REVIEW

Ocean acidification effects on calcifying macroalgae

Laurie C. Hofmann*, Kai Bischof

Marine Botany, Bremen Marine Ecology Centre for Research and Education, University of Bremen, Leobener Str. NW2, 28359 Bremen, Germany

ABSTRACT: Since the Industrial Revolution, the partial pressure of carbon dioxide (pCO_2) has been increasing and global ocean surface waters have absorbed 30% of the anthropogenic CO_2 released into the atmosphere. An increase in pCO_2 in surface ocean waters causes an increase in bicarbonate ions (HCO_3^-) and protons (H^+) and a decrease in carbonate ions (CO_3^{2-}), thereby decreasing the pH and the saturation state of the seawater with respect to CO_3^{2-}. These changes in ocean chemistry (termed ocean acidification) are expected to have negative impacts on marine calcifying organisms. Because calcifying marine primary producers are important to the carbon cycle and rocky shore habitat structure and stability, investigating how they will respond to future oceanic pCO_2 levels is a relevant and important topic of research. Due to a recent strong increase in the number of studies investigating the responses of calcifying marine macroalgae to elevated pCO_2, this review aims to present the state of knowledge on the response of calcifying macroalgae to ocean acidification alone and in combination with global and local stressors. We discuss the physiological responses of calcifying macroalgae to elevated pCO_2 within the contexts biogeography, taxonomy, and calcification mechanisms. Generally, coralline algae that deposit high-Mg calcite are most susceptible to high pCO_2, and polar species are particularly at risk. However, some dolomite-depositing species may be able to acclimate to high pCO_2. Calcifiers generally show sensitivity to overgrowth and outcompetition by noncalcifying algae when grown under elevated CO_2 conditions, and this trend could be amplified under conditions of high inorganic nutrients. However, it still remains unknown whether or not calcifiers will be able to adapt to their rapidly changing environments. We discuss the lack of research on this topic, and provide some suggestions for how this knowledge gap can be filled by future research.

KEY WORDS: Ocean acidification · Calcification · Macroalgae · Benthic communities · Eutrophication

INTRODUCTION

The purpose of this review is to discuss the state-of-the-art of research that has been conducted on calcifying macroalgae within the context of ocean acidification. Calcifying macroalgae serve important ecological functions in the marine environment, and have shown variable responses to CO_2-perturbation experiments, but are rare in naturally CO_2-enriched environments (Hall-Spencer et al. 2008, Fabricius et al. 2011, Porzi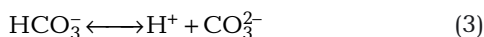o et al. 2011). Although the effects of global change on macroalgae have been thoroughly reviewed, specific attention to ocean acidification effects on calcifying macroalgae has been relatively brief (Koch et al. 2013). In order to gain a perspective on what factors control the sensitivity of calcifying macroalgae to ocean acidification, we discuss the reported physiological responses of calcifying macroalgae to elevated partial pressure of carbon dioxide (pCO_2) within the contexts biogeography, taxonomy and calcification mechanisms, and highlight the similar patterns of competitive interactions that occur be-

*Corresponding author: l.hofmann@uni-bremen.de

tween calcifiers and noncalcifiers under elevated CO_2 regardless of species and latitude. We first provide an introduction to the chemistry of ocean acidification, how it relates to calcification in the marine environment, and how the link between calcification and photosynthesis is an important factor influencing the response of calcifying macroalgae to elevated pCO_2. A short outline of calcification mechanisms among the calcifying macroalgae is provided, followed by a discussion of the literature and a meta-analysis of the physiological responses of calcifying macroalgae to ocean acidification within the context of biogeography and skeletal mineralogy. We discuss the differences in responses of calcifying macroalgae to elevated pCO_2 in polar (north of 66° N and south of 66° S), temperate (23 to 66° N and 23 to 66° S), Mediterranean and tropical (23° N to 23° S) regions. We also discuss knowledge gaps that should be filled in future CO_2-perturbation studies dealing with calcifying macroalgae.

OCEAN ACIDIFICATION AND ITS EFFECT ON OCEAN CHEMISTRY

Since the Industrial Revolution, the surface waters of the global oceans have absorbed one-third of the anthropogenic CO_2 released into the atmosphere (Siegenthaler & Sarmiento 1993, Sabine et al. 2004, Sabine & Feely 2007). As global CO_2 emissions continue to rise, the surface ocean waters will continue to absorb more CO_2. The dissolution of more CO_2 into ocean surface waters alters seawater chemistry by decreasing the pH and carbonate ion (CO_3^{2-}) concentration, which can have negative consequences for all marine organisms living in the surface layers as well as those living in deep layers due to potential changes in carbon cycling and shoaling of the carbonate saturation horizon. As CO_2 dissolves into surface oceans, it reacts with seawater to produce carbonic acid (Eq. 1), which dissociates into bicarbonate ions (HCO_3^-) and protons (H^+) (Eq. 2), resulting in a lower pH (hence the term ocean acidification). As a consequence, CO_3^{2-} ions react with the extra protons to produce more HCO_3^- ions that buffer the decrease in pH (Eq. 3):

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \qquad (1)$$

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \qquad (2)$$

$$HCO_3^- \longleftrightarrow H^+ + CO_3^{2-} \qquad (3)$$

Therefore the seawater becomes undersaturated with carbonate ions, which are the building blocks for calcium carbonate ($CaCO_3$) shells and skeletons of marine organisms.

CALCIFICATION IN THE MARINE ENVIRONMENT

Many marine organisms produce $CaCO_3$ skeletons and shells, including mollusks, echinoderms, corals and a variety of algae. Among the calcifying macroalgae, $CaCO_3$ is precipitated in 3 crystal forms: aragonite, calcite and magnesium calcite. Due to different structural characteristics, each crystal form has a different solubility in seawater, which is defined by Eq. (4):

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] \qquad (4)$$

The solubility product (K_{sp}) is different for each crystal form, and, for magnesium calcite, depends on the ratio of magnesium to calcium ions. Calcite crystals have a rhomboidal shape and this mineral is the least soluble form of $CaCO_3$. However, when the calcium (Ca^{2+}) ions are replaced by magnesium (Mg^{2+}) ions and the ratio of Mg:Ca becomes greater than 0.04, the $CaCO_3$ mineral is considered high-Mg calcite, which is the most soluble $CaCO_3$ crystal in seawater. Another form of calcite, dolomite ($Mg_{0.5}Ca_{0.5}[CO_3]$), is deposited along the cell rims in some tropical calcifying macroalgae and is less soluble in seawater than high-Mg calcite (Nash et al. 2012, Diaz-Pulido et al. 2014). Aragonite crystals have an orthorhombic shape, and are more soluble in seawater than calcite, but less soluble than high-Mg calcite. Some calcifying marine macroalgae deposit only aragonite or only calcite, while others can deposit both crystal forms under certain conditions (Ries et al. 2009). Furthermore, some are able to alter their Mg:Ca ratios depending on abiotic factors such as temperature, seawater carbonate saturation state and light (Andersson et al. 2008, Ries 2011a). The seawater saturation state of a particular mineral can be calculated by applying the parameters of Eq. (4) to Eq. (5), which relates the calcium and carbonate ion products to the solubility product expected when seawater is in equilibrium with the carbonate mineral:

$$\Omega = [Ca^{2+}][CO_3^{2-}]/K_{sp} \qquad (5)$$

When $\Omega = 1$, seawater is in equilibrium with the carbonate mineral, while $\Omega > 1$ indicates supersaturation and $\Omega < 1$ indicates undersaturation of the seawater with respect to the carbonate mineral. Because the saturation state of carbonate minerals is affected by increasing seawater CO_2 concentration, and the degree of change differs with latitude, our discussion of the effects of CO_2 on calcifying macroalgae has been separated by latitude (polar, temperate, and tropical) in this review.

