



# The potential environmental response to increasing ocean alkalinity for negative emissions

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## Abstract

The negative emissions technology, artificial ocean alkalization (AOA), aims to store atmospheric carbon dioxide (CO<sub>2</sub>) in the ocean by increasing total alkalinity (TA). Calcium carbonate saturation state ( $\Omega$ CaCO<sub>3</sub>) and pH would also increase meaning that AOA could alleviate sensitive regions and ecosystems from ocean acidification. However, AOA could raise pH and  $\Omega$ CaCO<sub>3</sub> well above modern-day levels, and very little is known about the environmental and biological impact of this. After treating a red calcifying algae (*Corallina* spp.) to elevated TA seawater, carbonate production increased by 60% over a control. This has implication for carbon cycling in the past, but also constrains the environmental impact and efficiency of AOA. Carbonate production could reduce the efficiency of CO<sub>2</sub> removal. Increasing TA, however, did not significantly influence *Corallina* spp. primary productivity, respiration, or photophysiology. These results show that AOA may not be intrinsically detrimental for *Corallina* spp. and that AOA has the potential to lessen the impacts of ocean acidification. However, the experiment tested a single species within a controlled environment to constrain a specific unknown, the rate change of calcification, and additional work is required to understand the impact of AOA on other organisms, whole ecosystems, and the global carbon cycle.

**Keywords** Ocean alkalinity · *Corallina* spp. · Calcification · Carbon dioxide removal · Artificial ocean alkalization

## 1 Introduction

To meet the Paris Agreement (United Nations Framework Convention on Climate Change 2015), which aims to limit global temperature change to below 2 °C, negative emission

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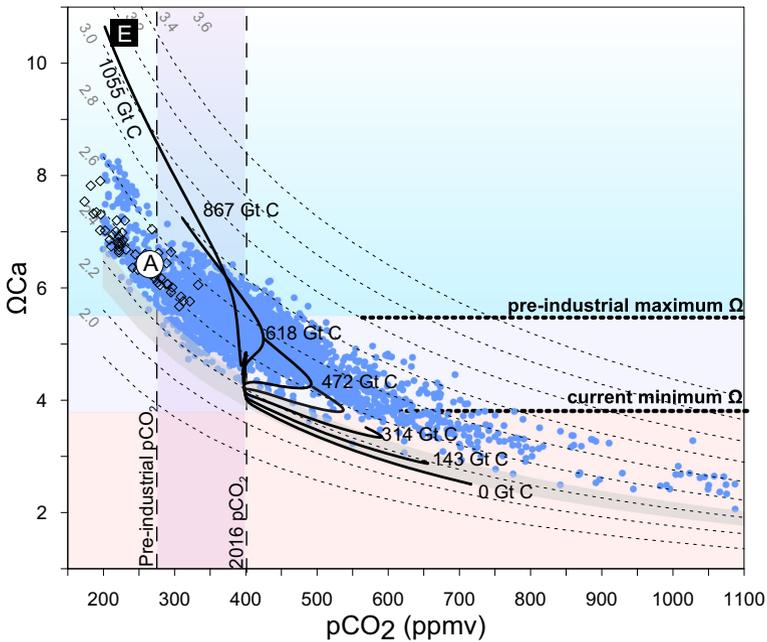
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technologies (NETs also known as “carbon dioxide removal”) may be needed in addition to severely reduced greenhouse gas emissions. One possible NET is artificial ocean alkalization (AOA) which stores atmospheric carbon dioxide ( $\text{CO}_2$ ) in the ocean as bicarbonate ions ( $\text{HCO}_3^-$ ) by increasing ocean total alkalinity (TA) (Kheshgi 1995). There are several proposals for increasing ocean TA. These include adding naturally occurring and abundant alkaline minerals, such as olivine ( $[\text{Mg}^{+2}, \text{Fe}^{+2}]_2\text{SiO}_4$ ) (Köhler et al. 2010), limestone ( $\text{CaCO}_3$ ) (Harvey 2008), or basalt (Beerling et al. 2018; Rigopoulos et al. 2017) to the ocean or land surfaces (Hartmann et al. 2013). Other proposals include accelerated limestone weathering (Rau and Caldeira 1999), electrochemical acceleration of silicate weathering (House et al. 2007; Rau et al. 2018), and the addition of lime ( $\text{CaO}$ ) or quick lime ( $\text{Ca}(\text{OH})_2$ ) to the surface ocean (Kheshgi 1995; Renforth et al. 2013). The overall objective of these proposals is to accelerate the natural weathering reactions which would otherwise take tens to hundreds of thousands of years to remove atmospheric  $\text{CO}_2$  by increasing ocean TA (Archer 2005; Lord et al. 2016).

An additional benefit of AOA is that it could alleviate regions from ocean acidification. Ocean acidification is the recent, and potential future, decrease in ocean pH and calcium carbonate saturation state ( $\Omega_{\text{CaCO}_3}$ ) caused by rising atmospheric  $\text{CO}_2$ . Ocean acidification has already influenced the marine environment by making it more difficult for some marine calcifiers to produce their calcium carbonate ( $\text{CaCO}_3$ ) shells (Doney et al. 2009). Artificially increasing ocean TA and the resulting increase in  $\Omega_{\text{CaCO}_3}$  would have the opposite effect, making it easier to calcify (Feng et al. 2017). Therefore, AOA could potentially allow ecosystems previously affected by reduced calcification (due to ocean acidification) to return to pre-industrial calcification values (Albright et al. 2016).

Although increasing ocean TA could be a way of alleviating ocean acidification, it could also increase ocean pH and  $\Omega_{\text{CaCO}_3}$  well above pre-industrial values, particularly in the regions where the alkaline minerals were added (Renforth and Henderson 2017; Feng et al. 2017) (Fig. 1). Therefore, if AOA was deployed, the ecosystems located close to where TA was increased could face significant changes. Most studies to date focus on what effect a decrease in pH and  $\Omega_{\text{CaCO}_3}$  will have on marine ecosystems (ocean acidification studies). There are a few studies, however, that have investigated the response following an increase in TA and  $\Omega_{\text{CaCO}_3}$ . Cripps et al. (2013) found that increased TA (raising pH up to 8.8 and  $\Omega_{\text{CaCO}_3}$  up to 12.6) caused abnormal acid-base balance and increased haemolymph pH in the marine calcifier *Carcinus maenas*. Albright et al. (2016) investigated the response of a coral reef flat to increased TA (raising pH to 8.3 and aragonite  $\Omega_{\text{CaCO}_3}$  to  $\sim 6$ ) and found that net community calcification increased. Further, a recent study by Gim et al. (2018) studied the ecotoxicological effects of increased  $\text{HCO}_3^-$  on various marine organisms, including both marine calcifiers and non-calcifiers. Their results showed a species-specific response to elevated  $\text{HCO}_3^-$ , suggesting that the ecosystem’s response to increased TA will not be easy to predict. There is still very little information on what impact TA addition will have on ecosystems and how marine organisms, including marine calcifiers, will respond to a large increase in TA.

