



# Skeletal mineralogy of geniculate corallines: providing context for climate change and ocean acidification research

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**ABSTRACT:** Marine species depositing high-magnesium (Mg) calcite (>8% MgCO<sub>3</sub>) are projected to be among the first to show response to the impacts of climate change, i.e. increased sea surface temperature (SST) and ocean acidification (OA), given the increasing solubility of calcite in seawater with increasing Mg content. Temperature is a major driver of Mg incorporation into the skeletons of calcifying macroalgae, and thus climate change may induce deposition of more soluble calcite, exacerbating responses to OA. Assessment of the skeletal Mg content of 3 geniculate, calcifying species of the genera *Corallina* and *Ellisolandia* (Rhodophyta, Corallinales), *C. officinalis*, *C. caespitosa* and *E. elongata*, sampled during 2012–2013 in the UK intertidal, demonstrated the existence of seasonal cycles in skeletal Mg. Seasonal cycles in skeletal Mg were also observed for herbarium collections of the Natural History Museum (British Museum), London, sampled during the recent past (1850–2010). Comparative sampling across a northeastern Atlantic latitudinal transect (Iceland to northern Spain) indicated a decreasing Mg content with increasing latitude for present-day *C. officinalis*, and relationships between SST and *Corallina* Mg content ( $r^2 = 0.45\text{--}0.76$ ) demonstrated the dominant influence of temperature on *Corallina* species skeletal mineralogy. *Corallina* and *Ellisolandia* species show lower absolute values of Mg content (0.11–0.16 mol% Mg/Ca), and smaller variation with change in SST (0.0028–0.0047 mol% Mg/Ca °C<sup>-1</sup>), than other temperate calcifying macroalgae studied to date. Over the period 1850–2010, no change in the magnitude of Mg incorporation by *C. officinalis* was detected in herbarium samples. However, the strong relationship between SST and Mg content indicates that projected increases in SST by 2100, which are far greater than temperature increases that occurred between 1850–2010, could have substantial impact on geniculate coralline algae skeletal mineralogy, and must be considered synergistically with the effects of OA.

**KEY WORDS:** *Corallina officinalis* · *Ellisolandia elongata* · *Corallina caespitosa* · Climate change · Ocean acidification · Mg/Ca ratio · Skeletal mineralogy

## INTRODUCTION

Since 1961, an excess of 80% of climate change-related atmospheric heating has been absorbed by the world's oceans, resulting in an increase in the global average sea surface temperature (SST) of

0.65°C between 1850 and 2005, according to the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report (Solomon et al. 2007). Concomitantly, ocean acidification (OA), the increasing acidity of the world's oceans attributed to uptake of anthropogenic CO<sub>2</sub>, has decreased the global

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average ocean pH by 0.1 relative to pre-industrial values, resulting in a 26% increase in hydrogen ion ( $H^+$ ) concentration and reduced biologically available carbonate ions ( $CO_3^{2-}$ ) (Feely et al. 2004, Doney 2006, Hoegh-Guldberg et al. 2007, Rhein et al. 2013). By 2100, climate change models predict increased global ocean average SST ranging from  $+0.6^\circ C$  to more than  $+3.0^\circ C$  and a further decrease in average ocean pH of 0.13 to 0.42 under IPCC Representative Concentration Pathways (RCPs) 2.6 and 8.5, respectively (Collins et al. 2013).

Varying responses of marine species to increases in SST and OA have been reported, with numerous studies predicting adverse effects of OA on those species that deposit calcium carbonate ( $CaCO_3$ ) as shells or skeletal structures (e.g. Gao et al. 1993, 2009, Langdon et al. 2000, Langdon & Atkinson 2005, Anthony et al. 2008, Kuffner et al. 2008, Zheng & Gao 2009, Cohen et al. 2009, Kleypas & Yates 2009, Dias et al. 2010, Dupont et al. 2010, Gao & Zheng 2010, Diaz-Pulido et al. 2012, Hofmann et al. 2012). Within the marine environment, different biogenic polymorphs of  $CaCO_3$  are deposited, each with different solubility in seawater (Ries 2011). Aragonite, the polymorph deposited by, for example, scleractinian coral species, is more soluble than pure calcite; however, the solubility of calcite increases with increasing magnesium ion ( $Mg^{2+}$ ) content substituting for calcium ( $Ca^{2+}$ ) ions (Andersson et al. 2008, Ries 2010, 2011). High-Mg biogenic calcite (i.e. greater than 8–12%  $MgCO_3$ ) is more soluble than aragonite in seawater (Andersson et al. 2008). Species depositing this polymorph are therefore likely to be more susceptible to the initial effects of OA (Gao et al. 1993, Morse et al. 2007, Kuffner et al. 2008, Ries et al. 2009, Ries 2010, Lombardi et al. 2011).

Red coralline macroalgae (Corallinales, Rhodophyta) are the most common high-Mg calcite producers, along with benthic foraminifera, bryozoans and echinoderms (Andersson et al. 2008). Coralline macroalgae comprise both geniculate genera (i.e. jointed or articulated), and non-geniculate genera, which are either encrusting, e.g. crustose coralline algae, or free-living nodules, known as rhodoliths or maerl (Irvine & Chamberlain 1994, Nelson 2009). Coralline algae have limited control over their calcification processes in that they are able to specify deposition of the calcite polymorph, as opposed to aragonite, but are unable to actively control the degree of Mg incorporation into their calcite skeletons (Ries 2010). Variation in Mg content is controlled by mechanisms including the Mg/Ca ratio of seawater, which

is only applicable over geological timescales (Ries 2006, 2010), and factors that influence growth rate, e.g. light availability (Andersson et al. 2008), the seawater carbonate saturation state (Andersson et al. 2008, Ries 2011, Egilisdottir et al. 2013), salinity (Kamenos et al. 2012) and temperature (Kamenos et al. 2008, Kuffner et al. 2008, Ries 2010, 2011). For example, observed decreases in the Mg content of calcite in coralline algae with increasing latitude have been attributed to concomitant decreases in light, seawater carbonate saturation and temperature (Chave 1954, Mackenzie et al. 1983, Andersson et al. 2008).

Within latitudes, temperature is the dominant influence on the skeletal Mg content of present-day coralline macroalgae (Kamenos et al. 2008). For example, seasonal cycles in Mg incorporation in the rhodolith species *Lithothamnion glaciale* (12.9–24.6 mol%  $MgCO_3$  range) and *Phymatolithon calcareum* (14.7–23.8 mol%  $MgCO_3$  range) show a strong positive regression ( $r^2 = 0.88–0.96$ ) with *in situ* seawater temperatures, with a change of 1.26 and 1.19 mol%  $MgCO_3$   $^\circ C^{-1}$  for the 2 species, respectively (Kamenos et al. 2008).

