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6 Chapter 4: Effects of ocean warming and acidification on rhodolith/maerl beds

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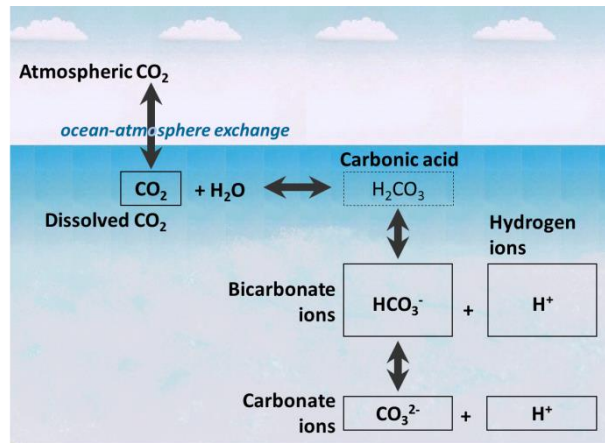
8 Ocean warming and acidification are currently under scrutiny since in combination they are
9 expected to reduce marine biodiversity and profoundly alter ecosystem function. Habitats
10 where coralline algae play an important ecological role, such as rhodolith and maerl beds, are
11 threatened by dissolution due to the high solubility of their high-magnesium calcite skeletons.
12 Those in the Arctic, where carbonate saturation levels are already low and falling, are of
13 particular concern. As well as direct corrosive effects on coralline algae, rising CO₂ emissions
14 are expected to have knock-on effects on ecosystems because reduced seabed habitat
15 complexity causes a reduction in biodiversity and simplifies food webs. We anticipate that
16 degradation of coastal calcareous habitats due to ocean acidification will facilitate a
17 proliferation of fleshy algae that may benefit from an increase in dissolved inorganic carbon,
18 to the detriment of calcified algae. It is not all doom and gloom: coralline algae have survived
19 previous mass extinctions and many species tolerate highly variable CO₂ levels. Which
20 species survive the Anthropocene will depend upon their ability to acclimate and adapt. These
21 topics warrant further research since coralline algae provide highly biodiverse habitats that
22 benefit commercially important species of fish and molluscs. Data so far suggest that 1) this
23 important algal group is especially vulnerable to ocean acidification and warming and 2)
24 protecting these habitats has long-term benefits, not least because coralline algae provide
25 habitat for species of commercial importance.

26

27 4.1 Climate change and ocean acidification

28 Anthropogenic emissions have increased the atmospheric carbon dioxide (CO₂) concentration
29 from 280 ppm prior to the beginning of the industrial revolution (1750) to more than 390 ppm
30 in 2013; this is *ca.* 100 ppm higher than at any time in the past 740,000 years. The present rate
31 of increase in atmospheric CO₂ and temperature is unprecedented in recent Earth history
32 (Hoegh-Guldberg et al. 2007).

33 Approximately 25 % of CO₂ emissions dissolve into the ocean, increasing *p*CO₂ in the surface
34 water and altering seawater carbonate chemistry (Canadell et al. 2007). This CO₂ reacts with
35 the water to form carbonic acid most of which dissociates into ions of hydrogen (H⁺) and
36 bicarbonate (CO₃²⁻) (Fig. 1). The increased concentration of H⁺ reduces pH (pH = -log₁₀[H⁺])
37 and carbonate ion (CO₃²⁻) concentration and increases the concentration of HCO₃⁻.