Coastal environments are a favourable site for alkalinity addition by providing geochemical and environmental benefits over open ocean AOA (Meysman and Montserrat 2017; Schuiling and de Boer 2010). An important feature of coastal ecosystems across the globe is red calcifying macroalgae (Corallinales; Akioka et al. 1999). Therefore, a global AOA scheme will likely impact both Corallinales and



**Fig. 1** Results from a three-box model mimicking significant features of the ocean carbon system (<http://www.noc.soton.ac.uk/jmodels/>; Chuck et al. (2005) reported in Renforth and Henderson 2017) showing the relationship between calcite saturation state ( $\Omega_{Ca}$ ) and  $pCO_2$  and associated ocean carbon storage (GtC) for various total alkalinity (TA) addition scenarios (RCP 6.0 business as usual and 0.5, 1, 1.5, 2, 3, 4 x TA addition) after 120 years. The contours represent average surface ocean (0–100 m depth) TA in  $mEq L^{-1}$  at 16 °C and 35% salinity. The black square shows the mean  $\Omega_{Ca}$  and  $pCO_2$  for the elevated alkalinity treatment (E), and the white circle shows the mean  $\Omega_{Ca}$  and  $pCO_2$  for the ambient alkalinity treatment (A) of this experiment. The blue circles show average  $\Omega_{Ca}$  and  $pCO_2$  of 23 coral reef locations (data from Cyronak et al. 2018). Empty diamonds show ocean  $\Omega_{Ca}$  and  $pCO_2$  reconstructed from Hönisch et al. (2009) for the past 2 Ma

coastal ecosystems. Corallinales are some of the most prolific producers of  $CaCO_3$ , particularly in temperate shallow coastal waters (Martin et al. 2007) producing high-magnesium calcite (HMC) (Basso 2012). HMC is the most soluble form of  $CaCO_3$  in the marine environment suggesting that HMC producers such as the Corallinales could be particularly vulnerable to ocean acidification (Andersson et al. 2008; Martin and Gattuso 2009; Hofmann et al. 2012a; Hofmann et al. 2012b; Williamson et al. 2014). However, Corallinales also grow in dynamic environments and so are used to relatively large daily and seasonal changes in carbonate chemistry which could promote resilience to changes caused by ocean acidification (Egilsdottir et al. 2013; Noisette et al. 2013). These variable results indicate that Corallinales' sensitivity to ocean acidification is complex and suggests that predicting Corallinales' sensitivity to AOA could be equally challenging.

This paper aims to investigate the potential environmental and biological responses to AOA by presenting results from an ex-situ experiment that tests how red calcifying algae, *Corallina* spp. (of the family Corallinales) responds to an increase in TA. *Corallina* spp. physiology (calcification, primary productivity, respiration, and photophysiology) was investigated for 3 weeks in an ex-situ experimental set-up.

## 2 Methods

### 2.1 Sample collection

*Corallina* samples were collected from Dunraven Bay, a rocky shore near Southerndown, South Wales (51°44.65' N, 03°60.73' W) during February 2018. The samples were carefully removed from their substrate making sure to obtain their encrusting base. Dunraven Bay consists of a heavily pitted limestone wave cut platform with rock pools. The rock pool temperature, pH, and salinity were measured on site using a temperature and pH combination electrode and refractometer. Photochemically active radiation (PAR) was measured at the water depth at which the *Corallina* was growing using a 4-pi LI-COR cosine-corrected quantum sensor respectively. The chemical and physical properties of the rock pool water are summarised in Table 1. *Corallina* samples were randomly selected from the rock pools found in the intertidal region of Dunraven Bay.

Two common species of red calcifying macroalgae (Corallinales) found in the UK are *Corallina officinalis* and *Corallina elongata* (Williamson et al. 2014). Frond morphology of the samples collected closely matched that of *C. officinalis*; therefore, the samples collected were decided to be most likely *C. officinalis*. However, morphological characters alone are often not sufficient enough to identify the Corallinales to subfamily taxonomic levels (Bailey and Chapman 1998), and because no formal identification was made (e.g., using DNA comparisons), the samples will be referred to as simply *Corallina* spp. herein.

The *Corallina* spp. samples and ~100 L of site water were transported back to Cardiff University. The site water was filtered using the methodology of Walsh et al. (2009) then stored in a flow-through chamber within a greenhouse. Twelve undamaged *Corallina* spp. samples that were visually free from epiphytes were chosen. Each sample had a similar number of fronds (8–10) and frond length (4–6 cm) and weight ~1 g (wet). The 12 *Corallina* spp. samples were submerged in 1-L glass chambers containing 400 mL of site water. Two blank 1-L bottles containing 400 mL of original seawater but no *Corallina* spp. sample were also prepared. These control bottles were used to account for any differences in carbonate chemistry not caused by the *Corallina* spp. samples.

### 2.2 Experimental set-up

The experimental set-up consisted of two TA treatments, an elevated TA treatment (elevated alkalinity) and an ambient TA treatment (ambient alkalinity). Every 48 h, each glass chamber was refreshed with 400 mL of filtered site water from the flow-through chamber. For the elevated alkalinity treatment, TA was increased by ~1000  $\mu\text{Eq L}^{-1}$  by adding 0.5 mol  $\text{L}^{-1}$   $\text{Na}_2\text{CO}_3$  and bubbling with ambient air for 2 h, to ensure that  $\Omega_{\text{CaCO}_3}$  did not exceed 10. This was carried out before being added to the *Corallina* spp. chambers. For the ambient alkalinity

**Table 1** Average  $\pm$  standard error chemical and physical properties of Dunraven Bay rock pool water

Parameter	Value during collection
Salinity	30
Temperature ( $^{\circ}\text{C}$ )	6.5 $\pm$ 0.05
Photochemically active radiation (PAR) ( $\mu\text{mol photons m}^{-2}$ )	150–740
pH	8.17 $\pm$ 0.05

treatment, TA was unmodified but was still bubbled with ambient air for 2 h to allow for consistency between the treatments. The carbonate chemistry for both the ambient and elevated alkalinity treatments is summarised in Table 2 and Fig. 2. For the first 7 days, four out of the 12 glass chambers containing *Corallina* spp. samples were refreshed with elevated TA (elevated 1) water and eight were refreshed with ambient TA water (ambient). On day 8 (and for the remainder of the experiment), four of the ambient TA *Corallina* spp. samples were then subjected to elevated TA water instead (elevated 2). Of the two blank chambers with no *Corallina* spp. samples, one was refreshed with elevated alkalinity water and the other with ambient alkalinity water every 48 h. Each glass chamber was placed in a 10 °C temperature-controlled fridge. Irradiance above the glass chambers was adjusted to  $\sim 200 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$ . The light source consisted of 39 W LED tubes (JBL Solar Ultra Marin Day, JBL Aquaria, Nelson, New Zealand) placed above the aquaria, and the photoperiod was adjusted to 12 h/12 h light/dark period. The samples were kept alive for 3 weeks.

### 2.3 Net calcification, primary productivity, and respiration

Before refreshing the seawater, 100 mL of the solution from the glass chambers was collected and filtered through 0.22  $\mu\text{m}$  filters (Minisart syringe filters, Sartorius, Germany). One hundred millilitres of both elevated and ambient alkalinity treatment seawater was also collected. The pH of each water sample was measured using a pH electrode (Mettler Toledo™, U.K.) calibrated with TRIS and AMPD seawater buffer solutions according to Dickson et al. (2007).

Gran titration (907 Titrando, Metrohm tiamo™, Switzerland), used to measure TA, was calibrated using reference measurements of carefully prepared  $\text{Na}_2\text{CO}_3$  standards (0.5, 1.0, and 1.25  $\text{mmol L}^{-1}$ ) in 0.7  $\text{mol L}^{-1}$  NaCl background medium according to Dickson et al. (2007). Accuracy and precision were determined by 6 titrations of an alkalinity standard (Batch 126) supplied by the University of California San Diego. The absolute error of the TA measurements was  $\pm 20 \mu\text{Eq L}^{-1}$ . Afterward, pH, TA, water temperature, and salinity were used to determine the other carbonate chemistry parameters (DIC,  $\text{pCO}_2$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ , and the saturation states of aragonite [ $\Omega_{\text{Ar}}$ ] and calcite [ $\Omega_{\text{Ca}}$ ]) by inputting the values into CO2SYS v2.1 (Pierrot et al. 2006). CO2SYS was run using the constants of Mehrbach et al. (1973) refitted by Dickson and Millero (1987).

The net calcification rate ( $\text{NCR} = \mu\text{mol CaCO}_3 \text{ gDW}^{-1} \text{ h}^{-1}$ ) was calculated from the change in TA before and after refreshing with the ambient/elevated alkalinity water (Eq. 1).

$$\text{NCR} = \frac{\Delta\text{TA} * v}{2 * \text{gDW} * h} \quad (1)$$

where  $v$  is the volume of water in the glass chamber (400 mL),  $\text{gDW}$  is the dry weight of the *Corallina* spp. samples in grams, and  $h^{-1}$  is the time elapsed in hours (48 h). The amount of  $\text{CaCO}_3$  precipitated ( $\mu\text{mol CaCO}_3$ ) was estimated using the alkalinity anomaly technique (Smith and Key 1975; Chisholm and Gattuso 1991) which assumes a decrease in TA by 2  $\mu\text{Eq}$  equals 1  $\mu\text{mol}$  of  $\text{CaCO}_3$  precipitated. Nitrogen uptake during primary productivity can also influence TA. However, the change in TA due to nitrogen uptake was calculated using calculation 39 in Wolf-Gladrow et al. (2007) and was found to be <4% of the overall TA change, therefore, was ignored. The blank chambers were used to account for any changes in TA not produced by *Corallina* spp.

