. 5). Atmospheric CO_2 concentration and sea ice extent were negatively correlated with the Mg/Ca ratios, while temperature was positively correlated (Fig. 6a–c). It is evident that the linear model, which considered the influence of all parameters, showed different results than an ordinary regression analysis of every single parameter (Fig. 6d–f).

Discussion

Is the atmospheric CO_2 concentration reflected in rhodolith Mg/Ca ratios?

When estimating the impact of environmental parameters on the Mg/Ca ratios, it has to be considered that our results so far rely on the analysis of a single specimen and therefore have to be considered preliminary. To demonstrate an ecologically significant relationship, it will be necessary to replicate our analyses with several rhodoliths. Nevertheless, our findings suggest that the Mg/Ca ratio within the skeleton of the rhodolith-forming coralline alga *L. glaciale* could reflect local atmospheric CO_2 concentrations. In contrast, sea ice extent (i.e. light) and water temperature appeared to play a comparatively minor role. Salinity was uncorrelated, supporting Wilson et al. (2004), who had shown that there is no influence on the productivity of *L. glaciale* except for very low values (15 PSU). While the width of the annual increments and therefore the growth of the analysed rhodolith did not change significantly within the observed time interval, the Mg/Ca ratio decreased continuously. The negative correlation of the atmospheric CO_2 concentration with the Mg/Ca ratio was demonstrated by all three analytical methods, Spearman's rank-order correlation, multiple linear regression analysis, and stepwise model selection based on the AIC for linear regression models. According to the findings by Ragazzola et al. (2016), a decline in magnesium can be interpreted in two different ways. One possibility is the biologically controlled loss of magnesium to decrease the solubility of the skeleton in a low-saturation environment. Coralline algae discriminate against magnesium in seawater because the concentrations in the skeleton calcite are several orders of magnitude below seawater values. While the role of magnesium during biomineralization is still unclear, it is evident that high magnesium concentrations increase calcite solubility (Mucci 1983). Another potential reason for the decrease in mgnesium is a loss of biological control on the biomineralization process (Ragazzola et al. 2016).

The negative relationship of low-light conditions (Williams et al. 2018), as well as the positive relationship of

Table 1 Compiled data from the Mg/Ca measurements (raw and smoothed data) and the environmental factors included in the analysis