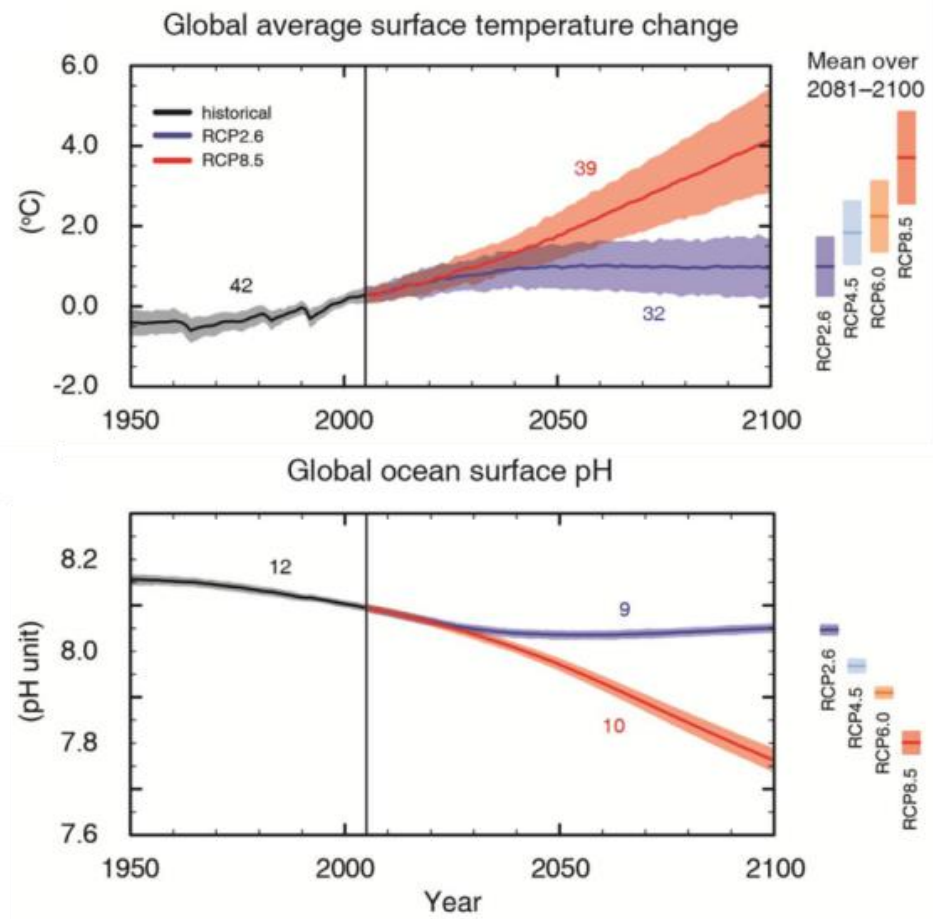
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39 **Fig. 1. Equilibrium between the three different species of dissolved inorganic carbon in seawater.**
 40 **Atmospheric CO₂ is absorbed at the surface of the oceans where it combines with the water molecules to**
 41 **form carbonic acid, which dissociates into bicarbonate, carbonate, and hydrogen ions. Different forms of**
 42 **dissolved inorganic carbon (DIC = [CO₂] + [HCO₃⁻] + [CO₃²⁻]) follow thermodynamic equilibria in**
 43 **seawater for the following reactions: CO₂ + H₂O ↔ H₂CO₃ ↔ HCO₃⁻ ↔ H⁺ + CO₃²⁻ + 2H⁺.**

44

45 During the 20th century, increasing atmospheric CO₂ caused the surface ocean to warm by
 46 0.7°C and to acidify by 0.1 pH units (Hoegh-Guldberg et al. 2007). The atmospheric CO₂
 47 concentration is expected to reach between 490 - 1370 ppm by 2100 causing a global mean
 48 surface temperature increase of between 0.3 to 4.8°C and a surface ocean pH decrease of
 49 0.06-0.32 units relative to the period 1986-2005 (IPCC 2013; Fig. 2). Ocean acidification and
 50 warming will not be regionally uniform; marine organisms in the Arctic region are thought to
 51 face more rapid and stronger warming and acidification than the global mean (Fig. 3).

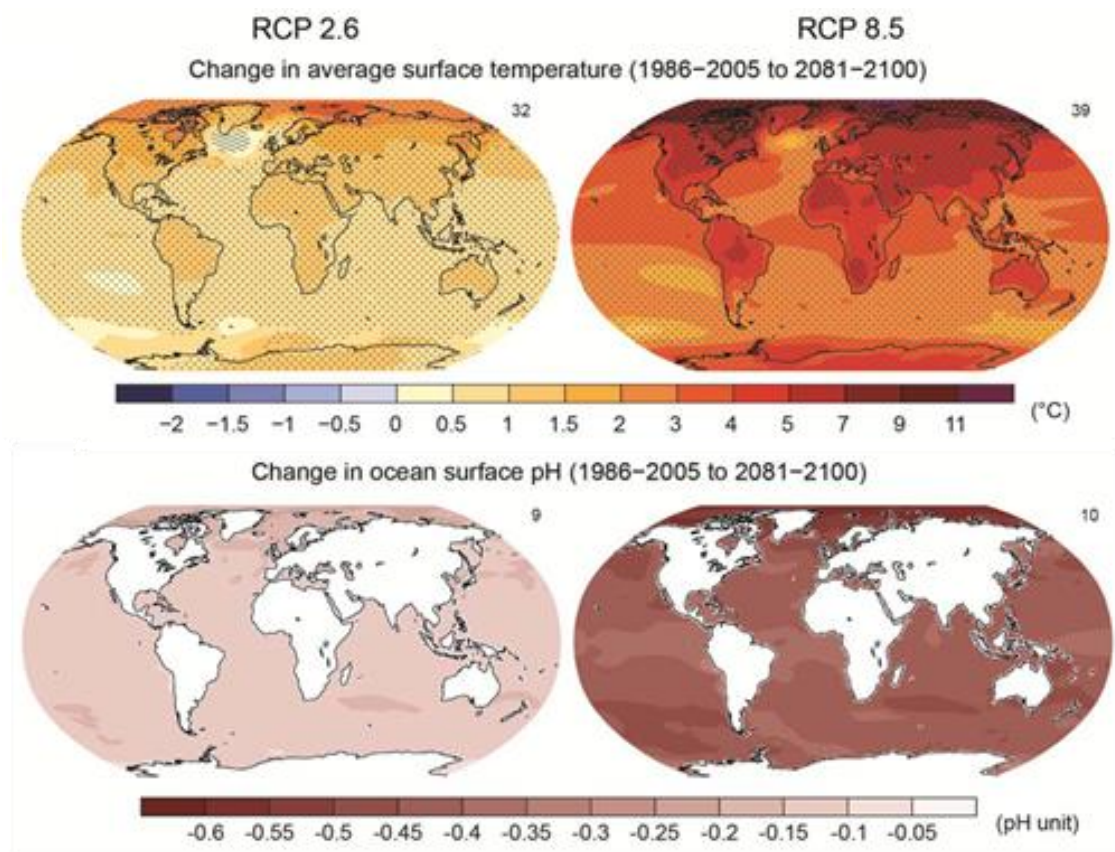
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54 **Fig. 2. Projected change in global annual mean surface temperature and global mean ocean surface pH,**
 55 **relative to 1986-2005 for Representative Concentration Pathway 2.6 (blue) and RCP8.5 (red) (Source:**
 56 **IPCC 2013).**