**Table 2** Average carbonate chemistry  $\pm$  standard deviation for elevated and ambient alkalinity treatments. TA = total alkalinity ( $\mu\text{Eq L}^{-1}$ ), DIC = dissolved inorganic carbon ( $\mu\text{mol L}^{-1}$ ),  $\text{pCO}_2$  = atmospheric partial pressure of  $\text{CO}_2$  ( $\mu\text{atm}$ ),  $\text{HCO}_3^-$  = bicarbonate ion concentration ( $\mu\text{mol L}^{-1}$ ),  $\text{CO}_3^{2-}$  = carbonate ion concentration ( $\mu\text{mol L}^{-1}$ ),  $\text{CO}_2$  = aqueous  $\text{CO}_2$  concentration ( $\mu\text{mol L}^{-1}$ ),  $\Omega_{\text{Ca}}$  = calcite saturation state, and  $\Omega_{\text{Ar}}$  = aragonite saturation state

Treatment	TA ( $\mu\text{Eq L}^{-1}$ )	DIC ( $\mu\text{mol L}^{-1}$ )	pH	$\text{pCO}_2$ ( $\mu\text{atm}$ )	$\text{HCO}_3^-$ ( $\mu\text{mol L}^{-1}$ )	$\text{CO}_3^{2-}$ ( $\mu\text{mol L}^{-1}$ )	$\text{CO}_2$ ( $\mu\text{mol L}^{-1}$ )	$\Omega_{\text{Ca}}$	$\Omega_{\text{Ar}}$
Elevated	$3454 \pm 105$	$2999 \pm 114$	$8.2 \pm 0.1$	$364 \pm 85.5$	$2632 \pm 151$	$362 \pm 64$	$13 \pm 3$	$8.8 \pm 1.6$	$5.6 \pm 1$
Ambient	$2694 \pm 114$	$2479 \pm 71$	$7.97 \pm 0.08$	$581 \pm 111$	$2288 \pm 48$	$171 \pm 34$	$21 \pm 4$	$4.1 \pm 0.8$	$2.7 \pm 0.5$

Calcification rates (CRs) for light and dark periods were also determined during week 1 and week 2. The 12 *Corallina* spp. chambers and two blank chambers were refreshed with 200 mL of elevated/ambient alkalinity water then left in either in light or dark conditions for 6 h. The pH was measured at the start of the 6 h (after being the water had been bubbled with ambient air) and again at the end of the 6 h. The pH and TA measured at the start and at the end of the 6-h experiment were then used to calculate how DIC changed over the course of the 6 hours. DIC was calculated using CO2SYS v2.1 (Pierrot et al. 2006). The change in DIC and the light and dark CRs were then used to estimate net primary productivity ( $NPP = -\mu\text{mol DIC gDW}^{-1} \text{ h}^{-1}$ ) and respiration ( $NR = +\mu\text{mol DIC gDW}^{-1} \text{ h}^{-1}$ ) values (Eq. 2).

$$NPP \text{ or } NR = \frac{\Delta\text{DIC}^* v}{gDW^* h} - CR(\text{dark}) / (\text{light}) \quad (2)$$

where  $CR(\text{dark})$  is the CR calculated from the change in TA in dark conditions and  $CR(\text{light})$  is the CR calculated from the change in TA in light conditions. Because the light and dark experiments occurred in an open-system, there may have been changes in pH caused by  $\text{CO}_2$  gas-solution transfer. The blank chambers were used to account for any changes in TA and pH not produced by *Corallina* spp. and used to correct light/dark CR, NPP, and NR for these changes.

The  $\text{CaCO}_3$  and organic carbon content of the *Corallina* spp. samples were also measured. First, the organic carbon ( $C_{\text{org}}$ ) content of the samples was measured by the loss in mass of the samples after combustion at  $500^\circ\text{C}$  for 6 h. Then, the  $\text{CaCO}_3$  content of the remaining ash was estimated using a FOGII Digital Calcimeter (BD Inventions P.C., Greece). Primary productivity rates ( $\text{mg } C_{\text{org}} \text{ gDW}^{-1} \text{ h}^{-1}$ ) were calculated assuming the ratio of  $\text{CaCO}_3$  to  $C_{\text{org}}$  content of the *Corallina* spp. did not change throughout the experiment and were equivalent to the measured cumulative alkalinity change.

The *Corallina* spp. dry weight ( $gDW$ ) used in Eqs. 1 and 2 is an average of the initial and end dry weight of the *Corallina* spp. Following the experiment, the *Corallina* spp. samples were dried at  $100^\circ\text{C}$  for 24 h to obtain the dry weight. The dry weight of *Corallina* spp. at the beginning of the experiment was estimated using the *Corallina* spp. dry weight at the end of the experiment minus the  $C_{\text{org}}$  produced (estimated from the combustion data) and cumulative  $\text{CaCO}_3$  produced (in grams).

## 2.4 Photophysiology

The photophysiology of the *Corallina* spp. samples was determined using PAM fluorometry. Rapid light curves (RLCs) were performed using a Walz Water-PAM fluorometer, after the chambers were refreshed with new site water, following the methodology of Perkins et al. (2006). Four replicate light curves were performed for both the elevated and ambient alkalinity treatments. RLC measurements were made on the tips of the upper-facing *Corallina* spp. fronds to avoid sampling potentially self-shaded frond regions and to minimise differential photoacclimation (i.e., due to differences in light history between upper and lower surfaces of fronds). RLCs were performed after each *Corallina* spp. sample was dark-adapted for 5 min.

Analysis of RLC was done using R v.3.4.1 (R Core Team 2013) and followed that described by Perkins et al. (2006) with curve fitting following the iterative solution of Eilers and Peeters (1988) to determine coefficients  $a$ ,  $b$ , and  $c$  and hence calculation of light curve parameters of relative maximum electron transport rate ( $rETR_{\text{max}}$ ), coefficient of light use

efficiency ( $\alpha$ ), and light saturation coefficient ( $E_k$ ). The shape of the RLC ( $rETR_{\max}$ ,  $\alpha$ ,  $E_k$ ) gives an indication to how efficient photosynthesis is. The first part of the RLC (the rise of the curve in the light limiting region) is proportional to the efficiency of light capture (effective quantum yield or  $\alpha$ ; Schreiber 2004), where the RLC peaks is used to determine the maximum photosynthetic capacity ( $rETR_{\max}$ ; Schreiber 2004). The interception of  $rETR_{\max}$  and  $\alpha$  determines the minimum saturating irradiance ( $E_k$ ; Sakshaug et al. 1997).  $E_k$  is related to how much light energy is either used for photosynthesis (photochemical quenching) or is emitted as fluorescence or converted to heat (non-photochemical quenching). The higher the  $E_k$  value, the more energy is used for photochemical quenching (Henley 1993). In the most simple terms, an increase in  $rETR_{\max}$ ,  $\alpha$ , and  $E_k$  suggests more efficient photosynthesis and a decrease in these values could suggest the *Corallina* spp. is becoming stressed.

The Genty parameter ( $F_v/F_m$ ) which is the approximate maximum light use efficiency in the dark-adapted state (Genty et al. 1989) and therefore gives an overall indication of the health of the *Corallina* spp. samples.  $F_v/F_m$  was calculated using R v.3.4.1 (R Core Team 2013). The Genty parameter is defined as:

$$F_v/F_m = (F_m - F_o)/F_m \quad (3)$$

where  $F_m$  is the maximum yield, and  $F_o$  is the minimum fluorescence yield in the dark-adapted state.