Given the positive relationship between SST and Mg incorporation into calcite (Kamenos et al. 2008), climate change-associated elevations in SST may lead to an increase in the relative proportion of more soluble calcite forms in coralline macroalgae, exacerbating the impacts of OA, as hypothesized for the bryozoan *Myriapora truncata* (Lombardi et al. 2011). Conversely, however, decreases in seawater carbonate saturation owing to OA itself may serve to decrease Mg content in coralline macroalgae. In the rhodolith *Neogoniolithon* sp., calcite Mg/Ca ratio decreased from 0.249 to 0.197 with a decrease in seawater aragonite saturation state from 2.5 to 0.7 (Ries 2011), and a decreased mol% Mg/Ca was observed in new structures formed by the geniculate *Ellisolandia elongata* during elevated  $pCO_2$  incubations ( $0.177 \pm 0.002$ ) compared to ambient conditions ( $0.190 \pm 0.003$ ) (Egilisdottir et al. 2013).

Multi-stressor studies examining the simultaneous impacts of increased SST and OA on the skeletal mineralogy of coralline macroalgae are currently lacking. When available, contextual interpretation of such results will depend on a clear understanding of the natural variation in the present-day carbonate skeletal mineralogy of these species, and its relationship with environmental conditions, in particular SST (Medakovic et al. 1995, Kamenos et al. 2008, Smith et al. 2012). In addition, given that present-day climate conditions, i.e. post-industrialization, are already sig-

nificantly shifted in comparison to pre-industrial times, examination of the skeletal mineralogy of coralline macroalgae to date, where possible, will further add to our capacity to predict and interpret potential future changes.

This study therefore assessed the present-day and recent-past (i.e. 1850–2010) variation in skeletal Mg incorporation in species of the cosmopolitan geniculate coralline genera *Corallina* and *Ellisolandia*, which are extremely ecologically important (Nelson 2009), yet relatively understudied in relation to climate change and OA. Erect, turfing species of *Corallina* and *Ellisolandia* are near-ubiquitous in temperate intertidal and subtidal environments (Smith et al. 2012), providing habitat for numerous small invertebrates, shelter via their physical structure from environmental stresses associated with intertidal habitats, and a substratum for the settlement of macro- and microalgae (Nelson 2009, Smith et al. 2012). Given these attributes, geniculate corallines are considered important autogenic ecosystem engineers (Jones et al. 1994, Nelson 2009), and as such, potential impacts of climate change-driven increases in SST and/or OA on these species could have serious implications for temperate coastal ecosystems and species therein (Hofmann et al. 2012).

The aims of the present study were to (1) quantify the present-day temporal and spatial patterns in Mg/Ca ratios of *C. officinalis* and *C. caespitosa* from the UK intertidal over a seasonal cycle; (2) examine interspecific variation in Mg/Ca ratios between *C. officinalis*, *C. caespitosa* and *Ellisolandia elongata*; (3) examine intraspecific variation in *Corallina* Mg/Ca ratios over small (within-site) to large (across

latitudes) spatial scales; (4) assess the recent-past (ca. 1850–2010) patterns in UK *C. officinalis* Mg/Ca ratios from herbarium collections of the Natural History Museum (British Museum), London; (5) examine the relationship between *Corallina* Mg/Ca ratios and SST; and (6) use these relationships to produce projections of *Corallina* skeletal mineralogy under future ocean conditions.

## MATERIALS AND METHODS

### Seasonal sampling

To examine present-day seasonal, within-site, and interspecific patterns in *Corallina* skeletal Mg/Ca ratios (mol% Mg/Ca), 12 samples each of *C. officinalis* and *C. caespitosa* were collected haphazardly by hand from within rock pools at each shore height where they occurred (Table 1) during December 2011 and March, June, September and December 2012 from Combe Martin, North Devon, UK (Fig. 1). To ensure sampling of discrete individuals, samples were collected at least 30 cm away from each other. Each sample consisted of a discrete basal portion and attached upright fronds. Sample replication of  $n = 12$  was selected by plotting  $n$  against cumulative mol% Mg/Ca variance. Cumulative variance decreased and saturated at  $n = 12$ –15 samples for both species (data not shown). Following collection, samples were mounted onto herbarium sheets using site seawater collected on the day of sampling, dried in a press, and stored on herbarium sheets until processing.

Table 1. Sampling site details (see also Fig. 1). SST: sea surface temperature. *C.*: *Corallina*; *E.*: *Ellisolandia*

Site	Location	Sampling months	Avg. (min–max) SST (°C)	Shore height sampled	Shore height relative to chart datum (m)	Species present	Estimated pool volume (m <sup>3</sup> )	Estimated pool depth (cm)
Combe Martin, UK	51°12'31" N, 4°2'19" W	Dec 2011	9.9 (8.9–11.4)	Upper	+ 5.5	<i>C. officinalis</i>	40	500
		Mar 2012	8.5 (7.0–10.2)			<i>C. caespitosa</i>		
		Jun 2012	14.2 (12–15.5)	Middle	+ 5.0	<i>C. caespitosa</i>	0.09	2–4
		Sep 2012	16.4 (13.4–17.6)	Lower	+ 3.5	<i>C. officinalis</i>	0.25	500
		Dec 2012	9.9 (8.9–11.4)					
Wembury Point, UK	50°18'53" N, 4°4'58" W	Jun 2012	13.8 (11.8–16.9)	Upper	+ 4.0	<i>C. officinalis</i>	0.25	500
				Lower	+ 2.3	<i>C. officinalis</i> <i>E. elongata</i>	0.25	500
Þorlákshöfn, Iceland	63°53'36" N, 21°23'45" W	Jul 2012	11.7 (10.1–13.6)	Lower	+ 1.5	<i>C. officinalis</i>	1.5	500
A Coruña, Spain	43°22'13" N, 8°24'54" W	Oct 2012	17.4 (16.2–19.7)	Lower	+ 2.0	<i>C. officinalis</i> <i>E. elongata</i>	0.125	500

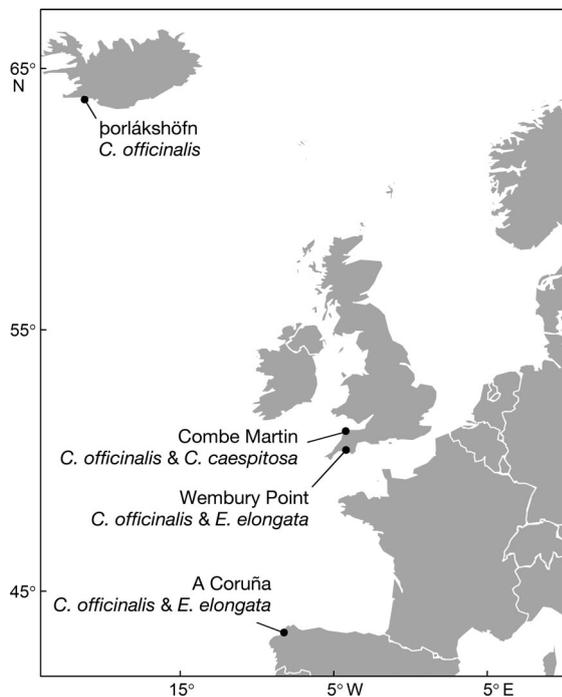


Fig. 1. Study sites in the NE Atlantic indicating *Corallina* and *Ellisolandia* species present at each site (see also Table 1)

### Comparative sampling

To examine spatial variation and interspecific differences in mol% Mg/Ca between UK sites, *Corallina officinalis* and *Ellisolandia elongata* were sampled from Wembury Point during June 2012 (12 individual plants per species and shore height present; Table 1) for comparison to Combe Martin data. To examine intraspecific variation in mol% Mg/Ca over a northeastern Atlantic latitudinal transect, *C. officinalis* was sampled ( $n = 12$  individual plants) from Iceland and northern Spain (Table 1), allowing differences to be assessed over 1418 miles (2282 km), with Combe Martin and Wembury Point located 542 and 480 miles (872 and 772 km) north from the northern Spain site, respectively (Fig. 1). Additionally, *E. elongata* was sampled from northern Spain for interspecific comparisons. Species identification was achieved by amplification of the *cox1* gene region and comparison with published sequences as per Walker et al. (2009).