57



58

59 **Fig. 3. Annual mean temperature and pH changes for the scenarios RCP2.6 and RCP8.5 in 2081-2100**
 60 **relative to 1986-2005 (Source: IPCC 2013).**

61

62 **4.2 Effects of ocean warming and acidification on seaweeds**

63 Global warming and ocean acidification will alter biochemical and physiological processes in
 64 seaweeds, causing changes in their ecological interactions (Koch et al. 2012, Harley et al.
 65 2012). Here we base predictions about the fate of rhodolith/maerl beds upon a growing body
 66 of information about the effects of warming and acidification on seaweeds in general and on
 67 coralline algae in particular. While some seaweed taxa seem likely to benefit from ocean
 68 warming and acidification, coralline algae are expected to be adversely impacted, putting the
 69 habitats they form at risk. This is a concern since beds of rhodoliths and maerl form highly
 70 biodiverse but very slow-growing habitats (Pena et al. 2014).

71

72 **4.2.1 Effects of ocean warming on seaweeds**

73 Temperature directly affects enzymatic processes and so alters rates of photosynthesis and
 74 growth; it also determines whether seaweeds can survive and reproduce and sets limits to their
 75 geographic distribution (Lüning 1990). Seaweeds, as with other organisms, have thermal
 76 performance curves that show beneficial effects of increased temperature at suboptimal
 77 temperature but detrimental effects above a threshold (Lüning 1990). In order for some
 78 individual species of seaweed to survive rising sea surface temperature they will need to
 79 acclimate (on short timescales), adapt (on medium and long timescales) or migrate (by

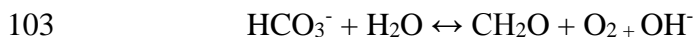
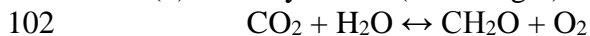
80 dispersion) (Wiencke & Bischof 2012). Seaweeds that are intertidal or have a broad
81 biogeographic range are more tolerant of temperature extremes than subtidal species and
82 those with narrower temperature ranges. The changes in temperature we see today are driving
83 a poleward shift in seaweed biogeographical regions (Wernberg et al. 2011). The tropical
84 region is widening polewards, to the detriment of organisms that occupy warm-temperate
85 regions and the cold-temperate regions are shrinking. Arctic seaweeds are at particular risk
86 due to warming winter temperatures (Wiencke & Bischof 2012). In coralline algae, a small
87 rise in temperature, within the range of temperature experienced in natural habitats, can
88 increase growth, photosynthesis and calcification in both temperate and tropical species
89 (Martin et al. 2006, Steller et al. 2007) but this has limits and rising temperature above these
90 levels is detrimental (Table 1). For example, Agegian (1985) showed that growth of tropical
91 *Porolithon gardineri* slowed dramatically at temperatures above 29-30°C. An increase of
92 +3°C above that normally experienced by coralline algae causes bleaching and adversely
93 affects health, survival, and the rates of photosynthesis and calcification in both tropical and
94 warm-temperate coralline algae (Anthony et al. 2008, Martin & Gattuso 2009, Diaz-Pulido et
95 al. 2011, Martin et al. 2013; Table 1).

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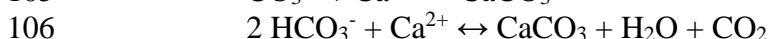
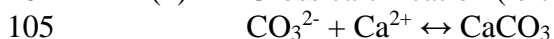
97 **4.2.2 Impact of ocean acidification on seaweeds**

98 Decreasing pH in the surface ocean will cause major shifts in seawater chemistry over the
99 course of this century that are likely to affect photosynthesis and calcification since these
100 processes use dissolved inorganic carbon (DIC: HCO_3^- , CO_3^{2-} and CO_2) as substrate

101 (1) Photosynthesis (left to right) and respiration (right to left) processes:



104 (2) Gross calcification (left to right) and dissolution (right to left) processes:

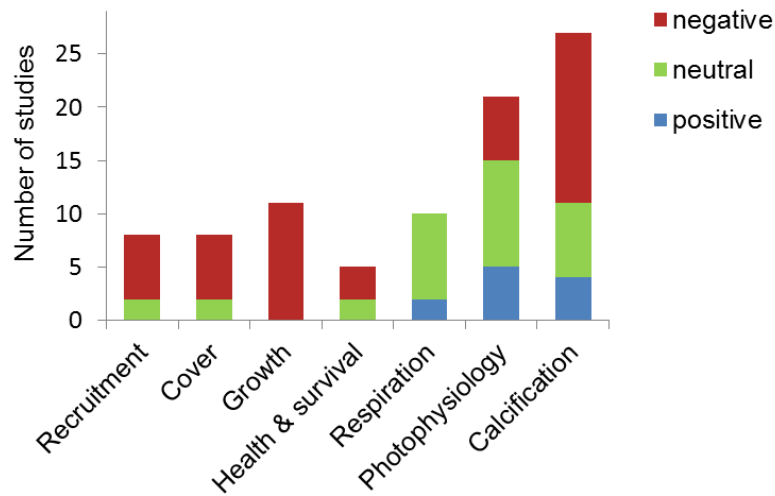


107 Algae can use dissolved CO_2 entering the cell by diffusion as the carbon source for
108 photosynthesis but most of them have carbon concentrating mechanisms which actively take
109 up HCO_3^- which is then converted to CO_2 in the cells (Raven et al. 2002, Hepburn et al. 2011,
110 Cornwall et al. 2012). This mechanism counteracts the limited availability of CO_2 in seawater
111 (Raven & Beardall 2003). An increase in seawater $p\text{CO}_2$ is expected to enhance photosynthesis
112 in primary producers that rely exclusively on CO_2 diffusion (Kübler et al. 1991) and may be
113 favourable to algae that can down-regulate their carbon concentrating mechanisms to save
114 energy (Hepburn et al. 2011, Cornwall et al. 2012, Raven et al. 2012).

115 Coralline algae are thought to be one of the groups of species most vulnerable to ocean
116 acidification due to the solubility of their high magnesium-calcite skeletons. Ocean
117 acidification is causing a decrease in the saturation state of calcium carbonate ($\Omega = [\text{Ca}^{2+}] \times$
118 $[\text{CO}_3^{2-}] / K_{\text{sp}}$) which is likely to affect the ability of marine calcifiers to form their carbonate
119 skeleton or shells by a decline in calcification rates (Kroeker et al. 2010). Although the
120 physiological response in terms of calcification is variable among taxa and species (Ries et al.
121 2009), seawater acidification is related to reduced growth rates in calcified macroalgae
122 (Kroeker et al. 2013). The recruitment and growth of coralline algae are usually negatively
123 affected under elevated $p\text{CO}_2$ (Table 1). Reductions in calcification rate at elevated $p\text{CO}_2$ have

124 been demonstrated for most coralline algae (Harley et al. 2012) but this response is variable
125 among species (Fig. 4, Table 1).

126



127
128

129 **Fig. 4. Summary of the expected direct effects of ocean acidification on coralline algae this century (based**
130 **on studies in Table 1). Negative, neutral and positive effects correspond to decreases, no change, and**
131 **increases in the processes, respectively. Photophysiology includes both photosynthesis and photosystem II**
132 **efficiency and relative electron transport rate.**

133

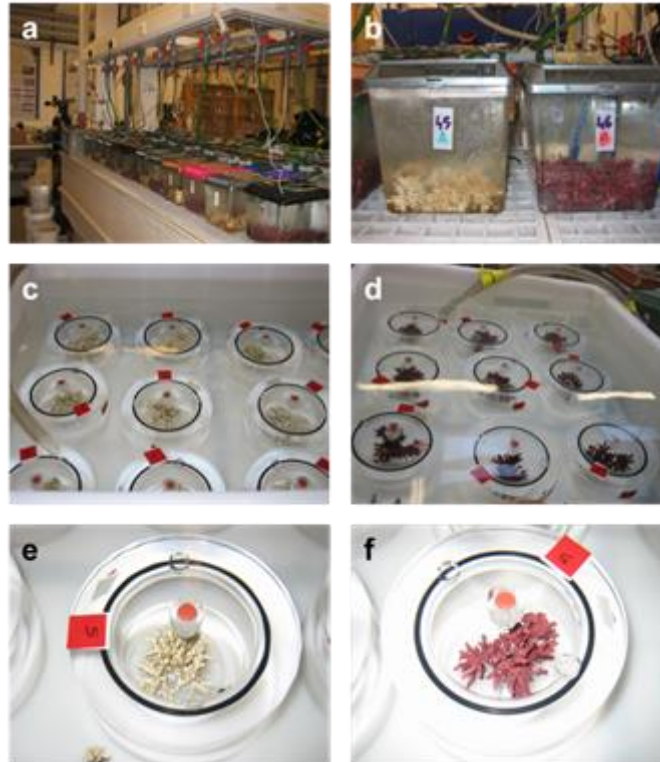
134 **4.2.3 Interactive effects of ocean warming and acidification on seaweeds**

135 While the effects of climate change and ocean acidification on seaweeds have mostly been
136 studied in isolation from each other, there is a lack of studies how these factors interact. The
137 combination of these two factors could however have a larger impact than alone. Recent studies
138 have effectively shown that the negative effect of ocean acidification on coralline algal
139 calcification is exacerbated by further ocean warming (Anthony et al. 2008). Some authors
140 reported a significant $p\text{CO}_2$ effect on coralline calcification, health and survival only in
141 combination with increased temperature, suggesting that elevated $p\text{CO}_2$ aggravates the
142 sensitivity of coralline algae to temperature (Martin & Gattuso 2009).