Due to the ecological importance of marine calcifying organisms in marine ecosystems and their contribution to coral reef accretion, sediment production, carbon cycling and habitat formation (see Nelson 2009), it is important to understand how they will respond to increasing surface ocean CO_2 concentrations, and how these responses differ among phylogenetic groups and latitudes. In the past few decades, there has been a large increase in ocean acidification research. In 2009, 165 peer-reviewed research articles were listed with the key word ocean acidification in the Web of Science, compared to 583 in 2013. Despite this increase in knowledge, there is no consensus as to how marine calcifiers as a whole will be affected by the expected changes in ocean chemistry, as different organisms have been shown to respond differently. Some are sensitive to elevated CO_2-induced low pH (e.g. Langdon et al. 2000, 2003, Leclercq et al. 2000, Guinotte et al. 2003, Jokiel et al. 2008, Andersson et al. 2009, Albright et al. 2010, Albright 2011) while others have shown mixed responses (Andersson et al. 2009, Ries 2009, Fabricius et al. 2011, Rodolofo-Metalpa et al. 2011, McCulloch et al. 2012). Therefore, this review aims to summarize the known impacts of elevated pCO_2 on calcifying marine macroalgae, and to identify the major patterns affecting their responses, such as their distribution, calcification mechanisms, and phylogeny. However, before summarizing the effects of ocean acidification on calcifying marine algae, a short introduction to the relationship between calcification and photosynthesis and calcification mechanisms among macroalgae is presented.

CALCIFICATION IN MACROALGAE

While calcification is expected to decline in macroalgae under elevated CO_2 due to undersaturation of calcium carbonate, the substrate for carbon fixation in photosynthesis is CO_2, and therefore a higher CO_2 concentration might be expected to stimulate photosynthesis. However, noncalcifying macroalgae have shown a variety of responses when grown under elevated pCO_2, indicating that some are not necessarily carbon-limited at the ambient oceanic CO_2 concentration or that they are able to down-regulate their carbon-concentrating mechanisms (CCMs) (Gao et al. 1991, 1993, García-Sánchez et al. 1994, Israel et al. 1999, Kübler et al. 1999, Zou 2005). Although the HCO_3^- concentration in seawater is approximately 200 times that of the CO_2 concentration at the ambient oceanic pH of about 8.1, many macroalgae have

the ability to convert HCO_3^- to CO_2 externally via the enzyme carbonic anhydrase (CA) or can actively transport HCO_3^- across their cell membranes, which is then converted to CO_2 inside the cell to be used for photosynthesis (Raven 1997, 2003, Sültemeyer 1998, Moroney & Somanchi 1999, Raven et al. 2012). Such CCMs concentrate dissolved inorganic carbon inside the cell at the site of Ribulose-1,5-bisphosphate carboxylase oxygenase (RubisCO), the enzyme responsible for carbon fixation. These mechanisms reduce the competition of oxygen for the enzyme by increasing the intracellular $CO_2{:}O_2$ ratio, thereby making it more efficient by reducing photorespiration (see Raven 1997, 2003, Raven et al. 2012 for reviews). CCMs have been reported in many macroalgal species, and are well documented and described among the green algae (Chlorophyta), and many of the red algae (Rhodophyta) and brown algae (Phaeophyta) also contain CCMs (Axelsson & Uusitalo 1988, Drechsler & Beer 1991, Axelsson et al. 1995, Mercado et al. 1998, Moulin et al. 2011, Raven et al. 2012). Algae that do not contain efficient CCMs, particularly those growing at depth, could be more stimulated by elevated pCO_2 than those that contain highly efficient CCMs, although algae that use HCO_3^- could also benefit by down-regulating their CCMs under elevated pCO_2 because such CCMs have high energy demands (see Wu et al. 2008). Differences in carbon uptake mechanisms among the calcifying macroalgae certainly plays an important role in their responses to elevated pCO_2 (Cornwall et al. 2012).

The relationship between photosynthesis and calcification in calcifying algae is complex and not completely understood. Photosynthesis has been shown to stimulate calcification rates in macroalgae (Borowitzka & Larkum 1976a,b, Borowitzka 1981, 1984). The mechanism of stimulation is thought to be that the consumption of CO_2 by photosynthesis increases the pH of the surrounding seawater, thereby increasing the saturation state of CO_3^{2-} and favoring $CaCO_3$ precipitation (Digby 1977a,b). Inversely, calcification may also stimulate photosynthesis by releasing CO_2 (McConnaughey 1991, McConnaughey & Falk 1991). However, the so-called 'carbon dioxide utilization theory' proposed by Digby (1977a,b) does not explain why some algae do not calcify, as all algae take up CO_2 via photosynthesis and subsequently increase the extracellular CO_3^{2-} saturation state. In coralline algae, specific cell wall polysaccharides produced by these algae are thought to be nucleation sites for $CaCO_3$ deposition (Borowitzka 1984, Bilan & Usov 2001). It is hypothesized that noncalcifying algae

produce CaCO₃ nucleation inhibitors (for example, herbivore deterrent phlorotannins), which would explain why they do not calcify (Borowitzka 1984, Borowitzka & Larkum 1987). The mechanisms of calcification in the 3 macroalgal groups are discussed briefly below.

Rhodophytes

The calcifying rhodophytes are a diverse group of organisms. Several genera within the orders Nemaliales and Nemastomatales deposit aragonite, while the Corallinales are the only calcifying macroalgae that deposit the highly soluble high-Mg calcite. The former deposit aragonite crystals on their cell or thallus surface only, while the latter deposit both on the cell surface and intercellularly in the cell walls (Littler 1976). An organic matrix in the cell wall has been shown to provide nucleation sites for calcification (Borowitzka 1984, Bilan & Usov 2001). As the cell walls are in contact with the external seawater, the high-Mg calcite skeleton of coralline algae may be highly susceptible to dissolution under ocean acidification conditions.

Chlorophytes

In the calcifying chlorophytes, the location of the calcification process within the alga is unique. The calcifying chlorophyte algae in the genus *Halimeda* deposit aragonite crystals on the surface of intercellular spaces between specialized structures called utricles. The chemical environment between the utricles is semi-separated from the external seawater, and therefore the algae have biological control over this internal environment via photosynthetic and respiratory processes (Borowitzka & Larkum 1977, Lee & Carpenter 2001). In the genera *Udotea*, *Penicillus*, and *Rhipocephalus*, a sheath surrounding the cell wall is formed, which is thought to facilitate calcification by creating a CO₂ diffusion barrier (Borowitzka 1984). The combination of having an aragonite skeleton and a semi-isolated calcification locus suggests that these algae might be less susceptible to ocean acidification than the red coralline algae.

Phaeophyceae

Only 2 genera within the Phaeophyceae are known to calcify. *Padina* spp. form lightly calcified fronds

made of aragonite. The aragonite crystals are deposited externally in a semi-enclosed space formed by infolding of the margin of the thalli (Okazaki et al. 1986). *Newhousia imbricata* is a calcified encrusting species that deposits mostly aragonite both extracellularly between frond layers and intercellularly within the cell wall matrices (Kraft et al. 2004).

The physiological and ecological function of calcification in macroalgae is not well understood. It is suggested that calcification provides structural support against wave action, protection against high light and defense against herbivory (Littler 1976), but the latter hypothesis is not strongly supported. Steneck (1983) suggests that calcifying macroalgae were prevalent before the most damaging feeding mechanisms (sea urchin teeth and parrotfish beaks) evolved, and studies have shown that some feeding generalists will eat calcified tissue (Pennings & Svedberg 1993, Hay et al. 1994). An alternative hypothesis is that calcification serves as a proton source for nutrient and HCO₃⁻ uptake, which provides a competitive advantage over noncalcifiers in oligotrophic conditions (McConnaughey & Whelan 1997). A combination of these factors, in addition to the production of antiherbivore secondary metabolites, most likely provide calcifiers with synergistic defenses against herbivory (Hay et al. 1994), structural stability and a physiological advantage over noncalcifiers under nutrient limiting conditions. Under elevated pCO₂, these advantages for calcifying macroalgae may be at risk and could result in shifting the ecological relationships between calcifiers and noncalcifiers.