Year	Mean Mg/Ca ratio ± SE	Mean Mg/Ca ratio ± SE (Gaussian 5-year average)	Increment width [µm]	Atmospheric CO_2 [ppm]* (annual mean)	Annual maximum core temperature WSC [°C]** (decadal average between 20 and 200 m water depth)	Salinity (PSU)** (decadal average between 20 and 200 m water depth)	Sea ice extent Fram Strait in April [10^3 km²]***
1976	0.088 ± 0.004	0.087 ± 0.004	397.14	NA	4.240	35.045	NA
1977	0.085 ± 0.005	0.085 ± 0.004	367.14	NA	4.234	35.040	NA
1978	0.084 ± 0.003	0.085 ± 0.004	350.00	NA	4.202	35.035	NA
1979	0.090 ± 0.008	0.086 ± 0.007	265.71	NA	4.217	35.034	661.250
1980	0.071 ± 0.006	0.078 ± 0.007	185.71	NA	4.372	35.038	607.500
1981	0.095 ± 0.012	0.091 ± 0.011	304.29	NA	4.480	35.040	573.750
1982	0.093 ± 0.009	0.089 ± 0.010	438.57	NA	4.539	35.039	711.875
1983	0.063 ± 0.013	0.069 ± 0.011	280.00	NA	4.515	35.034	490.000
1984	0.069 ± 0.008	0.068 ± 0.008	267.14	NA	4.533	35.035	426.875
1985	0.070 ± 0.005	0.068 ± 0.005	465.71	NA	4.622	35.029	677.500
1986	0.061 ± 0.005	0.064 ± 0.005	275.71	NA	4.704	35.024	761.875
1987	0.068 ± 0.005	0.067 ± 0.005	484.29	NA	4.806	35.016	586.250
1988	0.069 ± 0.003	0.070 ± 0.004	348.57	358.7	4.885	35.005	676.875
1989	0.076 ± 0.003	0.076 ± 0.004	287.14	357.0	4.848	34.991	549.375
1990	0.083 ± 0.010	0.080 ± 0.008	295.71	355.2	4.857	34.987	519.375
1991	0.076 ± 0.005	0.080 ± 0.007	351.43	356.1	4.920	34.986	518.750
1992	0.089 ± 0.010	0.089 ± 0.009	272.86	360.9	5.038	34.989	559.375
1993	0.100 ± 0.007	0.097 ± 0.010	341.43	357.8	5.085	34.987	452.500
1994	0.094 ± 0.022	0.092 ± 0.017	221.43	359.1	4.806	34.973	428.750
1995	0.073 ± 0.008	0.078 ± 0.010	375.71	361.3	4.792	34.984	486.875
1996	0.078 ± 0.005	0.076 ± 0.006	405.71	362.3	4.778	34.995	626.875
1997	0.069 ± 0.005	0.073 ± 0.005	498.57	363.2	4.796	35.007	568.125
1998	0.082 ± 0.005	0.078 ± 0.005	257.14	365.5	4.848	35.018	493.750
1999	0.069 ± 0.006	0.071 ± 0.006	278.57	370.9	4.853	35.025	423.750
2000	0.069 ± 0.005	0.068 ± 0.005	331.43	372.0	4.922	35.029	516.250
2001	0.064 ± 0.006	0.066 ± 0.005	508.57	370.9	4.953	35.042	564.375
2002	0.072 ± 0.004	0.071 ± 0.005	650.00	374.7	5.152	35.052	460.625
2003	0.075 ± 0.006	0.074 ± 0.006	580.00	378.0	5.505	35.082	522.500
2004	0.072 ± 0.008	0.074 ± 0.007	527.14	378.9	5.527	35.085	410.000
2005	0.079 ± 0.005	0.077 ± 0.006	754.28	380.5	5.545	35.082	505.000
2006	0.073 ± 0.008	0.073 ± 0.007	360.00	383.1	5.451	35.076	435.625
2007	0.068 ± 0.010	0.070 ± 0.010	332.86	384.1	5.353	35.082	475.000
2008	0.073 ± 0.011	0.071 ± 0.010	335.71	386.4	5.378	35.083	488.125
2009	0.070 ± 0.005	0.069 ± 0.007	211.43	387.0	5.344	35.088	482.500
2010	0.066 ± 0.009	0.069 ± 0.008	314.29	390.3	5.361	35.086	461.250
2011	0.085 ± 0.009	0.077 ± 0.011	240.00	392.5	5.271	35.082	456.250
2012	0.053 ± 0.022	0.060 ± 0.018	215.71	394.8	5.306	35.076	488.125
2013	0.063 ± 0.009	0.060 ± 0.011	324.29	397.3	5.375	35.077	519.375
2014	0.051 ± 0.007	0.053 ± 0.007	385.71	399.6	5.443	35.076	485.625
2015	0.049 ± 0.004	0.049 ± 0.004	232.86	401.2	5.585	35.077	423.125