143

144 **4.2.4 Physiological response of coralline algae to climate change and ocean acidification**

145 Photosynthesis, respiration, and calcification in coralline algae are usually determined from
146 measurements of oxygen, DIC and alkalinity in incubation chambers (Fig. 5). Most of these
147 studies show that coralline algal calcification is negatively affected under elevated $p\text{CO}_2$ (Table
148 1) and that this effect is exacerbated by warming (Anthony et al. 2008). However, some work
149 only shows a significant $p\text{CO}_2$ effect on calcification when this is combined with an increase in
150 temperature (Martin & Gattuso 2009) and some experiments have shown a positive effect of
151 moderate increases in $p\text{CO}_2$ (Smith & Roth, 1979, Ries et al. 2009, Martin et al. 2013, Kamenos
152 et al. 2013). Such responses may be related to the ability of the algae to maintain an elevated
153 pH at the site of calcification despite reduced external pH to facilitate CaCO_3 precipitation
154 (Borowitzka 1987, Ries et al. 2009, Hurd et al. 2011, Cornwall et al. 2013b).



156

157 **Fig. 5. Experimental set-up (a) with replicated aquaria (b) supplied with seawater at ambient or elevated**
 158 ***pCO*₂ containing alive or dead *Lithothamnion glaciale* maerl that were incubated in Perspex chambers for**
 159 **metabolic fluxes analyses (c,e, dead maerl and d,f, live). Photograph by Sophie Martin (Experiments**
 160 **performed at Plymouth Marine Laboratory).**

161 The response of coralline photosynthesis to increased *pCO*₂ is also variable among species with
 162 negative, neutral, positive and parabolic responses (Table 1) that can depend on the light levels
 163 used (Martin et al. 2013). Studies investigating the effect of increased *pCO*₂ on respiration
 164 showed no response for most species (Fig. 4). Very few studies of coralline algae have
 165 investigated photosynthesis, respiration, and calcification all together yet we know that these
 166 processes are complex and tightly linked. Photosynthesis affects calcification through the
 167 formation of the fibrous organic matrix of the cell walls where the nucleation of calcite crystals
 168 is thought to occur (Borowitzka, 1981). In addition, both photosynthesis and respiration affect
 169 calcification through changes in pH that occur in the cell walls at the site of calcification (Smith
 170 & Roth 1979, Gao et al. 1993) but also in the diffusion boundary layer between the algal surface
 171 and external seawater (Hurd et al. 2011). Photosynthesis (or respiration) increases (or
 172 decreases) pH and thereby increases (or decreases) CaCO₃ saturation state, promoting (or
 173 hindering) the precipitation of CaCO₃. Coralline algae are able to maintain calcification in the
 174 dark even at the relatively low pH values generated by respiration. Digby (1977) and Hofmann
 175 et al. (2012b) postulate that carbonic anhydrase may also play a role in the calcification of
 176 coralline algae by catalysing the conversion of CO₂ into HCO₃⁻ and then CO₃²⁻. The stimulation
 177 of carbonic anhydrase activity could help prevent a decrease in calcification at elevated *pCO*₂
 178 as reported for the Mediterranean crustose coralline alga *Lithophyllum cabiochae* (Martin et al.
 179 2013). However, carbonic anhydrase is also used by photosynthesis to convert HCO₃⁻ to CO₂.
 180 The maintenance or enhancement of calcification rates under elevated *pCO*₂ in *L. cabiochae*
 181 may thus be detrimental to photosynthesis, as indicated by reduced photosynthesis under
 182 elevated *pCO*₂ (Martin et al. 2013).

183 The physiological response of maerl to warming and ocean acidification has been investigated
184 in *Lithothamnion corallioides* which is a temperate species (Noisette et al. 2013b) and
185 *Lithothamnion glaciale* which is a cold-water species (Büdenbender et al. 2011, Kamenos et al.
186 2013). In *L. corallioides* diel (24h) calcification decreased by 50% at 750 μatm and 80% at
187 1000 μatm , and in *L. glaciale* the thalli dissolve under elevated $p\text{CO}_2$ (Büdenbender et al. 2011).
188 Kamenos et al. (2013) found that at night *L. glaciale* calcified in the control treatment but
189 dissolved in the low pH treatment. In both species calcification is less affected by $p\text{CO}_2$ in the
190 light than in the dark, although in *L. glaciale* upregulated calcification occurs at low pH cf.
191 control treatments during the day (Noisette et al. 2013b, Kamenos et al. 2013). High latitude
192 maerl beds are at risk as surface waters are becoming more corrosive which is expected to cause
193 dissolution of these habitats (Büdenbender et al. 2011). Tropical rhodolith beds may also be
194 affected since in multispecies rhodoliths, made up of *Lithophyllum*, *Hydrolithon* and *Porolithon*
195 spp., there is a decrease calcification by 20-250% between control and acidified conditions
196 (Jokiel et al. 2008, Semesi et al. 2009).