### Herbarium collections

*C. officinalis* from UK sites were selected to examine recent-past patterns in *Corallina* mol% Mg/Ca,

as they represented the largest collection of *Corallina* species held in the algal herbarium collections of the Natural History Museum (BM), London. These collections span from ca. 1850 to 2010, and are predominantly from donations made by individual collectors, not as established regular sampling initiatives, making samples over this period spatially and temporally heterogeneous, and lacking replication (Table S1 in the Supplement at [www.int-res.com/articles/suppl/m513p071\\_supp.pdf](http://www.int-res.com/articles/suppl/m513p071_supp.pdf)). In total, 112 *C. officinalis* samples were selected from the herbarium collections for use in the current study. Sub-sampling for analysis was conducted as detailed in the following section.

### Sample processing

In order to examine the skeletal Mg content most representing the time of collection during the present study, whilst allowing sufficient material for X-ray diffraction (XRD) analysis (see next section), the apical intergeniculum was sampled from 10–15 branches of each *Corallina* and *Ellisolandia* sample and pooled to comprise 1 sample for XRD analysis (Fig. 2). Growth of *Corallina* species is mostly restricted to a finite group of elongating and dividing apical cells (Colthart & Johansen 1973). Little data exists on the growth rates of geniculate corallines, but Colthart & Johansen (1973) reported rates of 2.2 mm per month

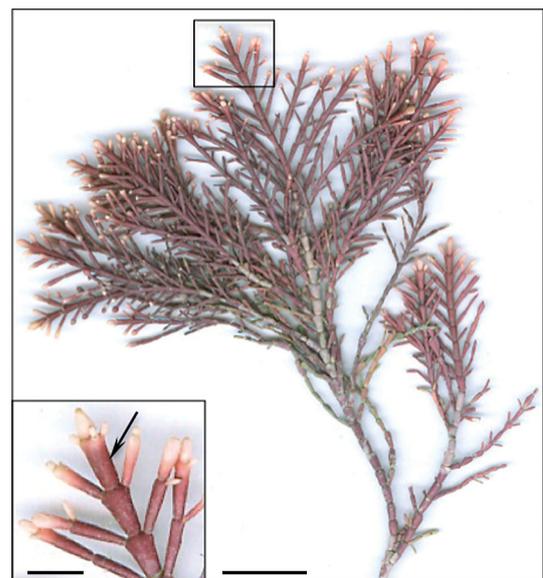


Fig. 2. Representative frond of *Corallina officinalis* collected from Combe Martin, UK (scale bar = 0.5 cm). Inset: apical region of frond branch (scale bar = 1 mm); arrow: apical intergenicula sampled for X-ray diffraction analysis

for *C. officinalis* at 12–18°C, corresponding to the production of a single 1 mm long intergeniculum per 12 d, and Hofmann et al. (2012) reported relative growth rates of  $1.97 \pm 0.15$  % fresh weight  $d^{-1}$  for the same species grown at 15°C with 50  $\mu\text{mol photons m}^{-2} \text{ s}^{-1}$  light intensity. Mol% Mg/Ca reported by the present study therefore likely represent Mg incorporation over approximately the previous 12 d before the time of sampling during periods of SST ranging from 12–18°C, and longer periods, given presumably lower growth rates, below these temperatures.

### X-ray diffraction analysis

All XRD analyses were conducted in the Mineralogy Department of The Natural History Museum, London. Samples were ground with a mortar and pestle and suspended in acetone (ca. 1:20 sample: acetone suspension). A few drops of the sample-acetone suspension were placed onto a single crystal sapphire substrate (zero-background holder). The dried samples were analysed using an Enraf-Nonius PDS120 diffractometer equipped with a primary Germanium (111) monochromator and an INEL 120° curved position sensitive detector (PSD). Operating conditions for the Co source were 40 kV and 40 mA. The horizontal slit after the monochromator was set to 0.14 mm to confine the incident beam to pure Co  $K\alpha_1$  radiation. The vertical slit was set to 5 mm.

Samples were measured in asymmetric flat-plate reflection geometry. Diffracted X-ray intensities were simultaneously collected over a 2-Theta range of 120° without angular movement of tube, sample or detector position. The tilting angle between incident beam and sample surface was kept constant at 6° and the sample was rotated during the measurements to improve particle counting statistics. Angular linearity of the PSD was calibrated using  $Y_2O_3$  as external standard. A full 2-Theta linearization of the PSD was performed with a least-squares cubic spline function.

The Mg content of the calcite skeletons of the *Corallina* and *Ellisolandia* species was derived from the position of the  $d_{104}$  reflection in the XRD pattern. All data of the present study fall into a compositional interval between 10 and 17 mol% Mg. A linear relationship between  $d_{104}$  value and Mg concentration of skeletal magnesian calcites was first reported by Chave (1952) over the range 2–16 mol% Mg. Considering compositions between 0 and 20 mol% Mg of biogenic and inorganic magnesian calcites, Mackenzie et al. (1983) concluded the  $d_{104}$  trend is equivalent to a straight line from calcite to disordered dolomite

or magnesite. Therefore, the present study derived the molar Mg content on the Ca site of magnesian calcites, i.e. the substitution of Ca ions for Mg ions in the crystal lattice of the calcite, using the linear relationship in Eq. (1):

$$\text{Mol\% Mg} = \frac{d_{104}^{\text{calcite}} - d_{104}^{\text{Mg-calcite (sample)}}}{d_{104}^{\text{calcite}} - d_{104}^{\text{magnesite}}} \quad (1)$$

where data for calcite and magnesite were taken from well-characterized standards of the National Bureau of Standards (PDF-2 database from International Centre for Diffraction Data; reference codes calcite [5-586] and magnesite [8-479]). Calculated  $d_{104}$  trendlines from Eq. (1) and an overall fit of 3 synthetic magnesian calcite studies (Goldsmith et al. 1961, Bischoff et al. 1983, Mackenzie et al. 1983) showed only minor differences in the compositional range between 0 and 20 mol% Mg. Deviations for a given  $d_{104}$  value were generally below 0.1 mol% Mg.