EFFECTS OF OCEAN ACIDIFICATION ON CALCIFICATION IN MARINE MACROALGAE

The effects of ocean acidification on calcification, photosynthesis and respiration in calcifying macroalgae are summarized in Table 1. Only experiments where pH was experimentally manipulated using CO₂ addition (rather than acid addition) are included in the summary, in an effort to eliminate studies where the carbonate chemistry did not mirror that expected for future surface oceans. In general, photosynthetic rates of calcifying macroalgae are not stimulated by elevated CO₂ conditions. The majority of studies have shown a decrease or no change in photosynthetic rates of calcifying macroalgae under elevated CO₂ conditions (Table 1); however, some recent studies have shown the ability of *Lithophyllum* spp. to acclimate to slow rates of ocean acidification (Table 1). Below, we provide an overview of the

Table 1. Summary of experimental pCO_2 effects on calcification (G) photosynthesis (PS) and respiration (R) in single species of calcifying macroalgae from different latitudes (P = polar, T = temperate, M = Mediterranean, Tr = tropical) and depths (T = tidepools, I = intertidal, S = subtidal) and presenting different morphologies (B = branched, CCA = crustose calcifying algae) and skeletal mineralogies (C = high-Mg calcite, A = aragonite, D = dolomite). The table is separated into 3 groups based on latitude (P, T, Tr) by dotted lines. Mediterranean species are included in the temperate category. Light intensity is reported as µmol photons m^{-2} s^{-1} unless otherwise stated. The responses of G, PS, and R are reported in relation to the control (ambient) CO_2 conditions, which are always listed in the first row for each species. Calcification responses are defined as an increase (↑), decrease (↓), no change (=), or parabolic with respect to CO_2 (p). Net dissolution was either observed (Y) or not observed (N) during the experiment. Some factors/parameters were not measured (–) or not reported (nr)

Species	Lat. (P, T, M, Tr)	Depth (T, I, S)	Morphology (CCA, B)	Skeletal minera-logy	pH	CO_2 (ppm)	$\Omega_{aragonite}$	Light intens.	Time of exp. to CO_2 (d)	G	Net dissol. (Y/N)	PS	R	Additional responses	Source
Lithothamnion glaciale	P	S	CCA	C	8.06	385	2.0	6.8	14	→	N	–	–		Büdenbender et al. (2011)
					7.74	883	1.1	6.8	14	→	N	–	–		
					7.7	989	1.0	6.8	14	→	N	–	–		
					7.52	1573	0.7	6.8	14	→	Y	–	–		
					8.07	388	1.9	0	14		Y	–	–		
					7.82	754	1.2	0	14	→	Y	–	–		
					7.72	958	1.0	0	14	→	Y	–	–		
					7.53	1563	0.7	0	14	→	Y	–	–		
Coralina pilulifera	T	I	B	C	8.2	350	nr	30	1	→					Gao et al. (1993)
					7.6	1600	nr								
Coralina elongata	T	T	B	C	8.09	362	3.1	30	21		N			Mg:Ca ratio lower in	Egilsdottir et al. (2012)
					7.94	547	2.3			=	Y (dark)	→	=	new structures grown	
					7.81	770	1.8			=	Y (dark)	=	=	under elevated CO_2	
					7.72	977	1.5			=	Y (dark)	=	=		
Coralina elongata	T	T	B	C	8.01	450	2.41	30	30			→			Noisette et al. (2013)
					7.88	637	1.88			=	N	=	=		
					7.80	770	1.58			=	N	=	=		
					7.70	1002	1.2930			=	Y (dark)	=	=		
Coralina officinalis	T	I	B	C	8.3	384	7.2	50	28	–	–	–	–	Growth decreased,	Hofmann et al. (2012b)
					7.84	1313	3.0			–	–	=	=	inorganic material decreased,	
					7.67	1939	2.0			–	–	=	=	P_{max} decreased	
Coralina officinalis	T	I	B	C	8.2	–	nr	50	14	–	–	←	=	$CaCO_3$ content decreased	Yildiz et al. (2013)
					7.7	–	nr			–	–				
Bossiella orbigniana	T	S	B	C	8.34	170	nr	5 mW cm^{-2}	0.08	p	N	–	–	Maximum calcification	Smith & Roth (1979)
					7.91	420	nr			p	N	–	–	rate at 1300 µatm CO_2	
					7.55	1300	nr			p	N	–	–		
					7.38	2400	nr			p	N	–	–		
					6.97	6900	nr			p	N	–	–		
					6.65	14600	nr			p	N	–	–		
					6.28	31200	nr			p	N	–	–		
Lithophyllum cabiochae	M	S	CCA	C	8.08	397	nr	6–35	365	↓/=	N	–	–	Short-term decrease in	Martin & Gattuso (2009)
					7.87	703	nr			↓/=	N	–	–	calcification followed by acclimation	
Lithophyllum cabiochae	M	S	CCA	C	8.01	384–424	3.0–3.8	natural	365	↑/=	–	→	=	Calcification increased only	Martin et al. (2013)
					7.87	693–714	2.0–2.7							in the summer	
Lithophyllum incrustans	M	I	CCA	C	8.2	370	nr	nr		–	–	–	–	Reproduction and growth	Cumani et al. (2010)
					8	550	nr			–	–	–	–	decreased	
					7.8	760	nr			–	–	–	–		

Table 1 (continued)

Species	Lat. (P, T, M, Tr)	Depth (T, L, S)	Morphology (CCA, B)	Skeletal mineralogy	pH	CO2 (ppm)	$\Omega_{aragonite}$	Light intens.	Time of exp. to CO2 (d)	G	Net dissol. (Y/N)	PS	R	Additional responses	Source
Lithophyllum incrustans	T	I	CCA	C	8.01; 7.88; 7.80; 7.70	450; 637; 770; 1002	2.41; 1.88; 1.58; 1.2930	30	30	=; →; →	Y (dark); Y (dark); Y (dark); Y (dark)	=; =; =	=; ←; ←	Higher occurrence of bleaching under high pCO2	Noisette et al. (2013)
Lithothamnion corallioides	T	S	CCA	C	8.01; 7.88; 7.80; 7.70	450; 637; 770; 1002	2.41; 1.88; 1.58; 1.2930	30	30	=; →; →	N; Y (dark); Y (dark)	=; =; =	=; →; =		Noisette et al. (2013)
Lithothamnion glaciale	P/T	S	CCA	C	8.03; 7.9; 7.81; 7.72	422; 589; 755; 1118	1.8; 1.3; 1.1; 1.0	20	90	–; –; –; –	–; –; –; –	–; –; –; –	–; –; –; –	Cell wall thickness, cell density, and growth decreased	Ragazzola et al. (2012)
Lithothamnion glaciale	P/T	S	CCA	C	8.18; 7.70	498; 1081	3.0; 1.67	90	80	←	N; Y	=	–; =	Exposure to abrupt change in pCO2 resulted in skeletal weakness	Kamenos et al. (2013)
Porolithon onkodes	Tr	S	CCA	D	8.00–8.4; 7.85–7.95; 7.60–7.70	135–460; 520–705; 1010–1350	3.3–6.6; 2.5–3.2; 1.5–2.0	700–1200	56	→; →	N; N; Y	→; →	=; =	Algae exposed to high pCO2 and high irradiance experienced bleaching	Anthony et al. (2008)
Porolithon onkodes	Tr	S	CCA	D	8.04; 7.86; 7.87	400; 660; 400–660	3.7–3.8; 2.7–2.8; 2.8	600	14	→; →	N; N; N	=; →	=; =	Algae from habitat with variable pCO2 less sensitive to variable pCO2 treatment (400–660 µatm)	Johnson et al. (2014)
Neogoniolithon sp.	Tr	nr	CCA	C	8.19; 8.05; 7.91; 7.49	359; 526; 802; 2593	3.1; 2.4; 1.8; 0.9	426 W m^{-2}	60	p; p; p; p	N; N; N; N			Mg:Ca ratio decreased	Ries et al. (2009), Ries et al. (2011a)
Hydrolithon sp.	Tr	S	CCA	C/D	8.1; 7.8	405; 811	4.0; 2.0	150; 150	5; 5	→	N; Y	=	=	Calcification not affected after 1 h, but decreased after 5 d	Semesi et al. (2009)
Hydrolithon onkodes	Tr	S	CCA	D	8.01; 7.95; 7.76	420; 530; 830	nr; nr; nr	336	21	p; p; p	–; –; –	–; –; –	–; –; –	Calcification highest at 530 µatm CO2	Johnson & Carpenter (2012)
Hydrolithon onkodes	Tr	S	CCA	D	8.18; 8.04; 7.94; 7.81; 7.7; 7.41	276; 385; 543; 740; 1036; 2072	4.6; 3.6; 3.0; 2.3; 1.9; 1.1	700	14	=; =; →; →; →	N; N; N; N; N; N	–; –; –; –; –; –	–; –; –; –; –; –		Comeau et al. (2013)