*Data recorded by the Zeppelin Observatory in Ny-Ålesund

**Data recorded by the Norwegian Polar Institute

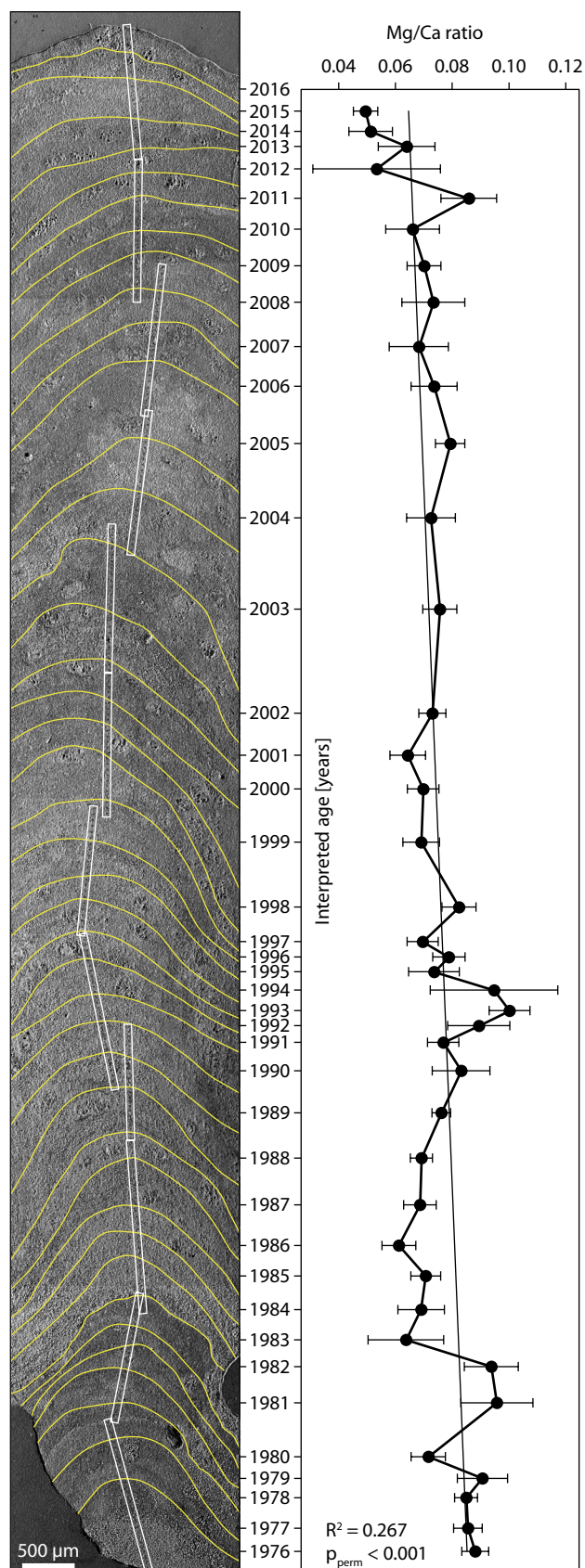***Data recorded by the National Snow and Ice Data Center

higher temperatures (Halfar et al. 2008; Kamenos et al.
2008), to the Mg/Ca ratio of coralline algal skeletons were
supported by our analysis. However, they were of subor-
dinate significance compared to the potential influence of
atmospheric CO_2 concentrations. Our results are in line with
the findings by Ragazzola et al. (2016), who showed that
specimens of *L. glaciale* grown under high aqueous pCO_2
conditions exhibited significantly lower magnesium concen-
trations than the control group.

Short-term versus long-term effects

There have been a number of attempts to predict the poten-
tial outcome of acidifying oceans on coralline algae, ranging
from uni-factorial short-term aquaria experiments (Comeau
et al. 2013) to long-term mesocosm setups (Jokiel et al.
2008). The results differ widely, partly depending on the
examined algal species, indicating a range of effects from
severe impacts on calcification (Fabricius et al. 2015) to the
apparent ability of coralline algae to actively regulate pH at
their site of calcification to maintain skeletal growth (Corn-
wall et al. 2017). Some studies indicate that the skeletal
structure of the algae is more sensitive to the rate, rather than
the magnitude, of ocean acidification (Kamenos et al. 2013).
This identifies one of the drawbacks of aquaria experiments
where CO_2 levels are raised unrealistically fast, compromis-
ing the ability of the algae to adapt to the sudden change in
conditions. The experimental conditions are often further
impaired by unrealistic ecological settings, rendering mean-
ingful predictions difficult.