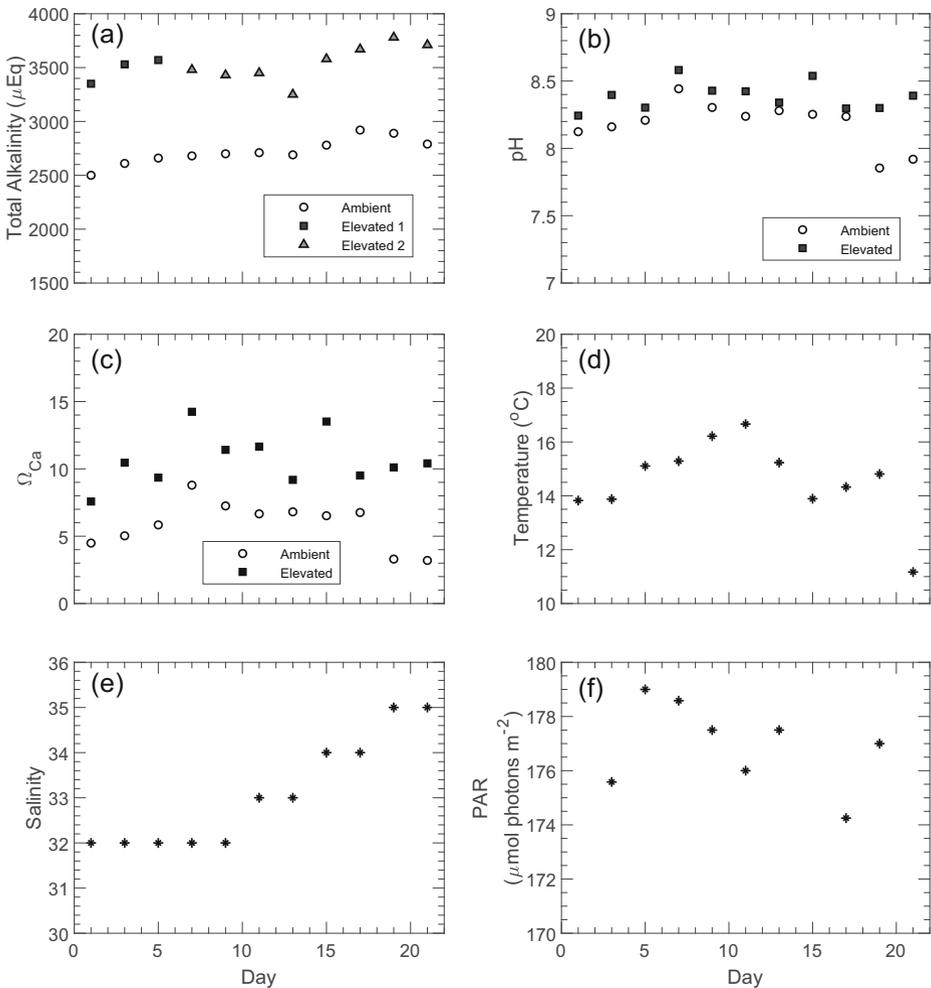
## 2.5 Data analysis

All figures were produced using either Grapher™ 13 (Golden Software, LLC) or MATLAB R2018b (MathWorks Inc., 2018). Where averages are given, the error is quoted as standard error ( $\pm$  S.E.) in the text, figures, or tables unless otherwise stated. All statistical analyses were performed using R v.3.4.1 (R Core Team 2013). Prior to all analyses, normality of data was tested using the Shapiro-Wilk test and examination of frequency histograms. Differences in parameters (NCR, NPP, NP,  $rETR_{\max}$ ,  $\alpha$ ,  $E_k$ , and  $F_v/F_m$ ) between the two alkalinity treatments were examined using Student's *t* test. Where data were not normally distributed, a Mann-Whitney *U* test was performed instead. Differences were deemed significant if  $p < 0.05$ . Linear regressions were performed to determine any significant relationships between NCR,  $rETR_{\max}$ ,  $\alpha$ ,  $E_k$ , and  $F_v/F_m$  and TA, pH, temperature, and irradiance (PAR). Additional linear regressions models were run to determine any significant relationship between NCR and photophysiology ( $rETR_{\max}$ ,  $\alpha$ ,  $E_k$ , and  $F_v/F_m$ ).

## 3 Results

### 3.1 Calcification

Throughout the experiment, TA, pH, and  $\Omega Ca$  were consistently higher in the elevated alkalinity treatment compared to the ambient alkalinity treatment (Fig. 2). *Corallina* spp. NCR was significantly higher (~60%) in the elevated alkalinity treatment compared to that in the ambient alkalinity treatment throughout the study period (Table 3, Fig. 3a). Average *Corallina* spp. NCR for elevated alkalinity was  $8.47 \pm 0.85 \mu\text{mol CaCO}_3 \text{ gDW}^{-1} \text{ h}^{-1}$  compared to  $5.34 \pm 0.61 \mu\text{mol CaCO}_3 \text{ gDW}^{-1} \text{ h}^{-1}$  for ambient alkalinity. The  $\text{CaCO}_3$  content



**Fig. 2** Physical and carbonate chemistry properties of the experimental set-up. **a** Total Alkalinity ( $\mu\text{Eq L}^{-1}$ ), **b** pH, **c** Calcite saturation state ( $\Omega_{\text{Ca}}$ ), **d** Temperature ( $^{\circ}\text{C}$ ), **e** Salinity, and **f** Photochemically active radiation (PAR;  $\mu\text{mol photons m}^{-2}$ ). Carbonate chemistry properties are divided into ambient alkalinity treatment (ambient; empty circles) and elevated alkalinity treatment which is further divided into elevated 1 (elevated 1; black squares) and elevated 2 (elevated 2; grey triangles). For elevated 1, total alkalinity was increased on day 1 and for elevated 2, total alkalinity was increased on day 8

measured at the end of the experiment was  $\sim 3\%$  higher for the *Corallina* spp. samples exposed to the elevated alkalinity treatments compared to the samples exposed to the ambient alkalinity treatment (Table 4). There was a significant positive linear relationship between NCR and TA, NCR and pH, and NCR and PAR (Table 5) with the strongest relationship between NCR and TA ( $R^2 = 0.3254$ ,  $p < 0.001$ ).

*Corallina* spp. NCRs were significantly higher ( $p < 0.05$ ) in the elevated 2 alkalinity treatment, where TA was increased after day 8, compared to the elevated 1 alkalinity treatment, where TA was increased straight away (Fig. 3a). Average *Corallina* spp. NCR for the elevated 1 alkalinity treatment was  $8.05 \pm 0.80 \mu\text{mol CaCO}_3 \text{ gDW}^{-1} \text{ h}^{-1}$  and for the elevated 2

**Table 3** Average *Corallina* spp. physiology values (NCR ( $\mu\text{mol CaCO}_3 \text{ gDW}^{-1} \text{ h}^{-1}$ ), LCR = light CR ( $\mu\text{mol CaCO}_3 \text{ gDW}^{-1} \text{ h}^{-1}$ ), DCR = dark CR ( $\mu\text{mol CaCO}_3 \text{ gDW}^{-1} \text{ h}^{-1}$ ), NPP ( $\mu\text{mol DIC gDW}^{-1} \text{ h}^{-1}$ ), NR ( $\mu\text{mol DIC gDW}^{-1} \text{ h}^{-1}$ ),  $r\text{ETR}_{\text{max}}$ ,  $F_v/F_m$ ,  $\alpha$ , and  $E_k$ . Significant codes: \*\*\* $p < 0.001$ , ns = not significant

Parameter	No. of samples		Average value		Standard error		Significance
	Elevated	Ambient	Elevated	Ambient	Elevated	Ambient	
NCR	60	47	8.47	5.34	0.85	0.61	***
CR (light)	8	8	12.43	8.83	1.02	0.64	ns
CR (dark)	8	8	2.29	-0.01	0.34	0.36	ns
NPP	8	8	-11.86	-5.87	1.47	0.79	ns
NR	8	8	0.645	-0.045	0.29	0.15	ns
$r\text{ETR}_{\text{max}}$	47	45	35	36	2	2	ns
$F_v/F_m$	47	45	0.68	0.69	0.02	0.02	ns
$\alpha$	47	45	0.13	0.13	0.01	0.01	ns
$E_k$	47	45	287	271	20	12	ns