### Predictive models

To examine the relationship between SST and skeletal Mg incorporation by *Corallina* species, present-day and recent-past derived mol% Mg/Ca ratios were regressed against locally reported SSTs which were obtained from the website<sup>1</sup> of the Centre for Environment, Fisheries and Aquaculture Science (CEFAS). For Combe Martin seasonal data, linear regression analysis was performed against monthly average SST recorded from 1992 to 2008 at CEFAS Stn 27, located at Ilfracombe (51° 20' 51" N, 4° 12' 67" W), approximately 8.8 km from Combe Martin. For mol% Mg/Ca derived from herbarium samples, average SST data were retrieved for the month of sample collection from the nearest CEFAS station to the point of collection recorded (Table S1 in the Supplement). Given the non-continuous nature of CEFAS SST data throughout time, SST values for 45 of 112 herbarium data points were available for regression analysis. Changes in the mol% Mg/Ca  $^{\circ}\text{C}^{-1}$  of *Corallina* species were derived from linear regression equations to SST. Regression equations derived for Combe Martin seasonal data were plotted using the monthly average SST data reported for the entire year from CEFAS Stn 27, to demonstrate the complete mol% Mg/Ca seasonal cycle for *C. officinalis* and *C. caespitosa*. Additionally, pooled

<sup>1</sup>[www.cefass.defra.gov.uk/our-science/observing-and-modelling/monitoring-programmes/sea-temperature-and-salinity-trends/station-positions-and-data-index.aspx](http://www.cefass.defra.gov.uk/our-science/observing-and-modelling/monitoring-programmes/sea-temperature-and-salinity-trends/station-positions-and-data-index.aspx)

monthly herbarium mol% Mg/Ca data ( $n = 112$ ) were modeled using a sine function regression (using Sigmaplot v.10 software) fitted to the apparent sine waveform of the data as a function of time.

### Statistical analysis

Prior to all statistical analyses, normality of data was tested using the Anderson-Darling test, and homogeneity of variance using Levene's test (significant differences from normality and homogeneity of variance were taken at the 5% significance level). All data were normally distributed and demonstrated homogeneous variance, or were transformed to meet these criteria as described below. All analyses were performed using Minitab v.14 software.

### Seasonal sampling

To examine differences in mol% Mg/Ca between sampling months, shore heights and species (*C. officinalis* and *C. caespitosa*) at Combe Martin, a nested ANOVA was performed with the factors 'Month', 'Shore height' and 'Species', with Species nested within Shore height, and the interaction terms 'Month × Shore height' and 'Month × Species'. Post hoc Tukey HSD analysis was used to examine significant differences highlighted by ANOVA analyses.

### Comparative sampling

As no significant difference in *C. officinalis* mol% Mg/Ca were evident between upper and lower shore Combe Martin or Wembury Point during June 2012, data from both shore heights were pooled per site for inter-site comparison. To examine differences in *C. officinalis* mol% Mg/Ca collected from Combe Martin and Wembury Point during June 2012 and from Iceland during July 2012, a 1-way ANOVA was performed with the factor 'Site'. To examine differences in mol% Mg/Ca between *C. officinalis* sampled in Combe Martin during September 2012 and northern Spain during October 2012, a *t*-test was performed with the factor 'Site'. Interspecific differences in mol% Mg/Ca of *C. officinalis* and *E. elongata* were examined by *t*-test comparison with the factor 'Species' between *C. officinalis* and *E. elongata* collected from lower shore Wembury Point during June 2012, and between *C. officinalis* and *E. elongata* collected from northern Spain during October 2012.

### Herbarium collections

Statistical differences in mol% Mg/Ca of herbarium data were examined using ANCOVA on square-root transformed data with the factors 'Location', 'Year' and 'Month' (covariate within 'Year'). The factor 'Location' was derived by categorizing herbarium samples into the county of collection.

## RESULTS

### Seasonal sampling

There was a significant difference in the mol% Mg/Ca of *Corallina officinalis* and *C. caespitosa* from Combe Martin in relation to 'Month' ( $F_{4,220} = 174.61$ ,

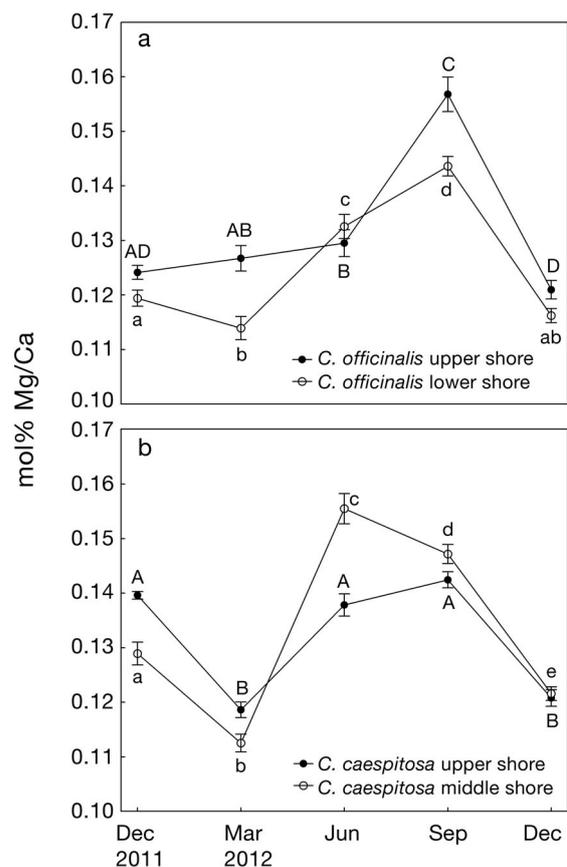


Fig. 3. Seasonal variation in mol% Mg/Ca of (a) *Corallina officinalis* from upper and lower shore, and (b) *C. caespitosa* from upper and middle shore of Combe Martin (mean  $\pm$  SE,  $n = 12$ ). Letters denote homogeneous subsets as determined by post hoc Tukey HSD analysis (at significance  $\alpha = 0.05$ ). Upper case letters refer to upper shore data and lower case letters refer to lower or middle shore data, respectively. Actual values (avg., min/max) are provided in Table S2 in the Supplement at [www.int-res.com/articles/suppl/m513p071\\_supp.pdf](http://www.int-res.com/articles/suppl/m513p071_supp.pdf)

$p < 0.0001$ ) (Fig. 3a,b). Highest mol% Mg/Ca was recorded for both upper (mean  $\pm$  SE:  $0.156 \pm 0.003$ ) and lower ( $0.143 \pm 0.001$ ) shore *C. officinalis* and upper shore *C. caespitosa* ( $0.142 \pm 0.001$ ) during September 2012, while middle shore *C. caespitosa* demonstrated maximal values during June 2012 ( $0.155 \pm 0.002$ ). Lowest mol% Mg/Ca were recorded during March 2012 for upper ( $0.118 \pm 0.001$ ) and middle ( $0.112 \pm 0.001$ ) shore *C. caespitosa*, and lower shore *C. officinalis* ( $0.113 \pm 0.002$ ), while upper shore *C. officinalis* demonstrated minimal values during December 2012 ( $0.120 \pm 0.001$ ). Homogeneous subsets determined from post hoc Tukey HSD analysis are demonstrated in Fig. 3a,b.