Data on the influence of ocean acidification on *L. gla-
ciale* are only available from aquaria experiments with a
duration of maximally one year (Büdenbender et al. 2011;
Ragazzola et al. 2012; Ragazzola et al. 2013; Ragazzola
et al. 2016). The present study is the first 'long-term study'
taking account of the longevity of coralline algae of at least
several decades (Teichert and Freiwald 2014). Additional-
ly, it reflects in situ growth in the natural ecosystem of the
algae, including interactions with grazers and fluctuations
in nutrient availability.

The influence of exposure time to acidified conditions has
already been highlighted for *L. glaciale* (Ragazzola et al.
2012; Ragazzola et al. 2013). In their first study, speci-
mens of *L. glaciale* were cultured under elevated pCO_2
levels (408, 566, 770, and 1024 µatm) for 3 months, and
again in a second study for 10 months. While the 3-month
specimens showed a reduction in the (inter and intra) cell
wall thickness but maintained normal growth rate, the
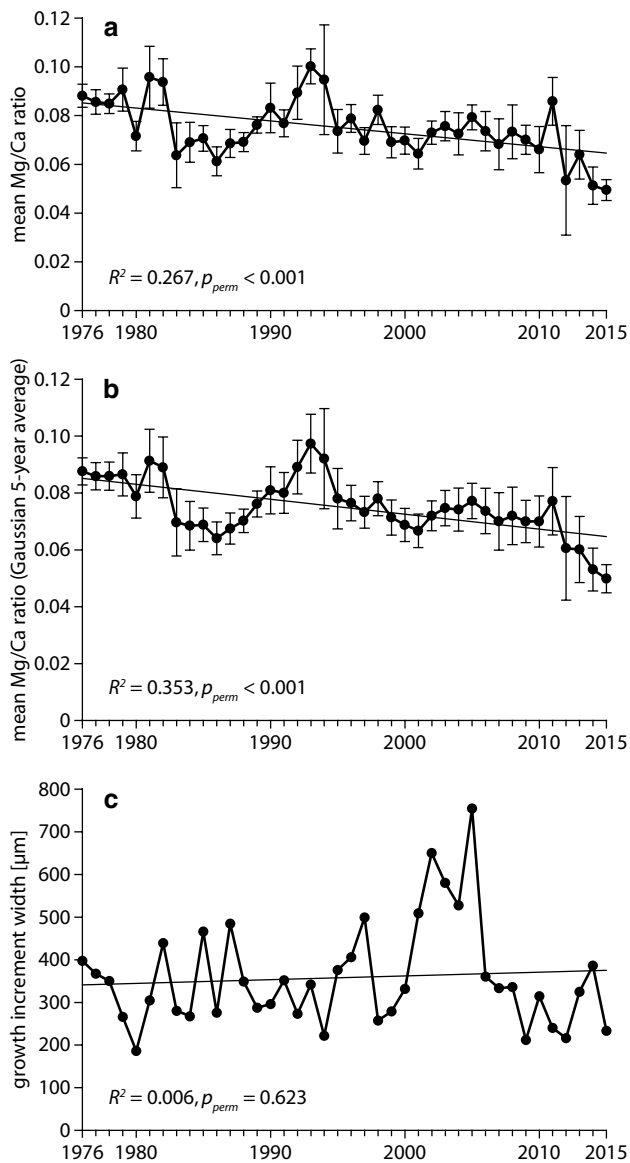10-month specimens showed that the (inter and intra) cell

Fig. 3 Mg/Ca and growth patterns. **a** Mean Mg/Ca ratios from 1976 to 2015, indicating a significantly decreasing trend. **b** Mean Mg/Ca ratios from 1976 to 2015, smoothed by a weighted moving average using a Gaussian kernel with standard deviation set to 1/5 of the window size (of n points). **c** Widths of annual growth increments from 1976 to 2015, indicating no significant trend

magnesium concentrations were correlated to elevated pCO_2 levels in their 3-month exposure. Aligned with our findings, this renders it likely that *L. glaciale* does not maintain the magnesium concentration in its skeleton over both short and long terms under elevated seawater pCO_2 levels, which are also controlled by atmospheric CO_2 concentrations to a certain degree.