Table 1 (continued)

Species	Lat. (P, T, M, Tr)	Depth (T, I, S)	Morphology (CCA, B)	Skeletal mineralogy	pH	CO$_2$ (ppm)	$\Omega_{\text{aragonite}}$	Light intens.	Time of exp. to CO$_2$ (d)	G	Net dissol. (Y/N)	PS	R	Additional responses	Source
Lithophyllum flavescens	Tr	S	CCA	C	8.18	276	4.6	700	14	→	N	–	–		Comeau et al. (2013)
					8.04	385	3.6				N	–	–		
					7.94	543	3.0			→	N	–	–		
					7.81	740	2.3			=	N	–	–		
					7.7	1036	1.9			=	N	–	–		
					7.41	2072	1.1			→	N	–	–		
Coralina sessilis	Tr	I	B	C	8.4	382	nr	985–6779 kJ m^{-2}	30	→	–	→	–		Gao & Zheng (2010)
					7.9	971	nr			→	–	–	–		
Halimeda opuntia	Tr	nr	B	A	8.1	nr	nr	nr	21	–	–	–	–	Smaller, denser aragonite crystals	Robbins et al. (2009)
					7.5	nr	nr			–	–	–	–		
Halimeda tuna	Tr	nr	B	A	8.1	nr	nr	nr	21	–	–	–	–	Smaller, denser aragonite crystals	Robbins et al. (2009)
					7.5	nr	nr			–	–	–	–		
Halimeda incrassata	Tr	nr	B	A	8.19	359	3.1	426 W m^{-2}	60	p	N	–	–		Ries et al. (2009), Ries et al. (2011a)
					8.05	526	2.4			p	N	–	–		
					7.91	802	1.8			p	N	–	–		
					7.49	2593	0.9			p	N	–	–		
Halimeda opuntia	Tr	S	B	A	8	440	2.5	150	14	→	N				Price et al. (2011)
					7.7	946	1.4			→	Y	→			
Halimeda taenicola	Tr	S	B	A	8	440	2.5	150	14	→	N	=			Price et al. (2011)
					7.7	946	1.4			→	N				
Halimeda macroloba	Tr	S	B	A	8.1	318	4.0	300	35	=	N	→	–		Sinutok et al. (2011)
					7.9	660	3.3			=	N	→	–		
					7.7	1066	2.1			=	N	→	–		
					7.4	2438	1.2				Y		–		
Halimeda cylindracea	Tr	S	B	A	8.1	318	4.0	300	35	=	N	←	–		Sinutok et al. (2011)
					7.9	660	3.3			→	N	→	–		
					7.7	1066	2.1			→	Y	→	–		
					7.4	2438	1.2				Y		–		
Halimeda macroloba	Tr	S	B	A	8.18	276	4.6	700	14	=	N	–	–		Comeau et al. (2013)
					8.04	385	3.6			=	N	–	–		
					7.94	543	3.0			=	N	–	–		
					7.81	740	2.3			=	N	–	–		
					7.7	1036	1.9			=	N	–	–		
					7.41	2072	1.1				N	–	–		
Halimeda minima	Tr	S	B	A	8.18	276	4.6	700	14	→	N	–	–		Comeau et al. (2013)
					8.04	385	3.6			→	N	–	–		
					7.94	543	3.0			→	N	–	–		
					7.81	740	2.3			→	N	–	–		
					7.7	1036	1.9			→–	N	–	–		
					7.41	2072	1.1				N	–	–		

major responses of these organisms according to their latitudinal distribution, taxonomy and calcification mechanisms. A meta-analysis of the studies conducted to date reveals that very few studies have been conducted on polar calcifying macroalgae, studies conducted for 2 to 4 wk show the highest number of negative responses with respect to calcification, and that longer-term studies result in more diverse responses, including potential acclimation and increases in calcification (Fig. 1). Furthermore, the majority of studies have been conducted on high-Mg calcite-depositing macroalgae, which show a wide variety of responses to elevated pCO_2, and very few studies have observed acclimation potential of calcifying macroalgae to elevated pCO_2 (Fig. 2), although most studies have not been designed to address acclimation or adaptation.

Polar environments

Surprisingly few studies have been conducted on the effect of high CO_2 on polar macroalgae, despite the fact that CO_3^{2-} saturation state is expected to decrease <1 first in polar surface oceans (Orr et al. 2005, Steinacher et al. 2009). Büdenbender et al. (2011) found decreased calcification rates in the crustose coralline alga *Lithothamnion glaciale* from northwest Svalbard under both winter and summer irradiance conditions when exposed to elevated CO_2, and net dissolution of the skeleton was observed at aragonite saturation levels between 0.9 and 1.1. The authors suggest that Arctic species of coralline algae could be the most severely affected by ocean acidification compared to temperate and tropical species, and that rhodolith beds in the Arctic could severely decrease within this century if CO_2 emissions continue at their current rate.

Temperate environments

Due to the broad distribution of *L. glaciale,* further studies have been conducted on this species collected from temperate environments (Burdett et al. 2012, Ragazzola et al. 2012, Kamenos et al. 2013), and all have reported reductions in the structural integrity of *L. glaciale* exposed to elevated pCO_2. Cell density, cell wall thickness, and growth of this species declined with increasing pCO_2 within a range of 422 to 1118 µatm CO_2 (Ragazzola et al. 2012). Changes in the cell structure increase the total strain energy and distribution of stress on the algal skeleton,
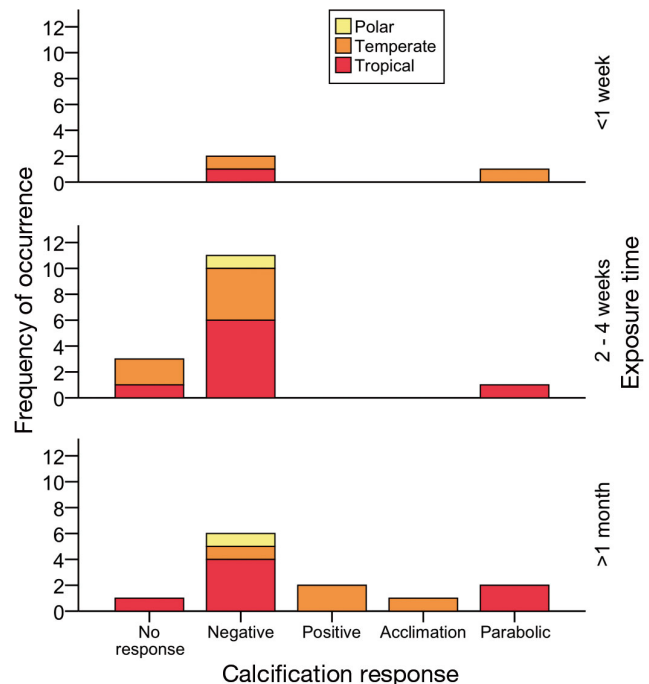