197

198 **4.2.5 Response of early life stages to ocean acidification and warming**

199 Although fragmentation is the main source of new thalli in beds of rhodoliths and maerl, they
200 are initiated through recruitment from spores (Foster 2001). Unfortunately, there is mounting
201 evidence that ocean acidification and warming will have negative impacts upon the
202 recruitment and growth of early life history stages of coralline algae (Agegian 1985, Jokiel et
203 al. 2008, Kuffner et al. 2008, Russell et al. 2009, Porzio et al. 2013, Bradassi et al. 2013;
204 Table 1). Kuffner et al. (2008) found that impacts on settlement led to 90% lower tropical
205 crustose coralline cover at pH 7.9 than at pH 8.2. Some coralline algal species show a
206 reduction in reproductive structures in areas with naturally high $p\text{CO}_2$ conditions (Porzio et al.
207 2011) and germination of spores in the laboratory reveal developmental abnormalities and
208 increased mortality in acidified conditions. Bradassi et al. (2013) found that in acidified
209 conditions the germlings of an intertidal species of coralline algae were able to fight
210 dissolution by up-regulating their rates of calcification; this must increase energy costs and
211 helps explain why coralline algae are replaced by fleshy algae in naturally high $p\text{CO}_2$
212 conditions (Hall-Spencer et al. 2008, Porzio et al. 2013).

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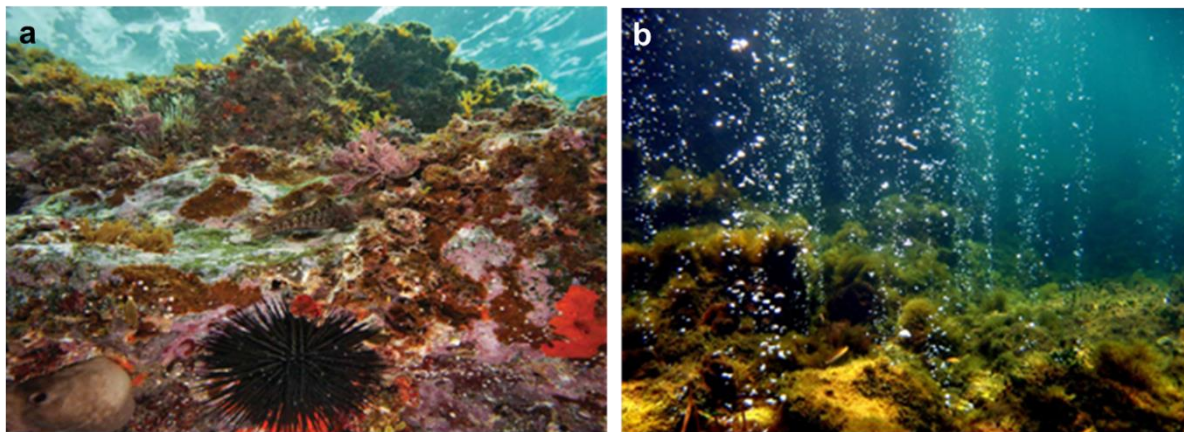
214 **4.2.6 Ecosystem level responses**

215 Most research into the effects of ocean warming and acidification has involved relatively
216 short-term (1 year or less) experiments on single species which makes it difficult to scale-up
217 and predict long-term effects at the community and ecosystem levels (Russell et al. 2013). To
218 tackle this, areas with naturally high CO_2 (and/or low pH and low calcium carbonate
219 saturation states) are being used to investigate which organisms can tolerate the long-term
220 consequences of ocean acidification and reveal how communities of primary producers
221 respond (Hall-Spencer et al. 2008, Johnson et al. 2012, Inoue et al. 2013). As with laboratory
222 and mesocosm experiments, the vent systems cannot accurately mimic future ocean
223 conditions; acidified areas are open systems so corallines can recruit from unaffected habitats
224 and grazing fish can swim in and out, these systems typically have large variations in
225 carbonate chemistry, and in some cases there are confounding factors that may mask or
226 amplify the effects of CO_2 . Some efforts have been made to determine the combined effects
227 of warming and acidification at such sites, although such work has so far been restricted to

228 corals, molluscs and bryozoans (Rodolfo-Metalpa et al. 2011). Some volcanic vents are
229 proving to be particularly useful ‘natural laboratories’ for the study of ocean acidification as
230 they reveal tipping points in recruitment, growth, survival and species interactions along
231 $p\text{CO}_2$ gradients (Porzio et al. 2011, 2013). Many species of microalgae, macroalgae and
232 seagrasses are remarkably tolerant of long-term exposures to high and variable carbon dioxide
233 levels at tropical and temperate CO_2 seeps (Johnson et al. 2012, 2013, Russell et al. 2013).
234 That they tolerate these conditions does not mean that they will necessarily thrive; seagrasses
235 for example lose the ability to defend themselves against herbivores and become over-run by
236 competing species of invasive seaweeds (Arnold et al. 2012).