Coralline acclimatization to elevated CO₂ and pCO₂ levels

There is evidence that coralline algae exert a strong biotic control over their skeletal structure and microenvironments where active calcification is occurring (e.g. Cornwall et al. 2017), including the species *L. glaciale* (Hofmann et al. 2018). Ragazzola et al. (2012) showed that *L. glaciale* was able to maintain net calcification at conditions slightly undersaturated in terms of aragonite ($\Omega_{Ar} = 0.98$). However, these specimens had been cultured in continuous light, simulating Arctic summer conditions. Hofmann et al. (2018) pointed out that long exposure of *L. glaciale* to darkness resulted in a pH of the thallus surface below the pH of seawater, suggesting that dissolution could still occur during Arctic winter. While maintaining the skeletal integrity is one of the main priorities of marine organisms living in a high CO_2 environment, all this comes at an ecophysiological cost. In coralline algae, there appears to be a possible shift in the energy budget from growth extension to maintaining structural integrity (Ragazzola et al. 2013). One interpretation of our findings over a 40-year time interval would be that *L. glaciale* is indeed able to maintain its growth rate under increasing atmospheric CO_2 concentrations, although the aqueous pCO_2 is controlled by it to a certain degree. Apart from this, a shift in the elemental composition of the skeleton can also be considered as an acclimation to elevated pCO_2 levels (Smith et al. 2012), because the polymorphs of $CaCO_3$ have different solubilities in seawater: aragonite is more soluble than pure calcite, and the solubility of calcite increases with its magnesium concentration, making high-magnesium calcite even more soluble than aragonite. Therefore, the observed decrease in the Mg/Ca ratio might be an ecophysiological tradeoff in *L. glaciale* to maintain its growth rate and possibly its cell wall thickness. It is also notable that the measured Mg/Ca ratios in our sample are at the lower range (5–10 wt%) of what is known for *L. glaciale* (11–25 wt%). Reasons might be that the other studies derive from earlier times (Clarke and Wheeler 1922), when CO_2 levels were lower than today (IPCC 2013), or because the analysed specimens were collected at lower latitudes (Kamenos et al. 2008), because ocean acidification appears to proceed faster in the Arctic Ocean than in other oceans (Qi et al. 2017).
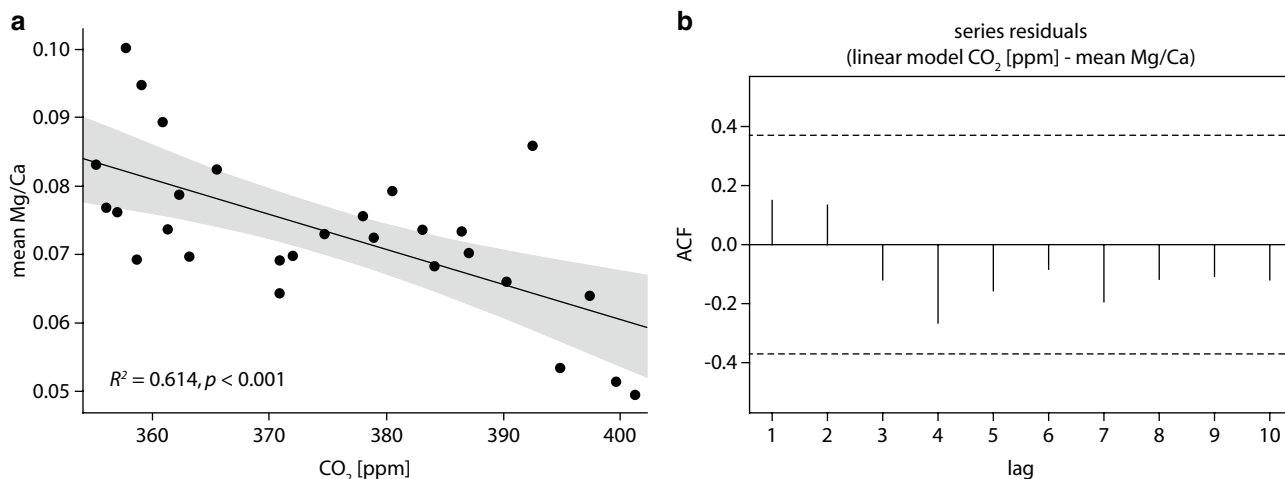
wall thickness was maintained, but there was a reduction in growth rate (linear extension) at all elevated pCO_2 levels. Regarding linear extension, our results differ in that we did not observe a significant trend over a 40-year period (Fig. 3c). A potential reason for this might be the relatively small difference between the minimal and maximal atmospheric CO_2 concentrations in our study (~46 μatm) compared to the larger differences in pCO_2 (~158 μatm) in the study by Ragazzola et al. (2013). As for the Mg/Ca ratio in *L. glaciale*, Ragazzola et al. (2016) showed that lower