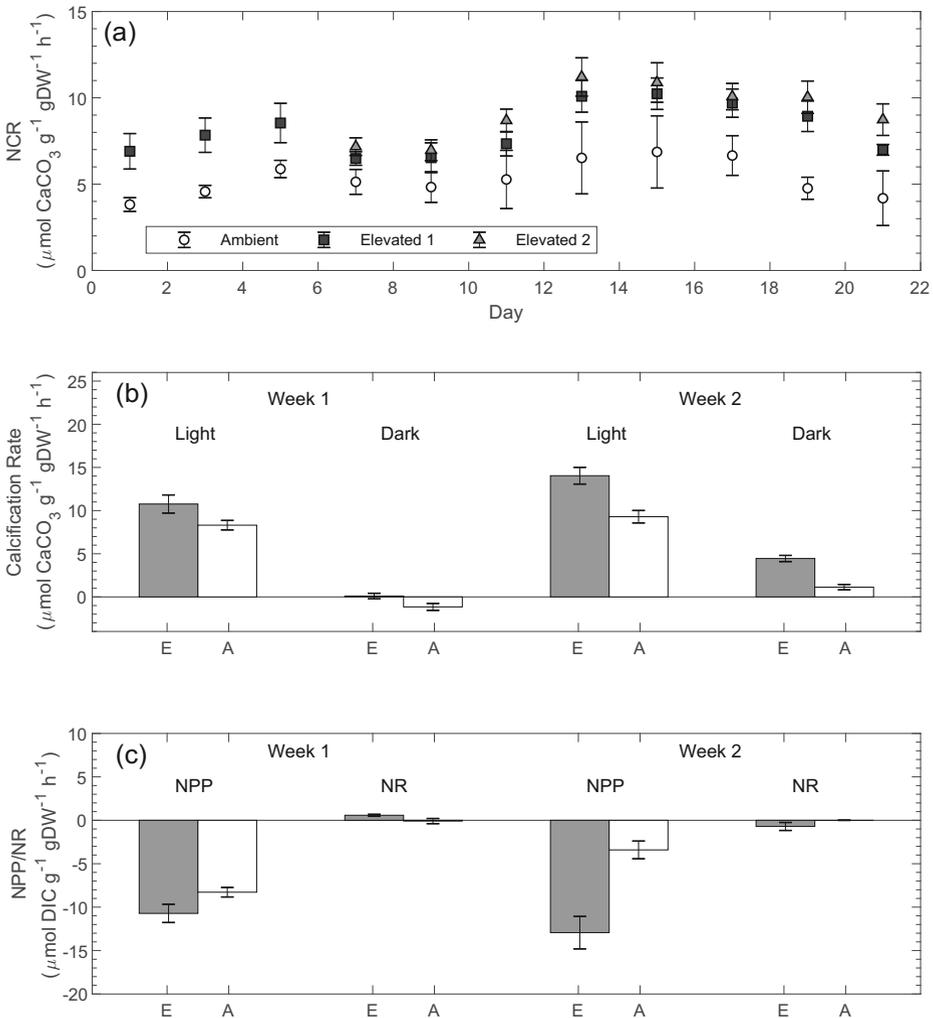
alkalinity treatment was  $9.34 \pm 0.84 \mu\text{mol CaCO}_3 \text{ gDW}^{-1} \text{ h}^{-1}$ . There was substantial temporal variation in *Corallina* spp. NCR for the ambient alkalinity treatment throughout the experiment. There was an initial increase of 74% from day 1 to 16 but then decreased back to the starting values by day 21, compared to a 40% increase in *Corallina* spp. NCR in the elevated 1 alkalinity treatment during the same time period (Fig. 3a).

*Corallina* spp. had higher rates of both light CR and dark CR when exposed to elevated alkalinity compared to the ambient alkalinity treatment. On average, the light CR was  $12.43 \pm 1.02 \mu\text{mol CaCO}_3 \text{ gDW}^{-1} \text{ h}^{-1}$ , which was 40% higher than the ambient alkalinity treatment ( $8.83 \pm 0.64 \mu\text{mol CaCO}_3 \text{ gDW}^{-1} \text{ h}^{-1}$ ; Table 3). *Corallina* spp. dark CR also substantially increased when exposed to the elevated alkalinity treatment compared to the ambient alkalinity treatment ( $2.29 \pm 0.34 \mu\text{mol CaCO}_3 \text{ gDW}^{-1} \text{ h}^{-1}$  compared to  $-0.01 \pm 0.36 \mu\text{mol CaCO}_3 \text{ gDW}^{-1} \text{ h}^{-1}$  respectively; Table 3). There was no significant difference between the alkalinity treatments for both the ambient and elevated alkalinity treatments (Table 3). The rates for *Corallina* spp. light and dark calcification increased from week 1 to week 2 (Fig. 3b).

### 3.2 Primary productivity (NPP) and respiration (NR)

After *Corallina* spp. were exposed to light conditions for 6 h, there was a substantial increase in pH for both the elevated and ambient alkalinity treatment water (increase of 0.57 and 0.67 respectively). This change in pH and in TA was used to estimate the rate of *Corallina* spp. NPP, which almost doubled when exposed to elevated alkalinity compared to the ambient alkalinity treatment. On average, the elevated alkalinity treatment NPP rate was  $-11.86 \pm 1.47 \mu\text{mol DIC gDW}^{-1} \text{ h}^{-1}$  and the ambient alkalinity treatment NPP rate was  $-5.87 \pm 0.79 \mu\text{mol DIC gDW}^{-1} \text{ h}^{-1}$ . The negative values indicate that  $\text{CO}_2$  was used up in photosynthesis.

After the *Corallina* spp. were exposed to dark conditions for 6 h, there was a decrease in pH for both the elevated and ambient alkalinity treatment water (decrease of 0.30 and 0.19 respectively). Both the elevated and ambient alkalinity treatments resulted in very low rates for NR ( $-0.29 \pm 0.39 \mu\text{mol DIC gDW}^{-1} \text{ h}^{-1}$  and  $0.58 \pm 0.20 \mu\text{mol DIC gDW}^{-1} \text{ h}^{-1}$  respectively).



**Fig. 3** Average *Corallina* spp. **a** net calcification rate (NCR;  $\mu\text{mol CaCO}_3 \text{ gDW}^{-1} \text{ h}^{-1}$ ), **b** light and dark *Corallina* spp. calcification rates ( $\mu\text{mol CaCO}_3 \text{ gDW}^{-1} \text{ h}^{-1}$ ), and **c** *Corallina* net primary productivity and net respiration (NPP/NR  $\mu\text{mol DIC g}^{-1} \text{ gDW}^{-1} \text{ h}^{-1}$ ) for the elevated (E) and ambient (A) alkalinity treatments. The elevated alkalinity treatment in (a) is further divided into elevated 1 (elevated 1; black squares) and elevated 2 (elevated 2; grey triangles). For elevated 1, total alkalinity was increased on day 1 and for elevated 2, total alkalinity was increased on day 8

There was a marked decrease in NPP rates for the ambient alkalinity treatment and a slight increase for the elevated alkalinity treatment going from week 1 to week 2 (Fig. 3c). Like the light and dark calcification rates, there was no significant difference between the elevated and ambient alkalinity treatments for NPP or NR.