Fig. 1. Meta-analysis of experimental studies (from 1987 to 2013) showing the frequency of 4 different calcification responses (no response, negative, positive, acclimation, or parabolic) reported in calcifying macroalgae exposed to elevated CO_2, grouped by latitude (polar = north of 66° N and south of 66° S, temperate = 23 to 66° N and 23 to 66° S, tropical = 23° S to 23° N), and the experimental time of exposure (<1 wk, 2–4 wk, >1 mo)
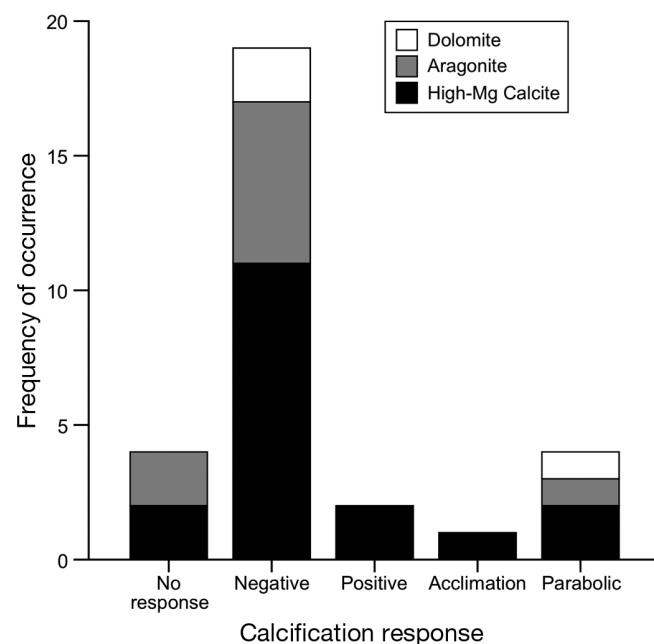

Fig. 2. Meta-analysis of studies (from 1987 to 2013) showing the frequency of calcification responses (no response, negative, positive, acclimation, or parabolic) reported for calcifying macroalgae exposed to elevated CO_2, according to the type of carbonate mineral deposited in the skeleton

and the authors suggest that these changes could make *L. glaciale* more susceptible to biological and physical erosion. Furthermore, cracks developed in the skeleton at 1181 µatm pCO_2, which may have resulted in increased dimethylsulphoniopropionate (DMSP) release. Nevertheless, the rate of pCO_2 increase has been shown to play an important role in the skeletal response of *L. glaciale* to elevated pCO_2, as rapid increases in pCO_2 weaken the skeleton more than gradual increases (Kamenos et al. 2013). In contrast to Büdenbender et al. (2011), Kamenos et al. (2013) reported increased calcification rates in *L. glaciale* under elevated pCO_2 conditions. Differences in the response of calcification rates in *L. glaciale* to elevated pCO_2 could be due to differences in light availability, which were more than 10 times higher in the case where calcification rates were stimulated under high pCO_2. Indeed, Teichert & Freiwald (2013) reported light incidence to be the strongest factor controlling growth rates in polar coralline algal communities. Therefore, limitations to growth, such as light, will be important factors influencing how calcifying macroalgae response to elevated pCO_2, particularly in polar environments.

Differences in carbonate mineral structure among coralline algae in temperate environments also influence species-specific responses to ocean acidification. Along a natural CO_2 gradient in the Mediterranean, 2 species of coralline algae (in contrast to the other red coralline algae present) did not decrease in cover along the natural CO_2 gradient (Porzio et al. 2011). *Hydrolithon cruciatum* and *Peyssonnelia squamaria* were actually more abundant at a heavily CO_2-impacted site than at the reference site. *P. squamaria* is an aragonite-depositing alga (James et al. 1988), and *Hydrolithon onkodes* has been shown to precipitate dolomite (Nash et al. 2011a,b), suggesting that other species in this genus may have the same ability and are therefore not as sensitive to pCO_2 as species that deposit Mg-calcite with higher Mg content.

Among other temperate coralline algae, reported responses include decreased calcification, growth, $MgCO_3$ content, total inorganic content and reproduction rates under elevated CO_2 (Martin & Gattuso 2009, Russell et al. 2009, Cumani et al. 2010, Hofmann et al. 2012a, Olabarria et al. 2013). In environments impacted by natural seafloor CO_2 vents, benthic and epiphytic crustose coralline algae (CCA) are much lower in abundance compared to unimpacted areas (Hall-Spencer et al. 2008, Porzio et al. 2011). Furthermore, Martin & Gattuso (2009) reported that elevated CO_2 aggravates the sensitivity of the Mediterranean species *Lithophyllum cabiochae* to ele-

vated temperature, indicating that the combination of these 2 abiotic factors could have severe implications for temperate CCA. On the other hand, the responses of CCA are strongly dependent on seasonality, and some species may be able to acclimate to rising CO_2 levels (Martin & Gattuso 2009, Martin et al. 2013). Associated communities will also influence the success of red coralline algae under future pCO_2 conditions. For example, kelp canopies may diminish the negative effects of elevated pCO_2 on associated coralline communities by buffering the acidification affect via higher photosynthetic rates (Tait 2014) and by increasing boundary layer thickness surrounding crusts (Cornwall et al. 2013). If productivity rates are high and water flow is optimum, calcifying macroalgae are able to alter the chemistry in the surrounding boundary layer in a way that buffers ocean acidification (Hurd et al. 2011). Under future pCO_2 conditions, boundary layer thickness will have to be optimized so that nutrient uptake is not limited, while the buffering capacity is maximized to counteract ocean acidification in order for these organisms to be successful.

Coralline algae use HCO_3^- as a substrate for calcification (Digby 1977a,b), and CA, the enzyme used in CCMs to concentrate inorganic carbon for photosynthesis, may act as a buffer for removing protons by converting some of the HCO_3^- into CO_2 (Tambutté et al. 2007), which can then be used for photosynthesis. Such a process is consistent with the hypothesis that calcification can stimulate photosynthesis in some algae (McConnaughey 1991, McConnaughey & Whelan 1997), and CA has been shown to play a role in the calcification process of many organisms (Kingsley & Watabe 1987, Al-Horani et al. 2003, Tambutté et al. 2007, Rahman et al. 2008). Although CA activity generally decreases in noncalcifying algae exposed to high pCO_2 (see Gao et al. 2012), the same pattern is not observed in calcifying macroalgae (Hofmann et al. 2013, 2014). The role of CA in macroalgal calcification has been largely ignored in ocean acidification studies, but due to the important role it plays in inorganic carbon uptake and accumulation, the activity of this enzyme and its genetic expression in macroalgae should be considered in future ocean acidification studies.

In contrast to the coralline algae, the brown alga *Padina pavonica* growing in a naturally CO_2-impacted site in the Mediterranean flourishes compared to in unimpacted sites. Despite a decrease in the amount of calcification, the algae growing in the impacted sites had higher chlorophyll content and higher relative electron transport rates (ETR) than

those growing in an unimpacted site (Johnson et al. 2012). Although some species of *Padina* have been shown to have CCMs and may even be able to use HCO_3^- (Israel & Hophy 2002, Raven et al. 2002, Enríquez & Rodríguez-Román 2006), their efficiency may differ from species to species. The stimulation of photosynthesis in *P. pavonica* under elevated CO_2 could be due to a poorly efficient CCM, or the down-regulation of its CCM, which allowed for energy real-location to other processes.

Tropical environments

Tropical calcifying macroalgae have been heavily investigated within the context of ocean acidification (Table 1) and show a variety of responses (Edmunds et al. 2013). Calcifying macroalgae contribute to reef accretion and carbonate sediment production in coral reef environments. Particularly algae in the genus *Halimeda* contribute heavily to sediment production, and diverse species of crustose calcifying algae act as a cement that maintains the structural integrity of coral reefs (see Adey 1998, Nelson 2009 for reviews). Furthermore, the calcifying brown alga *Padina* spp. is a food source for sea urchins (Sammarco 1982, Hereu 2006). Due to the differences in calcification mechanisms and the diverse responses of tropical calcifying macroalgae across taxa, they are discussed below in 3 taxonomic groups.