a

b

Fig. 4 Correlation between CO_2 concentration and mean Mg/Ca ratio. **a** Results of Spearman's rank correlation, confirming the general hypothesis that the Mg/Ca ratio within the skeleton of *L. glaciale*

declines successively with increasing atmospheric CO_2 concentrations. **b** Results of the autocorrelation function, indicating that the regression residuals are not autocorrelated

Table 2 Results of the multiple linear regression analysis, identifying atmospheric CO_2 concentrations before temperature to be significantly related to the Mg/Ca ratio, while salinity and sea ice extent do not show a significant correlation

Multiple $R^2_{adj} = 0.312$
ANOVA
$F = 5.417, p = 0.0018$

Variable	R^2	p-value
Atmospheric CO_2 concentration [ppm] (annual mean)	0.280	0.008
Annual max. core temp. WSC [°C] (decadal average)	0.185	0.039
Salinity (PSU, decadal average)	0.170	0.117
Sea ice extent Fram Strait in April [10^3 km^2]	0.013	0.367

Consequences for the rhodoliths and their ecosystem

The rhodoliths of Mosselbukta and elsewhere in Svalbard are important ecosystem engineers (Teichert 2014). Therefore, changes in the skeletal $CaCO_3$ production of the algae might impact the associated organisms. Our data suggest that linear growth of the rhodoliths so far did not decrease, and Ragazzola et al. (2013) showed that the cellular structure of the algae adapts after several months of experimental exposure.

Our data also propose that the chemical composition of the skeleton of *L. glaciale* changes by a reduction of the Mg/Ca ratio. We interpret this as a consequence of rising atmospheric CO_2 concentrations and coupled aqueous pCO_2. However, the hydrodynamic regime and seasonal fluctuations in the aqueous carbonate system are complex in Mosselbukta (Wisshak et al. 2019) and elsewhere in Svalbard (Sanz-Martín et al. 2018) so that aqueous pCO_2 is not always in equilibrium with CO_2 levels in the atmosphere. We nevertheless assume that a rising trend in atmospheric CO_2 concentration is mirrored in a trend of rising seawater pCO_2 and thus of local ocean acidification in Mosselbukta. Therefore, we propose that a decreasing Mg/Ca ratio in *L. glaciale* is

Table 3 Results of the stepwise model selection, identifying atmospheric CO_2 concentration as the significantly influencing variable, while sea ice extent and temperature have subordinate effects