Though significant interaction was observed between 'Month' and 'Species' ( $F_{4,220} = 19.92$ ,  $p < 0.0001$ ), no significant interspecific difference in mol% Mg/Ca was observed between Combe Martin *C. officinalis* and *C. caespitosa*. Similarly, no significant difference in mol% Mg/Ca was observed in

relation to 'Shore height', though significant interaction was apparent between 'Month' and 'Shore height' ( $F_{8,220} = 14.22$ ,  $p < 0.0001$ ). For *C. officinalis*, upper shore samples demonstrated higher mol% Mg/Ca than lower shore during all months except June 2012, whereas *C. caespitosa* from the mid shore had the highest mol% Mg/Ca in the summer, but had lower ratios than upper shore *C. caespitosa* collected in the winter and spring.

### Comparative sampling

A significant difference in *C. officinalis* mol% Mg/Ca was observed in relation to 'Site' ( $F_{2,59} = 9.44$ ,  $p < 0.001$ ), with post hoc Tukey HSD analysis demonstrating significantly decreased values in *C. officinalis* collected from Iceland during July 2012 and Combe Martin during June 2012 in comparison to Wembury Point, though no significant difference between Combe Martin and Iceland mol% Mg/Ca was apparent (Fig. 4a). Samples collected from lower shore Combe Martin in September 2012 demonstrated significantly lower mol% Mg/Ca in comparison to samples collected from northern Spain in October 2012 ( $T_{22} = -2.08$ ,  $p < 0.05$ ), though there was no significant difference between upper shore Combe Martin and northern Spain samples (Fig. 4b). No interspecific differences were observed between the mol% Mg/Ca of *C. officinalis* and *E. elongata* from either Wembury Point or northern Spain (Table S2 in the Supplement at [www.int-res.com/articles/suppl/m513p071\\_supp.pdf](http://www.int-res.com/articles/suppl/m513p071_supp.pdf)).

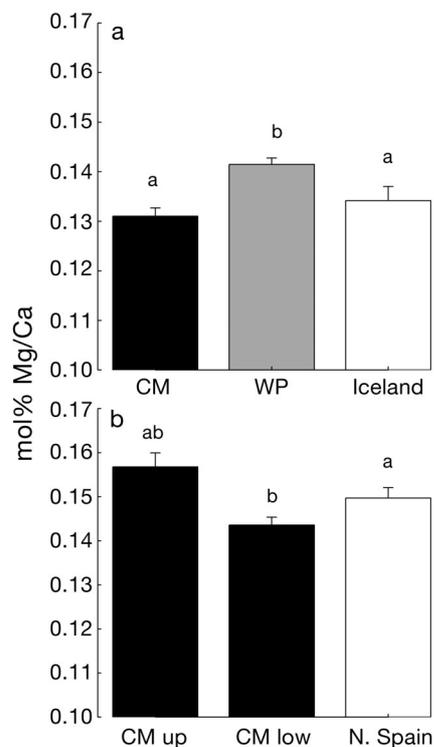


Fig. 4. (a) *Corallina officinalis* mol% Mg/Ca collected June 2012 from Combe Martin (CM) and Wembury Point (WP) (mean  $\pm$  SE,  $n = 24$ ), and July 2012 from lower shore Þorlákshöfn, Iceland (mean  $\pm$  SE,  $n = 12$ ). (b) *C. officinalis* mol% Mg/Ca (mean  $\pm$  SE,  $n = 12$ ) collected during September from Combe Martin upper (CM up) and lower (CM low) shore, and October from lower shore A Coruña, northern Spain. Letters indicate homogeneous subsets as determined from post hoc Tukey HSD analysis (at significance  $\alpha = 0.05$ )

### Herbarium collections

No significant difference in mol% Mg/Ca of *C. officinalis* apical tips was observed in relation to 'Location' or 'Year', though a significant difference was observed in relation to 'Month' ( $F_{10,111} = 7.46$ ,  $p < 0.001$ ), with 'Month' showing significant covariance within 'Year' ( $p < 0.05$ ). Average monthly mol% Mg/Ca of all herbarium data are presented in Fig. 5, demonstrating an apparent seasonal temporal pattern of mol% Mg/Ca as a function of month, effectively with summer maxima and late winter/spring minima.

### Temperature relationships

Significant linear relationships were identified between local SST and mol% Mg/Ca of Combe Martin

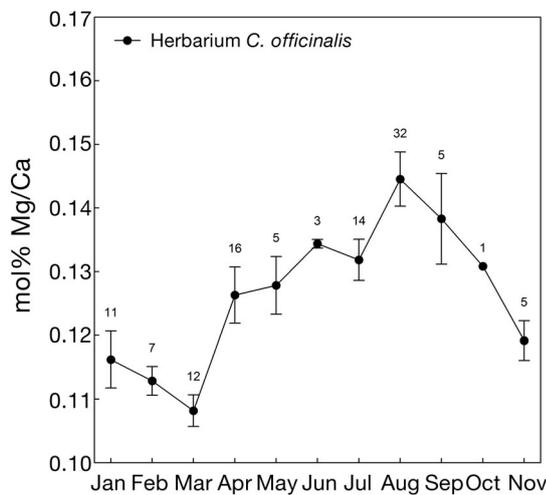


Fig. 5. Herbarium *Corallina officinalis* average monthly mol% Mg/Ca  $\pm$  SE (monthly average across all years, see Table S1 in the Supplement at [www.int-res.com/articles/suppl/m513p071\\_supp.pdf](http://www.int-res.com/articles/suppl/m513p071_supp.pdf)). Numbers represent sample size of the respective month

seasonally sampled *C. officinalis* (both upper and lower shore) and *C. caespitosa* (both upper and middle shore) (Fig. 6a,b, Table 2A). Based on these relationships, changes in Mg concentration of 0.0035 and 0.0037 mol% Mg/Ca  $^{\circ}\text{C}^{-1}$  were determined for upper and lower shore *C. officinalis*, respectively, and 0.0028 and 0.0047 mol% Mg/Ca  $^{\circ}\text{C}^{-1}$  for *C. caespitosa* upper and middle shore, respectively. Significant linear relationships were also identified between local SST and *C. officinalis* mol% Mg/Ca determined from  $n = 45$  herbarium samples (Fig. 6c, Table 2B), with a change in mol% Mg/Ca of 0.0036  $^{\circ}\text{C}^{-1}$  determined.

Mol% Mg/Ca were predicted using CEFAS SST data from Stn 27 for each month for both *C. officinalis* and *C. caespitosa* from Combe Martin (Fig. 7a). In addition, all herbarium data ( $n = 112$ ) grouped into month of collection demonstrated a clear sine wave-form function over time, with all equation parameters given significant at  $p < 0.001$  (Fig. 7b, Table 2B).