Chlorophytes

Within the genus *Halimeda*, there have been a variety of responses to ocean acidification experiments (Table 1). In general, the size of aragonite crystals in the skeleton decreases, while crystal density increases under pH conditions lower than 7.7 (Robbins et al. 2009, Sinutok et al. 2011). Some investigations on *H. opuntia* have shown decreased ETR and net dissolution at 946 ppm pCO_2, but Hofmann et al. (2014) found no effect of elevated pCO_2 on ETR or calcification rates in *H. opuntia* exposed to up to 1700 µatm pCO_2. Furthermore, Price et al. (2011) found no pCO_2 effect on the amount of $CaCO_3$ in *H. opuntia* skeletons. Discrepancies in reported responses of *H. opuntia* may be due to the difficulty in estimating calcification rates due to the high shedding rate of this species, and the more rapid rate of dissolution that probably occurs in shed (dead) segments compared to attached segments. *H. taenicola* on the other hand, showed no change in ETR, but a decrease in net calcification

and skeletal $CaCO_3$. In 2 studies, *H. macroloba* net calcification rates showed no response to CO_2 within the range of 276 to 1036 µatm pCO_2 (pH 8.1 to 7.7), but decreased at 2072 µatm (pH 7.4) in 1 of the 2 studies (Sinutok et al. 2011, Comeau et al. 2013). In *H. cylindracea*, no change in calcification rate was observed at 660 µatm, but net dissolution was observed at 1066 µatm pCO_2 (Sinutok et al. 2011). Another species, *H. incrassata*, showed a parabolic calcification response to CO_2-induced low pH, with a maximum calcification rate at pH 8.05 (606 ppm pCO_2) and no difference in calcification at pH 7.91 (903 ppm pCO_2) compared to current conditions (Ries et al. 2009). Finally, *H. minima* showed a decrease in calcification with increasing CO_2 (Comeau et al. 2013). Clearly, there has been a wide range of reported responses of *Halimeda* spp. to ocean acidification, which are likely due to differences in methods, light conditions, and perhaps differences in populations of *Halimeda*. However, based on studies to date, it is apparent that calcification in *H. macroloba* and *H. incrassata* is relatively insensitive to seawater CO_2 concentrations up to 900 µatm, while *H. minima* may be the most CO_2-sensitive of the species studied so far.

The mechanism of inorganic carbon uptake is an additional factor that could contribute to the variety of responses exhibited by *Halimeda* spp. to elevated pCO_2. Some *Halimeda* spp. are able to uptake HCO_3^- directly (Borowitzka & Larkum 1976b) and do not rely on external CA (de Beer & Larkum 2001). This ability is likely an advantage under high CO_2 conditions, but it is not clear if all species have this ability. Differences in CCMs could potentially explain why some *Halimeda* spp. are less sensitive than others to elevated CO_2. *Halimeda* spp. also show a wide range of morphologies. The width and number of utricle layers in the thallus may influence calcification, and therefore species like *H. macroloba* and *H. incrassata*, with 2 to 4 layers of relatively thick utricles may be less sensitive to pCO_2 than *H. minima*, which has only 1 or 2 layers of thin utricles (Verbruggen et al. 2004, Dijoux et al. 2012). Nevertheless, the combination of the semi-isolated location of calcification inside the utricular space and the deposition of aragonite are likely to make *Halimeda* spp. less susceptible to ocean acidification than the coralline algae.

Rhodophytes

CCA are extremely abundant in tropical reef environments and serve important ecological functions (Adey 1998, Nelson 2009). Unfortunately, they are

likely to be unsuccessful in future high-CO_2 oceans. Many studies have shown that across genera (*Litho-phyllum, Hydrolithon, Porolithon, Neogoniolithon*), calcification and photosynthetic rates decrease under elevated CO_2 conditions, as well as their cover and recruitment (Anthony et al. 2008, Jokiel et al. 2008, Kuffner et al. 2008, Andersson et al. 2009, Ries et al. 2009, Semesi et al. 2009, Campbell 2012, Comeau et al. 2013). However, recent evidence shows that the rate of change in pCO_2 is more important than the magnitude, that some species may be able to adapt, and others can alter their carbonate mineral structure to compensate for low pH (Table 1).

The mechanism and location of calcification proba-bly play a role in determining their sensitivity to low pH, but recent studies have suggested that increased dissolution rates, rather than decreased calcifica-tion rates, are the real threat to calcifying organisms under ocean acidification conditions (Ries 2011b, Rodolfo-Metalpa et al. 2011, Roleda et al. 2012). Therefore, the type of carbonate material deposited by a calcifying alga is important. Some species of coralline algae can decrease the Mg:Ca ratio of their skeletons in response to elevated CO_2 (Ries 2009, Egilsdottir et al. 2013), most likely as an attempt to decrease the solubility of the skeleton, thereby pre-venting rapid dissolution. The combination of de-creasing skeletal solubility by decreasing the Mg:Ca ratio and speeding up calcification rates may be an attempt by coralline algae to compensate for high dissolution that may be occurring under low pH con-ditions. Nevertheless, high-Mg calcite depositing species seem to be more heavily impacted by ele-vated CO_2 than aragonite-depositing macroalgae, with the exception of dolomite-depositing coralline algae (Nash et al. 2012, Diaz-Pulido et al. 2014). *Porolithon* spp. containing dolomite, a stable form of $CaCO_3$, are more resistant to dissolution under elevated CO_2 compared to algae that deposit high-Mg calcite (Nash et al. 2012). Furthermore, Diaz-Pulido et al. (2014) recently reported that dolomite accumulated in *Porolithon onkodes* exposed to high pCO_2 and temperature conditions expected under future CO_2 emissions scenarios. Therefore, shallow reefs consisting of dolomite-containing CCA will be more resistant to ocean acidification than reefs con-taining predominantly high-Mg calcite, due to the lower solubility of dolomite in seawater and the resistance to erosion by endolithic algae it provides (Nash et al. 2012, Diaz-Pulido et al. 2014). Reefs containing these organisms may be essential to providing protection and stability under future CO_2 conditions.

Phaeophyceae

To date, only one study has reported the effect of CO_2 on a calcifying phaeophyceae. Johnson et al. (2012) reported increased cover of *Padina australis* at sites naturally affected by elevated CO_2 in Papua New Guinea compared to unimpacted sites, despite a lower skeletal $CaCO_3$ content. They also reported a lower abundance of sea urchins at the CO_2-impacted sites, and hypothesized that *P. australis* could thrive at those sites due to lower grazing pressure. A wide range of calcium carbonate content in *Padina* spp. has been reported, even within the same species. Reported values for *P. pavonica* range from 9.3 to 63% of dry weight, while *P. japonica* and *P. sanctae-crucis* have 21 and 38%, respectively (Okazaki et al. 1986 and references therein, Johnson et al. 2012). The flexibility of $CaCO_3$ deposition in *Padina* spp. may influence the ability of these species to flourish under elevated CO_2. Johnson et al. (2012) speculates that the less calcified *Padina* may produce more herbivore-defense compounds, thereby decreasing the grazing pressure and allowing them to flourish despite low $CaCO_3$ content.