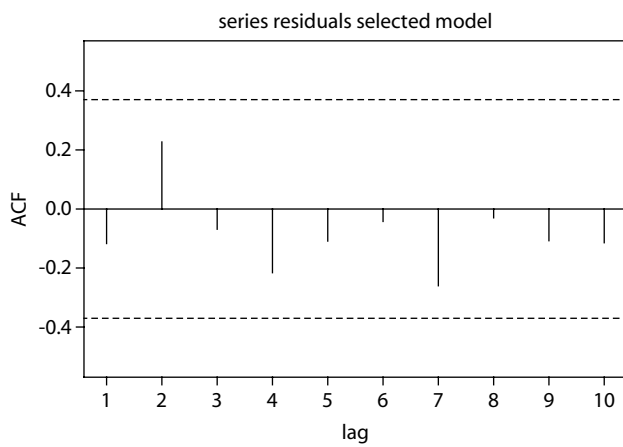| Overall model $AIC = -184.213$ $R^2_{adj} = 0.507$ $p < 0.001$	AIC for omitting parameter	Estimate	p-value
Atmospheric CO_2 concentration [ppm] (annual mean)	− 250.54	− 8.571^{-4}	< 0.001
Sea ice extent Fram Strait in April [10^3 km^2]	− 263.92	− 5.338^{-5}	0.076
Annual max. core temp. WSC [°C] (decadal average)	− 264.98	1.578^{-2}	0.133

Fig. 5 Results of the autocorrelation function for the linear model, indicating that the residuals of the final model are not autocorrelated

a reaction to rising aqueous $p\mathrm{CO}_2$ levels. As underlying mechanism, we envisage this as an acclimation of skeletal stability, because low-magnesium calcite is less soluble in acidified waters than high-magnesium calcite.

This leads us to the question whether decreasing Mg/Ca ratios also alter the mechanical properties of the alga's skeleton. Studies in materials science (Kunitake et al. 2012) demonstrated that the hardness (measured by nanoindentation and plane strain indentation modulus) of the CaCO_3 skeleton of the stiff penshell, *Atrina rigida* (Lightfoot, 1786), increases linearly with its magnesium content. It is assumed that magnesium hardens calcite by a solid solution hardening process, when magnesium substitutes for calcium in the calcite lattice (Kunitake et al. 2012). These authors point out that magnesium is a smaller cation than calcium and thus expected to create lattice distortions (i.e. a stress field) that hinders dislocation motion and thereby increases the hardness. The Mg/Ca ratio within their model organism *A. rigida* was ∼0.04 (at.%) and accounted for approximately 20% of
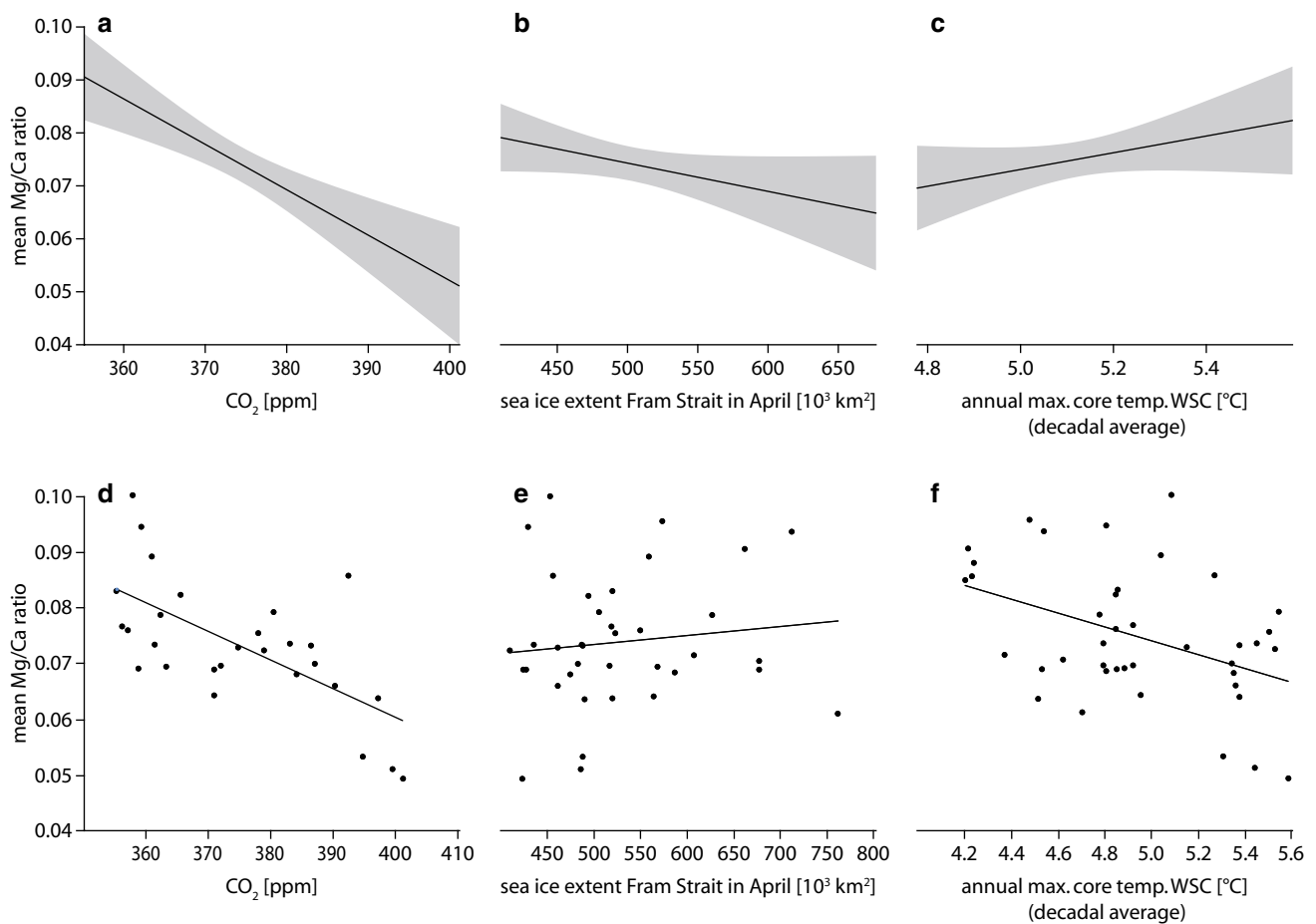