237 One clear pattern in studies at multiple natural CO_2 gradients is that the Corallinales are
238 adversely affected (Porzio et al. 2011, Fabricius et al. 2011) which is a particular concern
239 since this group of organisms underpin maerl, rhodolith habitat production (Hall-Spencer et
240 al. 2010). At Mediterranean CO_2 seeps the Corallinales dissolve at low carbonate saturation
241 states (Martin et al. 2008) and are outcompeted by heterokont algae as CO_2 levels increase
242 (Fig. 6). Epilithic diatoms, Dictyotales (e.g. *Dictyota* spp., *Padina* spp.) and Fucales (e.g.
243 *Cystoseira* spp., *Sargassum* sp.) thrive as CO_2 levels increase although *Padina* spp. loose
244 calcification (Porzio et al. 2011, 2013, Johnson et al. 2012). At the ecosystem level the
245 coralligenous habitats loose biodiversity as carbonate levels fall along transects of increasing
246 levels of CO_2 ; benthic recruitment is disrupted in calcified organisms (Cigliano et al. 2010);
247 some organisms such as soft corals and anemones are tolerant but many are physiologically
248 unable to cope with the increased CO_2 levels (Suggett et al. 2012, Calosi et al. 2013, Inoue et
249 al. 2013). Reefs formed by an association between coralline algae and vermetid molluscs are
250 expected to become extinct this century unless CO_2 emissions are reduces and emergency
251 conservation measures are taken (Milazzo et al. 2014).

252



253

254 **Fig. 6.** Sea urchin and coralline algae dominated rocky shore at (a) ambient CO_2 (photograph by David
255 Liittschwager, National Geographic) and (b) the loss of coralline algae and proliferation of diatoms and
256 phaeophytes at a CO_2 seep off Ischia, Italy (photograph by Luca Tiberti, Associazione Nemo).

257 Additional insights into the community-level effects of warming and ocean acidification are
258 beginning to come from longer-term multispecies laboratory experiments (Hale et al. 2011).
259 These also demonstrate that future increases in CO_2 are likely to have strong negative effects
260 on coralline algae and positive or neutral effects on noncalcified seaweeds both directly via
261 improved growth and indirectly via reduced consumption by calcified herbivores such as sea
262 urchins (Connell & Russell 2010, Diaz-Pulido et al. 2011, Cornwall et al. 2012, Olischläger et
263 al. 2012, Roleda et al. 2012, Olabarria et al. 2013). It is clear that the impact of climate

264 change and ocean acidification on rhodolith/maerl beds will depend on the combined
265 influence of direct environmental impacts on individual species and indirect effects mediated
266 by changes in interspecific interactions (Harley et al. 2012). For example, ocean acidification
267 may disrupt invertebrate recruitment to maerl/rhodolith beds by altering chemical settlement
268 cues associated with crustose coralline algae, as shown with coral recruits (Doropoulos &
269 Diaz-Pulido 2013).

270 Ocean warming and acidification degrade the habitat complexity of coralline algal sediments
271 with profound effects since these algae induce settlement and recruitment of numerous
272 invertebrates. The rapid rate of physicochemical change is predicted to cause a shift from
273 calcareous to fleshy algal-dominated coastal ecosystems (Hall Spencer et al. 2008, Hoegh-
274 Guldborg et al. 2007, Anthony et al. 2011, Diaz-Pulido et al. 2011). Given that
275 rhodolith/maerl habitats usually only form in waters that have high carbonate saturation states,
276 the spread of low saturation state waters in upwelling areas, lowered salinity water masses and
277 in polar waters, are likely to reduce their habitat complexity and thus cause biodiversity loss.
278 Beds of unattached coralline algae provide nursery grounds and habitat for numerous
279 commercial species of invertebrates and fishes (Kamenos et al. 2004a,b) so a decline in these
280 habitats due to dissolution is also likely to have serious consequences for society and
281 economy through the impact on fisheries.

282

283 **4.2.7 Impact on global C and CaCO₃ budget**

284 Rhodolith/maerl beds are a significant component of carbon and carbonate cycles in shallow
285 coastal ecosystems, being major contributors to CO₂ fluxes through high community
286 photosynthesis and respiration (Martin et al. 2005, 2007) and through high CaCO₃ production
287 and dissolution (Martin et al. 2006, 2007). The habitats formed by coralline algae are
288 expected to be degraded by ocean acidification and warming as they have slow growth rates
289 and are easily corroded due to their soluble high Mg-calcite skeletons. Any major decline in
290 coralline algae would have dramatic consequences since they cover vast areas of rock and can
291 form very extensive beds on sediments (Amado-Filho et al. 2012). Changes in the balance
292 between algal carbonate production and dissolution induced by elevated pCO₂ and
293 temperature in maerl and rhodolith beds may have major implications for carbon dynamics in
294 coastal systems by affecting the carbonate chemistry of the water column and the ability of
295 the oceans to take up atmospheric CO₂ (Andersson et al. 2005).