EFFECTS OF OCEAN ACIDIFICATION ON MACROALGAL COMMUNITIES

A summary of the studies conducted on macroalgal communities exposed to elevated CO_2 are shown in Table 2. To date, no studies have been conducted on macroalgal communities in polar environments. In both temperate and tropical macroalgal communi-ties, the relationship between calcifying and non-calcifying macroalgae under ocean acidification shifts in similar ways. In general, calcifying species are overgrown and eventually shaded by the noncalcify-ing species when CO_2 concentrations are elevated. The interactions between calcifying and noncal-cifying macroalgae under elevated pCO_2 are closely linked to carbon uptake mechanisms. For example, in a mesocosm study, photosynthesis in the rhodo-phyte *Chondrus crispus* was stimulated under ele-vated CO_2, while photosynthesis in the calcifying rhodophyte *Corallina officinalis* was not (Hofmann et al. 2012a). Both species use CA to dehydrate HCO_3^- into CO_2, but do not have an active HCO_3^- uptake mechanism and therefore must rely on diffusive CO_2 entry into the cell (Smith & Bidwell 1989, Ragazzola 2009). Higher CO_2 concentrations benefit the non-calcifying alga by increasing the diffusion gradient outside the cell relative to inside, while the calcifier

Table 2. Summary of CO_2 effects on macroalgal communities containing calcifiers and noncalcifiers. Morphology of the calcifying species is indicated as crustose calcifying algae (CCA), branched (B), or frond (F). For details and explanation of abbreviations and symbols, see Table 1. Responses are summarized as changes in cover of calcifying and turf/noncalcifying macroalgae as increase (↑), decrease (↓) or no change (=)

Community type & main calcifying species	Latitude (P, T, M, Tr)	Depth (T, I, S)	Morphology (CCA, B, F)	Skeletal mineralogy	pH	CO_2 (ppm)	$\Omega_{aragonite}$	Light	Salinity	Time of exposure to CO_2 (days)	Calcifier cover/ abundance	Turf/non-calcifying algae cover	Additional responses	Source
Kelp forest understory (*Lithophyllum* spp.)	T	S	CCA	C	8.1 8.1 7.95 7.95	222 210 306 298	1.98 1.88 1.38 1.34	34	nr	76 76 76 76	↑ ↓ ↓	↑ = ↑		Russell et al. (2009)
Rocky Intertidal macroalgae (*Corallina officinalis*)	T	I	B	C	8.22 8.01 7.69	385 665 1486	2.33 1.53 0.77	Natural	26–30 26–30 26–30	88 88 88	↓ ↓	↑ ↑		Porzio et al. (2011)
Volcanic CO_2 vent in Vulcano (*Padina pavonica*)	M	S	F	A	8.17–8.19 8.06 7.71 7.66	276–388 510 1244 1428	1.85–1.89 1.64 0.73 0.66	Natural	38 38 38 38	Reference site Permanent Permanent Permanent	↑ ↓ ↑	– – –	Lower $CaCO_3$ content, but higher chlorophyll and $rETR_{max}$; decrease in sea urchin and coralline algae cover	Johnsen et al. (2012)
Calcifying seagrass epiphytes (CCA)	M	S	CCA	C	8.17 8 7.6	309 542 1827	4.1 3.13 1.71	Natural	38	Reference site Permanent Permanent	↓ ↓	– –		Hall-Spencer et al. (2008)
CCA	M	S	CCA	C	8.14 7.83 6.57	334 957 20,812	3.91 2.43 0.19	Natural	38	Reference site Permanent Permanent	↓ ↓	↑ ↑		Hall-Spencer et al. (2008)
Synthetic assemblages (*Lithophyllum incrustans*)	M	I	CCA	C	7.99 7.91	704 897	nr nr	140–150	35	17	– –	– –	Understory biomass decreased, $MgCO_3$ decreased, but no response of PS or respiration	Olabarria et al. (2013)
Synthetic assemblages (*Corallina* sp.)	M	I	B	C	7.99 7.91	704 897	nr nr	140–150	35	17	– –	– –	Understory biomass decreased, $MgCO_3$ decreased, but no response of PS or respiration	Olabarria et al. (2013)
Volcanic CO_2 vent in Ischia	M	S	B, F, CCA	A, C	8.14 7.83 6.72	334 957 20,812	3.91 2.43 0.19	Natural	38 38 38	Reference site Permanent Permanent	↓ ↓	↑ ↓	Highest community complexity Dominance of few species, *H. cruciatum* and *P. squamaria* more abundant Simplified community with high dominance of few spp.	Johnson et al. (2012)
Volcanic CO_2 vent in Papua New Guinea (*Padina australis*)	Tr	S	F	A	8.19–8.31 7.78 6.68	276–388 1218 23,095	4.25–4.9 1.89 0.14	Natural	34 34 34	Reference site Permanent Permanent	↑ ↑	– –	Lower $CaCO_3$ content in calcifiers; decrease in sea urchin and coralline algae cover	Johnsen et al. (2012)
Calcifying seagrass epiphytes	Tr	S	CCA	C	8.19 7.86	437 1147	4.3 2.4	Natural	36 36	11 months 11 months	↓	↑		Campbell (2012)
CCA	Tr	S	CCA	C	8.17 7.91	400 765	2.74 1.55	Natural	35	51	↓	↑		Kuffner et al. (2008)
CCA	Tr	S	CCA	C	8.2 7.9	ca. 400 ca. 700	ca. 3 1–2	Natural	35	215	↓	=		Jokiel et al. (2008)
CCA	Tr	S	CCA	C	8.08 7.76	568 1147	2.8 1.4	Natural	35	1	↓	–	Calcification decreased	Andersson et al. (2009)

was negatively impacted due to the negative effects of CO_2 on growth rates, photosynthetic rates and calcification.

The implications of the results summarized above are that calcifying algae could be impaired under future ocean conditions if CO_2 levels continue to rise, due to overgrowth and outcompetition by noncalcifying species. In almost all cases, mesocosm and field experiments have reported outcompetition of calcifiers, particularly CCA, by noncalcifiers under manipulated CO_2 conditions, or even the lack of calcifying species at vent sites where CO_2 levels are naturally high (Table 2). On the other hand, the calcifying phaeophyceae *Padina* spp. seems to be an exception to the rule, as 2 species have been shown to increase cover with increasing CO_2 along natural gradients in both a Mediterranean and tropical environment (Johnson et al. 2012). Although it is well documented that future CO_2 concentrations could shift macroalgal community composition, it is still unclear how these changes might affect grazers, sedimentation, and the overall carbon cycling in benthic communities. Phase shifts on coral reefs resulting in fleshy algae-dominated communities have also occurred as a result of eutrophication and/or overfishing (e.g. Done 1992, Hughes 1994, Lapointe et al. 1997, Hoegh-Guldberg et al. 2007). A combination of these factors could be extremely detrimental to coral reef communities.

SYNERGISTIC EFFECTS

Several additional abiotic factors also influence the responses of calcifying macroalgal species and their associated communities to future environmental conditions. For example, rising temperature due to global warming is a large concern and has received considerable attention in recent decades (Sinutok et al. 2011, Martin et al. 2013, Olabarria et al. 2013, Reyes-Nivia et al. 2014). Sinutok et al. (2011) found that elevated temperature amplified the negative effects of CO_2 on 2 *Halimeda* spp. Olabarria et al. (2013) reported that the combination of elevated CO_2 and temperature drastically reduced the productivity of both noncalcifiers and calcifiers in macroalgae growing in rock pools. Martin et al. (2013) found that calcification in *Lithophyllum cabiochae* was stimulated by increased temperature under current CO_2 conditions, but the combination of high temperature and CO_2 negatively impacted net calcification rates. Furthermore, Reyes-Nivia et al. (2014) recently reported that *Porolithon onkodes* containing endolithic

algae was less susceptible to dissolution than *P. onkodes* without these associated organisms, but that the combination of high temperature and CO_2 expected under the SRES-A1F1 'business as usual' CO_2 emissions scenario (Meehl et al. 2007) significantly increased dissolution in *P. onkodes* regardless of the presence or absence of endolithic algae. The combination of ocean acidification and warming has also been shown to increase the susceptibility of CCA to grazing (Johnson & Carpenter 2012). Therefore, it is likely that the combination of elevated temperature and CO_2 will be detrimental for calcifying macroalgae in many environments.