From the combustion data and the  $\text{CaCO}_3$  to  $C_{\text{org}}$  ratio, it was estimated that, on average, a total of 0.09 g of  $C_{\text{org}}$  was produced by the *Corallina* spp. under the elevated alkalinity treatment and 0.07 g of  $C_{\text{org}}$  was produced by the *Corallina* spp. under the ambient alkalinity treatment (Table 4). Primary productivity was also estimated using the  $\text{CaCO}_3$  to  $C_{\text{org}}$  content

**Table 4** Results from CaCO<sub>3</sub> and organic carbon (C<sub>org</sub>) analysis of *Corallina* spp. samples and primary productivity rates (mg C gDW<sup>-1</sup> h<sup>-1</sup>) estimated from these values where gDW<sup>-1</sup> is the average dry weight of the *Corallina* spp. samples and *h* is time in hours. Error (±) estimated using error from Meyer et al. (2015)

Treatment	% of total weight		Ratio CaCO <sub>3</sub> :C <sub>org</sub>	Cumulative CaCO <sub>3</sub>		Cumulative C <sub>org</sub> (g)	Primary Productivity (mg C <sub>org</sub> gDW <sup>-1</sup> h <sup>-1</sup> )
	C <sub>org</sub>	CaCO <sub>3</sub>		(μmol)	(g)		
Ambient	26	58	0.45	1542	0.15	0.07	0.21 ± 0.06
Elevated 1	24	60	0.40	2306	0.23	0.09	0.31 ± 0.09
Elevated 2	26	59	0.44	2075	0.21	0.09	0.33 ± 0.10

ratio of the *Corallina* spp. samples. The primary productivity rates for *Corallina* spp. were ~ 50% higher for the elevated alkalinity treatments (elevated 1 and elevated 2) compared to that for the ambient alkalinity treatment (Table 4). The calculation of primary productivity was assumed that the rates were equivalent to the measured cumulative alkalinity change and that there was no variation in the ratio of CaCO<sub>3</sub> to C<sub>org</sub> content of the *Corallina* spp. throughout the experiment. However, Meyer et al. (2015) suggest as much as >±30% variation in the ratio of inorganic to organic carbon for calcareous algae may be possible. Therefore, this error (±30%) has also been taken into account for the primary productivity rates calculated using this ratio (Table 4).

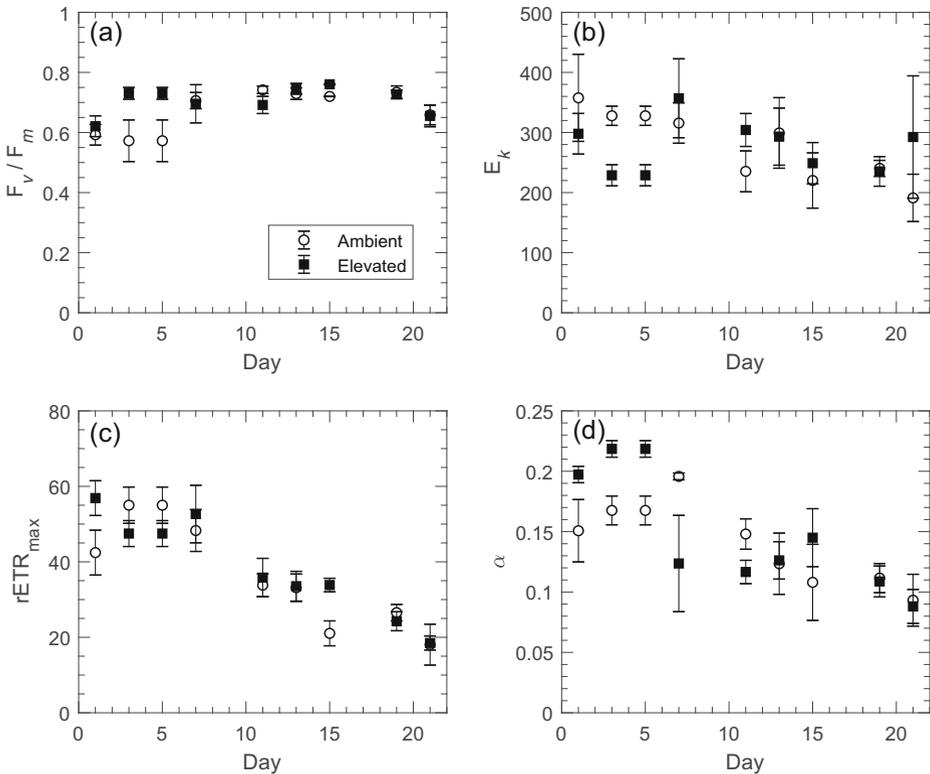
### 3.3 Photophysiology

*Corallina* spp. showed no significant difference in rETR<sub>max</sub>, F<sub>v</sub>/F<sub>m</sub>, α, and E<sub>k</sub> between the elevated and ambient alkalinity treatments (Table 3). There was a positive linear relationship between F<sub>v</sub>/F<sub>m</sub> and TA (R<sup>2</sup> = 0.1563, *p* < 0.01), rETR<sub>max</sub> and temperature (R<sup>2</sup> = 0.09817, *p* < 0.05), and α and PAR (R<sup>2</sup> = 0.0779, *p* < 0.05) (Table 4).

Both elevated and ambient alkalinity *Corallina* spp. F<sub>v</sub>/F<sub>m</sub> remained relatively constant throughout the study period, decreasing by 6% and 11% from 7 to 27 February respectively (Fig. 4a). Elevated alkalinity *Corallina* spp. E<sub>k</sub> also remained relatively constant throughout the study period, only decreasing by 2% from the 7 to 27 February, whereas ambient alkalinity *Corallina* spp. E<sub>k</sub> decreased by 47% from 7 to 27 February (Fig. 4b). *Corallina* spp. rETR<sub>max</sub>

**Table 5** Results from linear regression analysis of (a) *Corallina* spp. NCR (μmol CaCO<sub>3</sub> gDW<sup>-1</sup> h<sup>-1</sup>), F<sub>v</sub>/F<sub>m</sub>, E<sub>k</sub>, α, and rETR<sub>max</sub> in relation to TA (μEq L<sup>-1</sup>), pH, temperature (°C), and PAR (μmol photons m<sup>-2</sup> s<sup>-1</sup>) and (b) *Corallina* spp. NCR (μmol CaCO<sub>3</sub> gDW<sup>-1</sup> h<sup>-1</sup>) in relation to *Corallina* spp. rETR<sub>max</sub>, α, E<sub>k</sub>, and F<sub>v</sub>/F<sub>m</sub>. Relationship explained by the regression (R<sup>2</sup>), overall significance (sig), and number of observations (N). Significant codes: \**p* < 0.05, \*\**p* < 0.01, \*\*\**p* < 0.001, ns = not significant

a)	TA			pH			Temperature			PAR		
	R <sup>2</sup>	sig	N	R <sup>2</sup>	sig	N	R <sup>2</sup>	sig	N	R <sup>2</sup>	sig	N
NCR	0.3998	***	106	0.1141	***	106	2 × 10 <sup>-5</sup>	ns	106	0.05	*	83
F <sub>v</sub> /F <sub>m</sub>	0.1563	**	56	0.0689	ns	56	0.05	ns	56	0.01	ns	56
E <sub>k</sub>	0.0039	ns	56	0.0039	ns	56	0.03	ns	56	1.43 × 10 <sup>-4</sup>	ns	56
rETR <sub>max</sub>	0.0058	ns	56	0.0203	ns	56	0.10	*	56	0.04	ns	56
α	0.0008	ns	56	0.0648	ns	56	0.05	ns	56	0.08	*	56
b)	rETR <sub>max</sub>			α			E <sub>k</sub>			F <sub>v</sub> /F <sub>m</sub>		
	R <sup>2</sup>	sig	N	R <sup>2</sup>	sig	N	R <sup>2</sup>	sig	N	R <sup>2</sup>	sig	N
NCR	0.0996	*	56	0.0814	*	56	0.004	ns	56	0.210	***	56



**Fig. 4** Average elevated alkalinity (black squares) and ambient alkalinity (empty circles) *Corallina* spp.  $F_v/F_m$  (a),  $E_k$  (b),  $rETR_{max}$  (c), and  $\alpha$  (d) over the study period. Error bars show standard error. All parameters are dimensionless

and  $\alpha$  saw similar decreases throughout the study period; elevated alkalinity *Corallina* spp.  $rETR_{max}$  and  $\alpha$  decreased by 67% and 55% respectively, and ambient alkalinity *Corallina* spp.  $rETR_{max}$  and  $\alpha$  decreased by 38% and 57% respectively (Fig. 4c, d). There was a positive linear relationship between NCR and both  $rETR_{max}$  ( $R^2 = 0.09212$ ,  $p < 0.05$ ) and  $F_v/F_m$  ( $R^2 = 0.213$ ,  $p < 0.001$ ) (Table 4).