## DISCUSSION

### Present-day mol% Mg/Ca cycles

*Corallina* species in the northeastern Atlantic have clear seasonal cycles in skeletal Mg incorporation, as demonstrated by seasonal variability in mol% Mg/Ca of present-day *C. officinalis* and *C. caespitosa* recorded during this study. These findings are in line with previous work that have demonstrated season-

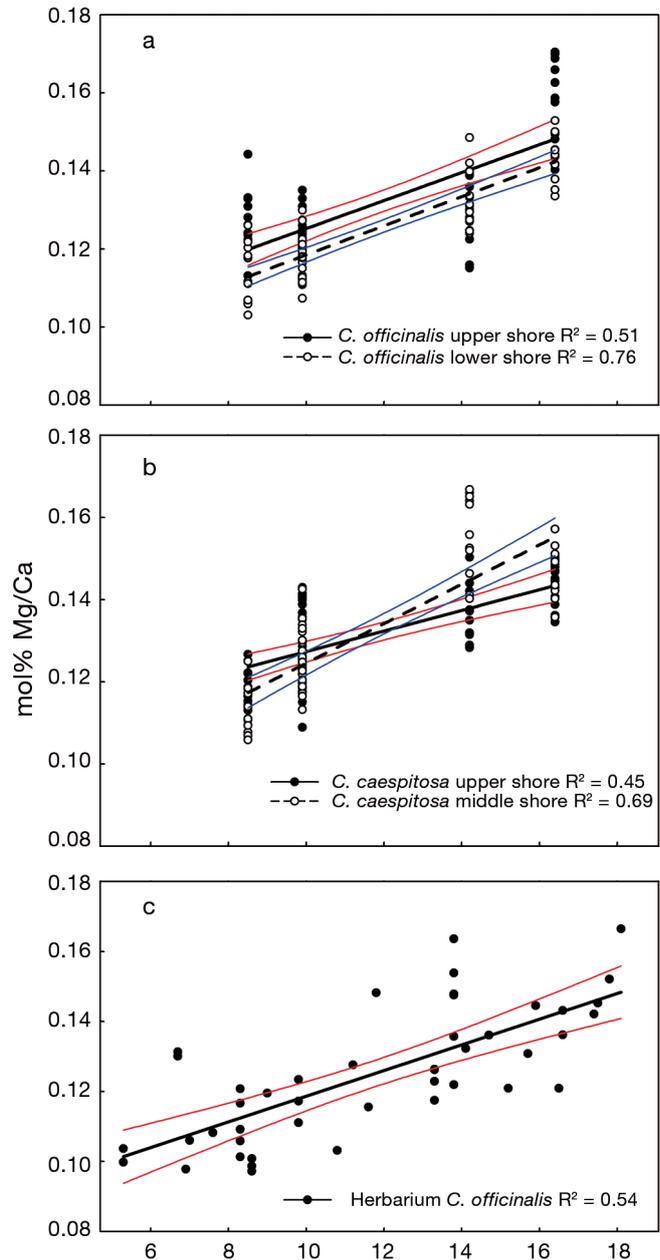


Fig. 6. Mol% Mg/Ca–temperature relationships for (a) *Corallina officinalis* collected from upper and lower shore and (b) *C. caespitosa* collected from upper and middle shore, from Combe Martin, and (c) herbarium *C. officinalis* (see Table 2A for relationship equations). All regressions were significant at  $p < 0.0001$  (Table 2A) and are displayed with 95% confidence intervals (red and blue lines) of predictions made from least-squares regressed linear relationships

ally cyclic patterns of Mg/Ca ratios in rhodoliths (Kamenos et al. 2008), corals (Mitsuguchi et al. 1996) and other calcifying species (Chave 1954), and support the assertion that the Corallinaceae are a group with consistently high Mg content (ca. 10 mol% or more) (Vinogradov 1953).

Table 2. (A) Mol% Mg/Ca–temperature relationships for *Corallina officinalis* and *C. caespitosa* from Combe Martin, and herbarium *C. officinalis* matched to sea surface temperature (SST). (B) Mol% Mg/Ca–month relationship for all herbarium *C. officinalis* samples, where month is represented by values 1 to 11 (January to November) (see also Figs. 6 & 7). na: not applicable

A								
Species	Shore height	Relationship ( $y = mx + c$ )	R <sup>2</sup>	m SE	c SE	r	p	n
<i>C. officinalis</i>	Upper	Mol% Mg/Ca = 0.00358 SST + 0.0894	0.51	±0.0004542	±0.005522	0.71	<0.0001	60
	Lower	Mol% Mg/Ca = 0.00372 SST + 0.0813	0.76	±0.0002699	±0.003281	0.87	<0.0001	60
<i>C. caespitosa</i>	Upper	Mol% Mg/Ca = 0.00286 SST + 0.1022	0.45	±0.0003628	±0.004410	0.67	<0.0001	60
	Middle	Mol% Mg/Ca = 0.00479 SST + 0.0766	0.69	±0.0004138	±0.005030	0.83	<0.0001	60
<i>C. officinalis</i> (herbarium)	na	Mol% Mg/Ca = 0.00367 SST + 0.0819	0.54	±0.0005073	±0.006247	0.74	<0.0001	45
B								
Species	Relationship ( $y = y_0 + b \sin(2\pi(x/c) + d)$ )		R <sup>2</sup>	SE	r	p	n	
<i>C. officinalis</i> (herbarium)	Mol% Mg/Ca = 0.1270 + 0.0145 sin[2π(Month/11.2423) + 3.5493]		0.47	y <sub>0</sub> ± 0.0013 b ± 0.0015 c ± 0.9944 d ± 0.3211	0.68	<0.0001	112	

Concentrations and seasonal ranges of Mg in geniculate *Corallina* and *Ellisolandia* species are towards the lower end of those reported for other coralline macroalgae from similar geographic regions. For example, Combe Martin *C. officinalis* Mg content (expressed as mol% MgCO<sub>3</sub>) ranged from approximately 10–17 mol% MgCO<sub>3</sub> and *C. caespitosa* from 10–16 mol% MgCO<sub>3</sub>. These concentrations and ranges are noticeably lower than those reported for the rhodoliths *Lithothamnion glaciale* (12.9–24.6 mol% MgCO<sub>3</sub>) and *Phymatolithon calcareum* (14.7–23.8 mol% MgCO<sub>3</sub>) from Scotland (Kamenos et al. 2008), though are in the same range as those reported for the geniculate coralline *E. elongata* from France (0.177 ± 0.002 mol% Mg/Ca) (Egilsdottir et al. 2013).