Light quantity and quality is another important factor influencing the physiological responses of calcifying macroalgae to ocean acidification. Gao & Zheng (2010) found that UV exposure amplified the negative effects of CO_2 on growth, photosynthesis and calcification in the coralline alga *Corallina sessilis*. Yildiz et al. (2013) also emphasized the importance of light quality in dictating the response of *C. officinalis* to ocean acidification. Martin et al. (2013) reported that calcification in *Lithophyllum cabiochae* was unaffected by elevated pCO_2 for most of the year, except in summer, when light intensity was highest and calcification rates increased. The skeletal composition of macroalgae modulates the quality and quantity of light that is absorbed for photosynthesis. Therefore, another likely explanation for the different effects of CO_2 on photosynthesis in calcifying macroalgae is the difference in skeletal structure and composition and how it affects light absorption. Because the skeletons of many coralline algae and some *Halimeda* spp. have less inorganic carbon under elevated CO_2 conditions, the light scattering properties of the skeleton are affected and therefore also the amount and quality of light that reaches the light harvesting complexes. The scattering properties of calcified skeletons have been shown to be very important for light harvesting by the photosymbiotic algae in corals (Enríquez et al. 2005, Terán et al. 2010). With a less calcified skeleton, perhaps the light harvesting complexes of some calcifiers receive less light than under normal conditions, and therefore maximum photosynthetic rates decrease. Because eutrophication and high suspended sediment loads often occur together due to land runoff, and ocean acidification can alter the strength of the influence of light on macroalgal communities (Russel et al. 2011), these factors are also likely to be interacting in marine environments in ways which are difficult to manipulate in the lab. Seasonal changes are also important to consider, due to differences in tempera-

ture and light availability. Therefore, more experimentally manipulated field work, for example *in situ* nutrient or temperature enrichment along a natural CO_2 gradient over a seasonal cycle, must be done in order to better predict community responses to elevated CO_2 and other changing environmental factors.

Inorganic nutrient availability is also likely to have synergistic effects in combination with elevated pCO_2. Although CO_2 alone affects the carbon and nitrogen metabolism of macroalgae, the response is also dependent on inorganic nutrient history and availability. CO_2 is therefore affecting nutrient assimilation, but exactly how nutrient assimilation is affected depends on the concentration and types (nitrate, ammonium and/or phosphate) of inorganic nutrients available. In *C. officinalis*, phosphate and nitrate uptake rates have been shown to decrease as a function of increasing CO_2 concentration, despite elevated nitrate reductase activity (Hofmann et al. 2013). If nitrate uptake is reduced under elevated pCO_2, then the production of nitrogen-rich metabolites becomes more energy costly, which could lead to an increase in the production of nitrogen-free metabolites, such as DMSP (Stefels 2000). Some calcifying macroalgae have been shown to produce DMSP in a diel cycle, with production highest at night when the carbonate saturation state of the seawater is lowest (Burdett et al. 2013), and under manipulated pCO_2 conditions (Burdett et al. 2012). Increased DMSP production by macroalgae could influence atmospheric DMS levels and influence grazing pressure (Van Alstyne et al. 2001, Van Alstyne & Houser 2003).

In contrast to temperate calcifying species, tropical calcifiers grow in oligotrophic environments where inorganic nutrients are usually limiting. An addition of nutrients could stimulate their growth (Delgado & Lapointe 1994, Teichberg et al. 2013) and affect their response to elevated pCO_2 (Hofmann et al. 2014); however, inorganic nutrient enrichment also stimulates the growth of noncalcifying macroalgae (see Valiela et al. 1997 for review). Therefore, excess nutrients could amplify the shift from calcifiers to noncalcifiers under elevated CO_2 conditions, due to the ability of noncalcifying algae to rapidly take up and assimilate inorganic nutrients and carbon compared to calcifiers (Delgado & Lapointe 1994, Hoegh-Guldberg et al. 2007). To date, no studies have investigated pCO_2 and nutrient enrichment effects on tropical calcifying macroalgae and their associated communities, but Russell et al. (2009) reported that elevated nutrients exaggerated the expansion of non-

calcifying algae to the disadvantage of calcifiers in a kelp understory. Therefore, calcifiers may be especially at risk in eutrophied environments. Nevertheless, if grazing pressure increases under elevated CO_2 and inorganic nutrient conditions, as is the case with turf algae in kelp communities (Falkenberg et al. 2014), the high growth rates of noncalcifying macroalgae may be constrained relative to calcifying macroalgae.

The *in situ* CO_2 conditions in the local habitat where calcifying macroalgae grow may also influence their responses to elevated pCO_2. Noisette et al. (2013) reported that temperate species of coralline macroalgae growing in environments with naturally strong pH variations were not more resistant to elevated pCO_2 than species growing in a stable pH environment. Rather, skeletal mineralogy was likely the more important factor controlling the calcification response of the 3 species investigated. On the other hand, Johnson et al. (2014) reported that *P. onkodes* collected from a habitat with high pCO_2 variability were more resistant to high pCO_2 than individuals collected from a habitat with stable pCO_2, although both populations decreased calcification rates when exposed to 660 µatm pCO_2. Because *P. onkodes* is a dolomite-depositing alga, populations growing in the pCO_2-variable environment may have accumulated dolomite in their skeletons (which has been shown to occur in this species; Diaz-Pulido et al. 2014), making them more resistant to experimental pCO_2 conditions.

CONCLUSIONS

We conclude that many calcifying macroalgae are sensitive to ocean acidification, but that variations in their responses are due to calcification mechanisms, skeletal mineralogy, carbon uptake mechanisms and local environmental conditions. Because calcification is not the only process affected by ocean acidification (other physiological processes including photosynthesis, growth and nutrient uptake and assimilation are also involved), the consequences of elevated pCO_2 on these organisms are complex, and will be influenced by temperature, light, nutrient availability and seasonal cycles. The implications of these changes for benthic communities are large, including shifts in community composition, higher susceptibility to grazing and higher bioerosion rates. In temperate and polar environments, seasonal changes interact with elevated CO_2 and complicate our understanding of the future

response of macroalgae to ocean acidification. At the community level, significant changes in macroalgal communities have been shown to occur under elevated CO_2 in temperate and tropical environments. These changes often result in communities dominated by noncalcifiers, with the exception of communities where *Padina* spp. are common, in which case they also become prominent under elevated CO_2 conditions despite decreases in skeletal inorganic carbon. In situations where inorganic nutrients are in excess, the trend towards communities dominated by noncalcifiers could become amplified, especially in tropical environments. We therefore conclude that ocean acidification is a relevant threat to macroalgal communities, across all latitudes, and that additional abiotic factors such as temperature and eutrophication may amplify the negative effects of elevated CO_2 on these communities. Communities dominated by dolomite- and aragonite-depositing calcifying species will be the most resistant to future ocean acidification, but polar calcifying macroalgae may be at the highest risk, due to the fact that they deposit high-Mg calcite. Many questions remain when it comes to investigating the performance and competition of macroalgae under elevated CO_2 concentrations that are expected to occur by the end of the century. Differences in CCMs, including ion transport mechanisms, the inorganic carbon substrate used for photosynthesis, and the activity and location of carbon and inorganic nutrient uptake and assimilation-related enzymes in calcifying macroalgae are areas that should be further explored in order to provide a better understanding of their individual responses to elevated pCO_2. Investigating the reproductive success, recruitment and survival of macroalgae under changing abiotic conditions is also crucial to understanding how they will fare under future ocean conditions. Furthermore, gene expression should be investigated, to determine which genes in macroalgae are strongly affected by ocean acidification and how changes in gene expression relate to their physiological responses. Finally, their adaptive capabilities must be investigated, in order to determine if the responses of individuals are representative of future responses, or if acclimation of individuals will eventually allow for adaptation of species to cope with their rapidly changing environment. In particular, studies manipulating pCO_2 with a slow rate of change are needed. The balance between the rate of adaptation and the rate of environmental change is an important factor that will control whether or not adaptation will occur.

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