## 4 Discussion

Results from this study show that increased TA can influence *Corallina* spp. physiology. *Corallina* spp. net calcification rate significantly increased by ~60% and  $CaCO_3$  content increased by ~3% when exposed to elevated alkalinity compared to the ambient alkalinity treatment. This is due to an increase in both light and dark calcification rates under increased TA. However, due to the small sample sizes, there was no significant difference between the alkalinity treatments for light and dark calcification rates. Other, non-statistically significant, physiology changes included *Corallina* spp. net primary productivity increasing and net respiration rates decreasing when exposed to elevated alkalinity compared to ambient alkalinity. There was no significant difference between the alkalinity treatments for *Corallina* spp.

photophysiological parameters. These results have important implications constraining the environmental impact and efficiency of NETs such as increasing ocean alkalinity.

#### 4.1 Calcification

The strongest regression relationship for net calcification rates (NCR) was with TA ( $R^2 = 0.3998$ ,  $p < 0.001$ ) suggesting that the higher rates of calcification for the elevated alkalinity treatment were due to the increase in TA. The increase in TA caused calcite  $\Omega_{\text{CaCO}_3}$  to increase by 114% resulting in *Corallina* spp. NCR to increase by ~60% and  $\text{CaCO}_3$  content to increase by ~3%. Higher  $\Omega_{\text{CaCO}_3}$  creates more favourable conditions for *Corallina* spp. to produce  $\text{CaCO}_3$ . This finding is consistent with that of Hofmann et al. (2012a) where *C. officinalis* growth rate and inorganic carbon content increased by ~50% and ~3%, respectively, when calcite  $\Omega_{\text{CaCO}_3}$  increased by 194% (due to a decrease in  $\text{pCO}_2$ ). A similar response was seen for a coral reef flat where the aragonite  $\Omega_{\text{CaCO}_3}$  increased by approximately 50% (due to increased TA) resulting in an increase of NCR by approximately 7% (Albright et al. 2016).

Contrary to this, Williamson et al. (2017) found that a 34.2% increase in calcite  $\Omega_{\text{CaCO}_3}$  (despite TA and  $\text{HCO}_3^-$  decreasing by 2.4% and 9.3% respectively) occurred with a ~65% decrease in *C. officinalis* light calcification rates. The increase in  $\Omega_{\text{CaCO}_3}$  was most likely caused by a decrease in  $\text{pCO}_2$  (~28.5%). This discrepancy between the investigations may be explained by their different methodologies. This study and the investigations by Hofmann et al. (2012a) and Albright et al. (2016) purposely altered the carbonate chemistry compared to Williamson et al. (2017) who did not. Instead, Williamson et al. (2017) investigated the response of *C. officinalis* to a tidal emersion. Williamson et al. (2017) concluded that factors such as temperature and light levels had the strongest influence on *C. officinalis* calcification rates, not the carbonate chemistry. Therefore, in an ex-situ environment where temperature and light levels were held constant, like this study, carbonate chemistry may have more influence over calcification rates.

In-situ light and dark calcification rate (CR) values from Williamson et al. (2017) are summarised and compared to values from this study in Table 6. The in-situ values are from *C. officinalis* in Combe Martin, North Devon, and were sampled during winter when in-situ temperature and PAR were most similar to the temperature and irradiance values of this study.

**Table 6** Comparison of *Corallina* spp. physiology (LCR = light CR ( $\mu\text{mol CaCO}_3 \text{ gDW}^{-1} \text{ h}^{-1}$ ), DCR = dark CR ( $\mu\text{mol CaCO}_3 \text{ gDW}^{-1} \text{ h}^{-1}$ ), NPP ( $\mu\text{mol DIC gDW}^{-1} \text{ h}^{-1}$ ), NR ( $\mu\text{mol DIC gDW}^{-1} \text{ h}^{-1}$ ),  $\text{rETR}_{\text{max}}$ ,  $\alpha$ ,  $E_k$ , and  $F_v/F_m$ ) to in-situ winter *C. officinalis* physiology. LCR, DCR, NPP, and NR values are the averages from week 1 and week 2

	In-situ		This study	
	Max	Min	Elevated	Ambient
LCR	4 <sup>a</sup>	2 <sup>a</sup>	12	9
DCR	-0.40 <sup>a</sup>	-0.25 <sup>a</sup>	2.29	-0.01
NPP	-15 <sup>a</sup>	-5 <sup>a</sup>	-12	-6
NR	5 <sup>a</sup>	5 <sup>a</sup>	-0.29	0.58
$\text{rETR}_{\text{max}}$	120 <sup>b</sup>	100 <sup>b</sup>	35	36
$\alpha$	0.11 <sup>b</sup>	0.1 <sup>b</sup>	0.13	0.13
$E_k$	800 <sup>b</sup>	700 <sup>b</sup>	287	271
$F_v/F_m$	0.3 <sup>b</sup>	0.2 <sup>b</sup>	0.68	0.69

<sup>a</sup> From Williamson et al. (2017)

<sup>b</sup> From Williamson et al. (2014)

Both elevated and ambient alkalinity treatment *Corallina* spp. light and dark CR were higher compared to the in-situ values. This could be explained by the higher TA values at Dunraven Bay (2694- $\mu\text{Eq L}^{-1}$ ) compared to North Devon ( $\sim 2300 \mu\text{Eq L}^{-1}$ ).

Negative values for calcification rates suggest that instead of calcification, dissolution occurred. Based on previous studies, as summarised in Table 6, this is not unheard of for *Corallina* spp. and can be explained by an increase in respiration occurring when dark. At the organism level, respiration can generate internal  $\text{CO}_2$  which lowers internal  $\Omega_{\text{CaCO}_3}$  and so can promote  $\text{CaCO}_3$  dissolution over calcification (Koch et al. 2013). However, dark dissolution (negative values), rather than calcification (positive values) only occurred for the ambient alkalinity treatment in week 1 (Fig. 3b). Dark calcification, rather than dissolution, has previously been documented for *Corallina* spp. (Williamson et al. 2017; Pentecost 1978; Lee and Carpenter 2001). Whether calcification or dissolution occurs is believed to be strongly related to the rock pool  $\Omega_{\text{CaCO}_3}$  (Williamson et al. 2017). In the elevated alkalinity treatments (and ambient alkalinity treatment in week 2),  $\Omega_{\text{CaCO}_3}$  was higher, so despite internal  $\text{CO}_2$  increasing due to respiration, the water  $\Omega_{\text{CaCO}_3}$  would have remained high enough to promote calcification rather than dissolution. This is supported by the substantial increases between elevated and ambient alkalinity treatment dark CR for both week 1 and week 2 (Fig. 3b).

## 4.2 Photophysiology

The relatively constant values in  $F_v/F_m$  values suggest little decline in *Corallina* spp. “health” throughout the experiment. However, there was a reduction in *Corallina* spp.  $\text{rETR}_{\text{max}}$ ,  $\alpha$ , and  $E_k$  for both the elevated and ambient alkalinity treatments. This suggests less effective photosynthesis at the end of the experiment compared to the start, which may be expected for a multi-week ex-situ experiment.

In-situ photophysiology values from Williamson et al. (2014) were used for comparison to the ex-situ values from this study (Table 6). Williamson et al. (2014) investigated the photophysiology of *C. officinalis* in Combe Martin, North Devon, during winter 2013 (when in-situ temperature and PAR were most similar to the temperature and irradiance values of this study). However, caution should be taken with comparing the photophysiology values as the weather and light conditions would not be exactly the same as those at Dunraven Bay at the time of sampling of this study. For both the elevated and ambient alkalinity treatments, *Corallina* spp.  $\text{rETR}_{\text{max}}$  and  $E_k$ 's values were lower than in-situ *C. officinalis*  $\text{rETR}_{\text{max}}$  and  $E_k$  values. Further, values of  $\alpha$  from this study were slightly higher than the in-situ values (Table 6). Therefore,  $\alpha$  is relatively higher compared to  $\text{rETR}_{\text{max}}$  and  $E_k$ , which suggests that the *Corallina* spp. in this experiment have become acclimated to low light (Perkins et al. 2016). This is likely due to the lower irradiance values (100–200  $\mu\text{mol photons m}^{-2}$ ) of the experimental set-up compared to typical values at Dunraven Bay (150–740  $\mu\text{mol photons m}^{-2}$ ).