Biogenic Mg-calcites have been demonstrated to go through a maximum solubility at approximately 24 mol% MgCO<sub>3</sub>, with the most insoluble Mg-calcite containing about 2 mol% MgCO<sub>3</sub> (Plummer & Mackenzie 1974). Given this increasing solubility of calcite with increasing Mg content, variation in skeletal mineralogy between coralline species has been suggested to impact their vulnerability to OA (Gao et al. 1993, Morse et al. 2007, Andersson et al. 2008, Kuffner et al. 2008, Ries et al. 2009, Ries 2010, Lombardi et al. 2011, Smith et al. 2012). In this regard, northeastern Atlantic species of the genera *Corallina* and *Ellisolandia* may demonstrate reduced susceptibility to the impacts of OA on skeletal growth and dissolution in comparison to other high-Mg calcite-depositing coralline species, in particular rhodoliths, from similar geographic regions. The seasonal range

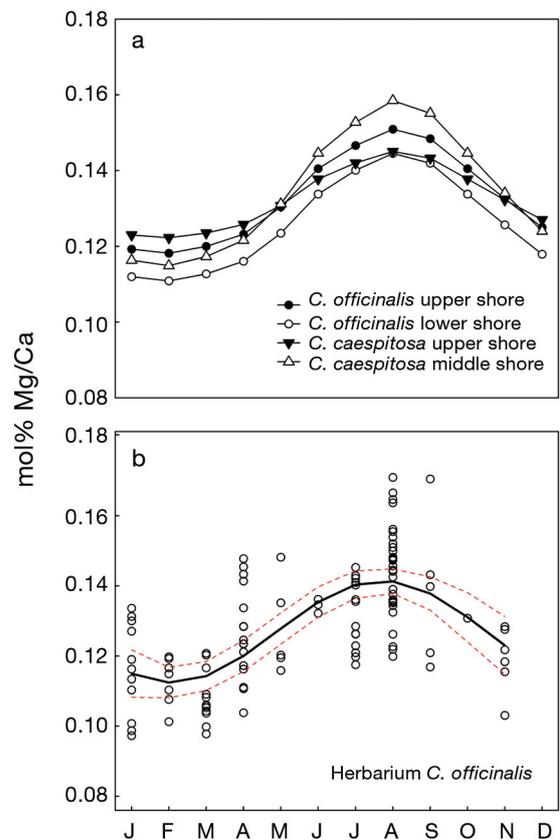


Fig. 7. (a) Predicted seasonal cycles in mol% Mg/Ca of *Corallina officinalis* upper and lower shore, and *C. caespitosa* upper and middle shore, from Combe Martin, calculated using average monthly sea surface temperature (SST) reported from CEFAS Stn 27 and linear regression equations shown in Table 2A. (b) Herbarium *C. officinalis* mol% Mg/Ca (n = 112) with fitted sine waveform function in relation to month, showing 95% confidence intervals (dashed red lines) (see Table 2B for model equation)

of *Corallina* Mg content reported here (approximately 0.11–0.16 mol% Mg/Ca) would correspond to a solubility product range (the equilibrium constant for a solid substance dissolving in an aqueous solution) of approximately  $-7.95$  to  $-7.69$  (log K at 25°C and 0.98 bar CO<sub>2</sub>) based on Plummer & Mackenzie (1974, their Table 3). For comparison, *P. calcareum* of Kamenos et al. (2008) would have a seasonal solubility product range of approximately  $-7.65$  to  $-7.15$ , the less negative values indicating increased solubility. This supports recent work that has demonstrated differential susceptibility of rhodolith and crustose coralline algae to OA conditions in comparison to geniculate coralline species (Noisette et al. 2013).

### Temperature relationships and inter/intra-specific mol% Mg/Ca patterns

Significant positive relationships identified between the mol% Mg/Ca of *C. officinalis* and *C. caespitosa* and local SST ( $R^2 = 0.45$ – $0.76$  across our data; Fig. 6) highlight that under present climatic conditions, Mg incorporation by *Corallina* species is closely related to ambient seawater temperature. This is in agreement with data for rhodolith species from a similar geographic region (Kamenos et al. 2008), which have been highlighted as robust Mg-palaeotemperature proxies (Kamenos et al. 2009), and several marine calcifying species from numerous regions (Chave 1954). For example, Chave (1954) observed that in all groups of calcitic organisms where sufficient data are available, a linear or near-linear relationship exists between skeletal Mg content and the water temperature in which the organisms grew.

While strong Mg–temperature relationships have been identified in numerous studies, Mg content is known also to be a function of growth rate, which is affected by several other abiotic parameters (Moberly 1968, Andersson et al. 2008, Ries 2010, 2011). For marine macroalgae, temperature and irradiance are 2 fundamental parameters controlling productivity, growth and distribution (Luning 1990, Lobban & Harrison 1994). For calcifying species, carbonate chemistry also plays a crucial role in regulating calcification and thus growth processes (Andersson et al. 2008, Ries 2010, Egilisdottir et al. 2013). In intertidal habitats, temperature, irradiance and carbonate chemistry are interdependent, showing covariance over both long (i.e. seasonal) and short (i.e. diurnal) time periods (Ganning 1971, Truchot & Duhamel-Jouve 1980, Morris & Taylor 1983). While our data indicate a significant relationship between

*Corallina* skeletal Mg concentrations and SST, we cannot rule out the potential influence of other factors, e.g. irradiance, on Mg incorporation via effects to growth. Multifactorial laboratory incubations with manipulation of temperature, irradiance and carbonate chemistry are required to disentangle the individual roles of these factors.

Interspecific vital effects on Mg incorporation were found by the present study to be lacking or weak within the genus *Corallina* and between species of *Corallina* and *Ellisolandia* (previously all members of *Corallina*), as per the conclusions of Ries (2010). Different *Corallina* and *Ellisolandia* species sampled simultaneously from the same location within sites showed no significant difference in mol% Mg/Ca, while intraspecific differences in mol% Mg/Ca were evident between both local sites (i.e. Combe Martin and Wembury Point) and across latitudes. At the small spatial scale (within sites), differences in skeletal Mg content can be related to position on shore and thus the varying influence of abiotic conditions. Regular, short-term fluctuations in temperature and other abiotic parameters (e.g.  $p\text{CO}_2$ , O<sub>2</sub>, salinity, nutrient concentrations and irradiance) are experienced in intertidal rock pools inhabited by *Corallina* and *Ellisolandia* species (Ganning 1971, Daniel & Boyden 1975, Morris & Taylor 1983, Egilisdottir et al. 2013). During daylight emersion, irradiance drives increases in rock pool water temperature and photosynthetic utilization of  $p\text{CO}_2$ , increasing pH and carbonate saturation due to effects on the carbonate chemistry equilibrium. During nighttime emersion, the opposite trends are apparent, with conditions potentially corrosive to calcite established through production of  $p\text{CO}_2$  by respiration processes and subsequent decreases in pH and carbonate saturation (Ganning 1971, Truchot & Duhamel-Jouve 1980, Morris & Taylor 1983). All of these dynamics may potentially impact geniculate coralline algae growth and calcification and thus Mg incorporation. In this regard, rock pools higher up a shore will experience longer periods of tidal emersion and therefore more extreme fluctuations in abiotic parameters, while lower shore rock pools, and the species therein, will be more influenced by ambient seawater conditions, e.g. SST. This trend is present in our data, whereby stronger regression of *Corallina* mol% Mg/Ca to ambient SST is observed the further down a shore the species was collected. In addition, rock pool size may influence the degree of variability in abiotic conditions and thus skeletal Mg incorporation. Larger and deeper pools, for example, are known to have more stable conditions (Ganning 1971). The extremes

in mol% Mg/Ca of *C. caespitosa* collected from middle shore pools in comparison to upper pools likely relate to extremes in abiotic conditions experienced in these small/shallow middle shore pools (volume: ca. 0.09 m<sup>3</sup>, depth: ca. 2–4 cm), in comparison to upper shore pools (ca. 40 m<sup>3</sup> volume and 500 cm deep) (Table 1).