Fig. 6 Visualization of the linear model and comparison with ordinary regression analysis. **a** Negative influence of atmospheric CO_2 concentration on the Mg/Ca ratio. **b** Negative influence of the sea ice extent on the Mg/Ca ratio. **c** Positive influence of temperature on the

Mg/Ca ratio. **d–f** Ordinary regression analyses for the environmental parameters atmospheric CO_2 concentration, sea ice extent, and temperature to illustrate their apparent correlation functions with the Mg/Ca ratio if parameters are not considered simultaneously

the increased hardness of this bivalve skeleton compared to abiogenic calcite mineral. It is not known if these data can be extrapolated, but as the Mg/Ca ratio of *L. glaciale* ranges one magnitude higher (0.11–0.25 wt%, Smith et al. 2012), the influence of the magnesium concentration on its skeletal hardness might be even higher. However, the skeletal hardness in molluscs could also be related to the shell structure, in addition to its mineralogy.

The skeletal stability of rhodoliths may not simply depend on the hardness but also on other parameters of the skeletal ultrastructure and architecture, including the arrangement and size of the cells. Using finite element analysis, Ragazzola et al. (2012) showed that under elevated pCO$_2$, *L. glaciale* suffered from an increased strain energy under mechanical stress, thus indicating that the algal skeleton stores more strain energy per volume and has more internal energy available to propagate cracks and cause catastrophic breakage when damaged. Whether this holds true also for rhodoliths in their natural environment remains to be demonstrated.

Rhodoliths at the Svalbard shelf are exposed to a variety of mechanical stressors, including activity from predators and grazers (Wisshak et al. 2019) and increasing wave action (Melbourne et al. 2015). Increased calving activity of glaciers caused by global warming might be an additional factor, because drifting icebergs scour rhodolith beds and cause massive breakage (Teichert et al. 2012, 2014). Future studies on the long-term effects of aqueous pCO$_2$ should thus consider the impacts of ocean acidification on the stability of the coralline algal skeleton from rhodolith beds around the globe.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interest.

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