There was no statistically significant difference in *Corallina* spp.  $\text{rETR}_{\text{max}}$ ,  $\alpha$ ,  $E_k$ , and  $F_v/F_m$  between the elevated and ambient alkalinity treatments (Table 3). However, there was a significant positive linear relationship between  $F_v/F_m$  and TA ( $R^2 = 0.1563$ ,  $p < 0.01$ ) suggesting that increasing TA could have influenced *Corallina* spp. photosynthetic rates. However, because the *Corallina* spp. are low-light acclimated (relatively low  $\text{rETR}_{\text{max}}$  compared to  $\alpha$ ),

the low-light levels may have had a stronger influence on the photophysiology than alkalinity. This could partly explain why there was no similar increase in  $rETR_{max}$ ,  $\alpha$ , and  $E_k$  when TA was increased.

### 4.3 Primary productivity and respiration

Despite there being very little difference in photophysiology between alkalinity treatments, *Corallina* spp. primary productivity rates (NPP) did increase under elevated alkalinity. However, a note of caution is due here since the chambers were an “open system” and so DIC would have been lost as  $CO_2$  through gas-solution diffusion. Therefore, primary productivity was also estimated using the  $CaCO_3$  to  $C_{org}$  content ratio of the *Corallina* spp. samples. The primary productivity rates estimated this way were approximately ten times larger than the NPP rates estimated using Eq. 2 (once converted to  $mg\ C\ gDW^{-1}\ h^{-1}$  from  $\mu mol\ DIC\ gDW^{-1}\ h^{-1}$ ). This is most likely due to buffering of  $CO_2$  from ambient air during the experiment which would mean a smaller change in pH than what would otherwise occur in a closed system. However, both the primary productivity rates estimated from the  $CaCO_3$  to  $C_{org}$  content ratio and from Eq. 2 were higher for the elevated alkalinity treatment compared to the ambient alkalinity treatment (30% higher for Eq. 2 calculated NPP rates and 52% for the  $CaCO_3$  to  $C_{org}$  content ratio calculated NPP rates), therefore, suggesting that increasing TA can increase primary productivity.

Because both calcification and photosynthesis take place in the cell wall, there is a strong relationship between light calcification and photosynthesis. During photosynthesis, internal  $CO_2$  decreases causing  $\Omega_{CaCO_3}$  to increase and so promotes calcification (Borowitzka 1982; Koch et al. 2013). This increase in photosynthesis (NPP rather than photophysiology) under elevated alkalinity could partly explain why *Corallina* spp. net calcification also increased under increased TA. Strong correlations between *C. officinalis* photosynthesis and calcification have previously been reported by Williamson et al. (2017) and Pentecost (1978) with  $R^2$  values of 0.65 and 0.886 respectively.

Increasing TA resulted in a greater increase in dark calcification rate (~200% increase from ambient to elevated) compared to light calcification (40% increase from ambient to elevated). Therefore, implying that the increase in *Corallina* spp. NCR was due to higher  $\Omega_{CaCO_3}$  (from increasing TA) preventing dissolution occurring at night (increased dark calcification) rather than an increase in photosynthesis removing  $CO_2$  in the day causing an increase in  $\Omega_{CaCO_3}$  (increased light calcification). Supporting this, in-situ *C. officinalis* primary productivity rates were slightly less than the *Corallina* spp. primary productivity rates in this study for both the elevated and ambient alkalinity treatments (Table 6). This suggests that *Corallina* spp. was not fully productive in this experimental set-up despite having higher calcification rates compared to in-situ values.

The near zero and slightly negative values of *Corallina* spp. respiration rates (NR) are unusual. Respiration produces  $CO_2$ ; therefore, DIC would be expected to increase (Eq. 4) and positive values for NR were expected. The decrease in pH which occurred after the *Corallina* spp. were exposed to dark conditions for 6 h also implies that  $CO_2$  was being produced due to respiration. However, because the respiration and primary productivity experiments took place in an open system, they can only give an estimation of NR and

NPP values and so these results need to be interpreted with caution.

$$\text{DIC} = \text{CO}_2 + \text{HCO}_3^{2-} + \text{CO}_3^{-} \quad (4)$$

#### 4.4 Potential for increasing ocean alkalinity as a negative emissions technology and for ocean acidification mitigation

Increasing TA did not appear to be detrimental for *Corallina* spp. with respect to calcification or photosynthesis. Based on these findings, solely for *Corallina* spp. and hence not fully representative of the marine coastal environment, increasing TA (and  $\Omega_{\text{CaCO}_3}$ ) could be used to alleviate some of the impacts of ocean acidification. However, if artificially increasing ocean alkalinity (AOA) increases  $\Omega_{\text{CaCO}_3}$  to beyond the pre-industrial maximum, there still could be detrimental impacts. For example, Hofmann et al. (2012b) found that increased calcification rates were associated with lower growth rates and lower protein levels which could limit population growth.

A potential downfall to AOA leading to increased calcification rates is the potential increase in oceanic  $\text{pCO}_2$  which would eventually exchange with the atmosphere and therefore, decrease the efficiency of the oceanic sink for atmospheric  $\text{CO}_2$ . However, this study has shown that for *Corallina* spp., there was also an increase in primary productivity (which uses up of  $\text{CO}_2$ ) which suggests that *Corallina* spp. could still be an overall sink for atmospheric  $\text{CO}_2$ , therefore, suggesting that AOA would still be an effective method of reducing atmospheric  $\text{CO}_2$  despite an increase in carbonate production. However, only one species was studied, and future investigations should look at the response to different species of marine calcifiers to see if the same results occur.

Biogeochemical modelling studies suggest that using AOA as the sole response to mitigating carbon emissions would increase global surface water calcite  $\Omega_{\text{CaCO}_3}$  to between 6 and 7.5 (Paquay and Zeebe 2013; Ferrer-González and Ilyina 2016; Ilyina et al. 2013). This is lower than the increase in  $\Omega_{\text{CaCO}_3}$  in this study (calcite  $\Omega_{\text{CaCO}_3} = \sim 9$ ). However, modelling studies have suggested that if TA is added to smaller more specific regions (e.g., coastal seas) rather than homogeneously across the whole ocean, the changes in  $\Omega_{\text{CaCO}_3}$  could be much greater in these regions. Feng et al. (2017) predict that coastal aragonite  $\Omega_{\text{CaCO}_3}$  could increase to between 7 and 16 if TA is added continuously. This is much greater than the increase in this study (aragonite  $\Omega_{\text{CaCO}_3} = 5.6$ ). Therefore, if localised AOA was to be deployed, there may be global increases in carbonate production similar or even higher than that which occurred in this study. This suggests that the magnitude of the increase in calcification rates would depend on how and where TA was added. For example, localised TA increases may lead to very large changes in  $\Omega_{\text{CaCO}_3}$ , potentially leading to large increases in carbonate production producing  $\text{CO}_2$  and so reducing the efficiency of AOA as a NET. This may not be seen if TA is increased homogeneously across the open ocean resulting in a reduced increase in  $\Omega_{\text{CaCO}_3}$ . Therefore, further research into how calcification and primary productivity respond to different TA manipulation scenarios (different  $\Omega_{\text{CaCO}_3}$ ) is needed.

## 5 Conclusions

This study set out to investigate the biological and environmental impact of increasing ocean alkalinity as a NET. This investigation has shown that increasing TA did not significantly affect *Corallina* spp. respiration or photophysiology but did cause a significant increase in calcification rates (NCR increased by 60% compared to a control) and a substantial, if not

significant, increase in primary productivity. The increase in carbonate production appears to be due to both increased  $\Omega_{\text{CaCO}_3}$  preventing dissolution occurring at night and, to a lesser extent, an increase in photosynthesis leading to an increase in light calcification. The results from this study suggest that artificially increasing ocean alkalinity as a NET may not be detrimental to the marine calcifiers such as *Corallina* spp. and that it could be used to mitigate against the effects of future ocean acidification. Therefore, increasing ocean alkalinity still appears to be an effective method at removing atmospheric  $\text{CO}_2$  to achieve negative emissions. To develop a more in-depth understanding of the environmental response to increasing ocean alkalinity as a NET, additional studies are needed to investigate the impact of increasing TA on other marine calcifiers under different TA addition scenarios.

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