Across latitudes, intraspecific differences in *C. officinalis* mol% Mg/Ca observed during summer and autumn may suggest that decreases in light, seawater carbonate saturation and temperature caused a decrease in Mg concentration in *Corallina* with increasing latitude (Chave 1954, Mackenzie et al. 1983, Andersson et al. 2008). This data should, however, be interpreted with caution, given the reduced sampling frequency in Iceland and northern Spain, and comparisons between different sampling months across latitudes. Additionally, samples of *C. officinalis* collected from Þorlákshöfn in southwest Iceland may experience warmer conditions than implied by its location just south of the Arctic Circle. Despite the higher latitude, southwest coastal Iceland experiences a relatively moderate temperature regime due to the domination of the Irminger Current, a relatively warm offshoot from the North Atlantic Current, which results in summer SST over 10°C (Jiang et al. 2001). As such, 'latitudinal' differences in *C. officinalis* mol% Mg/Ca may be reduced between e.g. southwest Iceland and the UK. To fully elucidate potential gradients in mol% Mg/Ca of geniculate coralline algal species across latitudes, sampling over complete seasonal cycles is required at a range of latitudes.

### Recent past (i.e. 1850–2010) mol% Mg/Ca cycles

Despite the sporadic nature of herbarium collections, analysis of *C. officinalis* samples housed in the algal herbarium of the Natural History Museum (BM), London, enabled investigation into recent past cycles in Mg incorporation by *Corallina* species in the northeastern Atlantic, providing important information with regard to natural variability in *Corallina* skeletal mineralogy. Herbarium collections can thus represent an important resource for climate change and OA research (though see Huisman & Millar 2013 for a discussion of herbarium limitations).

Notably, over the period ~1850–2010, no significant change in the mol% Mg/Ca ratio of herbarium *C. officinalis* was detected during the present study, while within-year variability strongly reflected present-day seasonal cycles in skeletal Mg incorporation of *Corallina* species in terms of both absolute concen-

trations and ranges. The influence of SST on *Corallina* Mg incorporation was also supported by significant positive regression of herbarium *C. officinalis* mol% Mg/Ca cycles with locally reported SSTs. Our herbarium data thus confirm our present-day seasonal cycles in mol% Mg/Ca, strengthens the relationship between Mg incorporation and SST in *Corallina* species, and indicates that within the intertidal, such seasonal cycles have not changed significantly over the last ca. 150 yr (see below).

### Predictive models

*Corallina* mol% Mg/Ca and SST relationships enable projection of *Corallina*'s skeletal mineralogy. Given the change in herbarium *C. officinalis* skeletal Mg content expected with temperature (Table 2B), we would expect an increase of approximately 0.23 mol% MgCO<sub>3</sub> with the increase in global average SST of 0.65°C over the period 1850–2005 caused by climate change (Solomon et al. 2007). Such an increase in Mg concentration was not observable in herbarium samples over the period ~1850–2010, most likely owing to the sporadic nature and lack of replication of herbarium collections, and intraspecific variation in *Corallina* Mg concentration within and between sites. Additionally, simultaneous decreases in skeletal Mg content owing to decreased seawater carbonate saturation caused by concomitant OA over this period may have occurred (Ries 2011, Egilisdottir et al. 2013). However, had an increase of 0.23 mol% MgCO<sub>3</sub> occurred since 1850 in relation to increased SST, our data indicate that this would represent an increase of just 3.2% of the seasonal variation experienced by *C. officinalis* in the UK intertidal. It is therefore unlikely that cycles in intertidal *C. officinalis* Mg incorporation have been significantly impacted by climate change over the last ~150 yr.

By 2100, climate change models predict increased global ocean average SST ranging from +0.6°C to more than +3.0°C and a further decrease in average ocean pH of 0.13 to 0.42 under IPCC RCP2.6 and RCP8.5, respectively (Collins et al. 2013). A 3°C increase in SST could cause an increase in *C. officinalis* and *C. caespitosa* Mg content of approximately 1.1 mol% MgCO<sub>3</sub>, corresponding to approximately 32% of the seasonal variability in Mg concentration currently experienced by these species in the northeastern Atlantic. During periods of highest skeletal Mg content (i.e. August), *Corallina* mol% Mg/Ca would increase to approximately 0.15, while in cooler months (i.e. February), mol% Mg/Ca of approxi-

mately 0.12 would be expected, giving a new solubility product range (log K at 25°C and 0.78 bar CO<sub>2</sub>) of approximately –7.74 to –7.93 (Plummer & Mackenzie 1974). Although maximum Mg concentrations remain substantially less than observed in present-day rhodolith species (Kamenos et al. 2008), increases in the Mg content of *Corallina* may have impacts on skeletal growth and dissolution. This may be particularly important given *Corallina*'s intertidal habitat, where rock pool pCO<sub>2</sub> can naturally reach 1000 µatm during dark tidal emersion periods due to respiration processes, causing significant decreases in rock pool carbonate saturation, and thus conditions corrosive to skeletal CaCO<sub>3</sub> (Ganning 1971, Daniel & Boyden 1975, Morris & Taylor 1983, Egilsdottir et al. 2013).

Over the long term, reductions in seawater carbonate saturation owing to OA that will occur simultaneously with increases in SST may serve to decrease skeletal Mg concentrations, and therefore solubility/potential vulnerability to OA, and should also be considered when projecting future responses of calcifying organisms. For example, Egilsdottir et al. (2013) demonstrated an average reduction of 0.013 mol% Mg/Ca in new structures formed by *E. elongata* in acidified conditions. This represents approximately 39% of the annual Mg variation experienced by present-day UK *Corallina* populations, of a similar magnitude to the increase projected with +3°C SST. However, as multi-stressor incubation studies (i.e. increased temperature and decreased calcite saturation) have not been conducted with *Corallina* or *Ellisolandia* species to date, it is currently unknown which of these stressors (if either) will have a dominant influence on skeletal mineralogy and thus solubility under future oceanic conditions.

The potential impacts of climate change (increased SST and OA) on calcifying species of the genera *Corallina* and *Ellisolandia* will be complex and should be addressed by multi-stressor future scenario incubations. Given the intertidal nature of these important ecosystem engineers (Nelson 2009), the results of such studies would benefit from knowledge of the natural variation in temperature and seawater carbonate chemistry currently experienced during periods of tidal emersion. Results of the present study demonstrate the present-day and recent-past skeletal mineralogy of temperate geniculate coralline algal species, the relationship between skeletal Mg content and SST, and place climate change and OA-induced changes in the skeletal mineralogy of these species into meaningful context with regard to present-day seasonal cycles.

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