296 In temperate maerl beds, *L. corallioides* calcification is expected to decrease by up to 80% at
297 1000 µatm pCO₂, relative to present day conditions of pCO₂ (Noisette et al. 2013b). This
298 would cause a reduction in CaCO₃ precipitation from a current value of *ca.* 500 g CaCO₃ m⁻²
299 y⁻¹ (Martin et al. 2007) to less than 100 g CaCO₃ m⁻² y⁻¹ in the near future under 1000 µatm
300 pCO₂ (Noisette et al. 2013b). The net calcification in maerl/rhodolith beds could even become
301 negative because the production of CaCO₃ will be exceeded by its dissolution (Martin &
302 Gattuso 2009). Arctic maerl beds are at particular at risk due to seawater becoming corrosive
303 to algal carbonate since live specimens of polar *L. glaciale* are corroded under elevated pCO₂
304 (Büdenbender et al. 2011). Dissolution also occurs in the dark in live maerl under elevated
305 pCO₂ in temperate maerl species (Noisette et al. 2013b; Kamenos et al. 2013). As maerl beds
306 are also composed of dead thalli, dissolution is likely to strongly increase; dissolution of dead
307 *L. glaciale* thalli increases by more than 10 fold from ambient condition to elevated pCO₂ of
308 *ca.* 1100 µatm (Kamenos et al. 2013). Precipitation and dissolution of CaCO₃ contribute to
309 the global CO₂ balance through shifts in the seawater carbonate equilibrium. The precipitation

310 of one mole of CaCO_3 ($\text{Ca}^{2+} + 2\text{HCO}_3^- \leftrightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$) releases *ca.* 0.6 moles of
311 CO_2 in seawater (Ware et al. 1992). In that way, the CO_2 released by calcification in
312 maerl/rhodolith beds will also be reduced. These changes will thus have major implications
313 for both carbon and carbonate budgets in coastal systems.

314

315 **4.2.8 Acclimation and adaptation**

316 The coralline fossil record for the past 300 Million years shows they have been able to survive
317 past mass extinctions including periods of very high CO_2 (Wood 1999). However, the present
318 rate of ocean change may be too rapid for genetic adaptation of habitat-forming coralline
319 algae. Work at CO_2 vents that are 100s of years old indicates that corallines have a limited
320 capacity to acclimate to ocean acidification, since most species are intolerant of chronic
321 exposures to increases in $p\text{CO}_2$ levels predicted this century and those that can survive are
322 outcompeted by fleshy algae (Martin et al. 2008, Porzio et al. 2011, Fabricius et al. 2012).
323 Localised seeps with high CO_2 levels are not well suited to the study of coralline algal
324 adaptation since they are open to colonization by algal spores from outside the acidified areas
325 and so presently we have no knowledge about the ability of rhodolith/maerl species to adapt
326 to present day rates of warming and acidification. We find it striking, however, that
327 rhodolith/maerl beds are common along the Atlantic seaboard of the Americas, where
328 carbonate saturation states are high, but they are scarce along the Pacific seaboard where
329 carbonate saturation states are low.

330 Adaptation is the evolutionary response of a population over multiple generations to
331 environmental changes but, according the current magnitude and rate of ocean warming and
332 acidification, the potential for evolutionary adaptation is limited in organisms with long
333 generation times such as coralline algae. However, coralline algae may have the potential to
334 adjust to modified environment within their lifetime (acclimation). In particular, the ability of
335 organisms to tolerate significant temperature and/or $p\text{CO}_2$ fluctuations may be a result of
336 adaptation (a genetic trait shared by the population) and/or acclimation (owing to phenotypic
337 plasticity of the individual). Organisms surviving in highly variable environments are likely to
338 be more robust. For instance, Egilisdottir et al. (2013) reported that coralline algae inhabiting
339 variable environments where $\text{pH}/p\text{CO}_2$ fluctuates naturally are likely to exhibit fewer negative
340 responses to elevated $p\text{CO}_2$ than those inhabiting relatively stable environments, supporting
341 the assumption of a greater resilience of organisms acclimated and/or adapted to highly
342 variable $\text{pH}/p\text{CO}_2$ environments of future ocean acidification.

343 Coralline algae may be able to tolerate ocean acidification through changes in the composition
344 of their skeletons (Agegian 1985, Ries et al. 2009, Egilisdottir et al. 2013). A decrease in
345 mMg/Ca ratio would confer resilience to elevated $p\text{CO}_2$ as this would lower the solubility of
346 their skeletons. However, it is questionable whether mineralogical plasticity associated with a
347 decrease in Mg incorporation will help since warming simultaneously increases Mg
348 incorporation (Agegian 1985). Dolomite (MgCO_3) rich crustose coralline algae have 6- to 10-
349 fold lower rates of dissolution than predominantly Mg-calcite species (Nash et al. 2013).
350 Dolomite-rich crustose coralline algae are widespread in shallow wave-exposed habitats in the
351 tropics but have not been recorded in cooler waters suggesting that its formation may be
352 constrained by temperature. Thus dolomite intracellular calcification may confer an advantage
353 on tropical corallines but not those found at higher latitudes (Nash et al. 2011). It is clear that
354 elevated $p\text{CO}_2$ weakens the skeletal structure in the high latitude maerl species *L. glaciale*
355 (Ragazzola et al. (2012).

356 Society can also help mitigate adverse effects of warming and acidification. In the NE
357 Atlantic steps have been taken to remove damaging dredging, fishing and aquaculture
358 practices to protect maerl beds in a network of protected areas (Chapter ##). If this approach
359 is adopted world-wide the reduced pressure on coralline algal systems would help increase
360 their resilience to the adverse effects of acidification and warming.

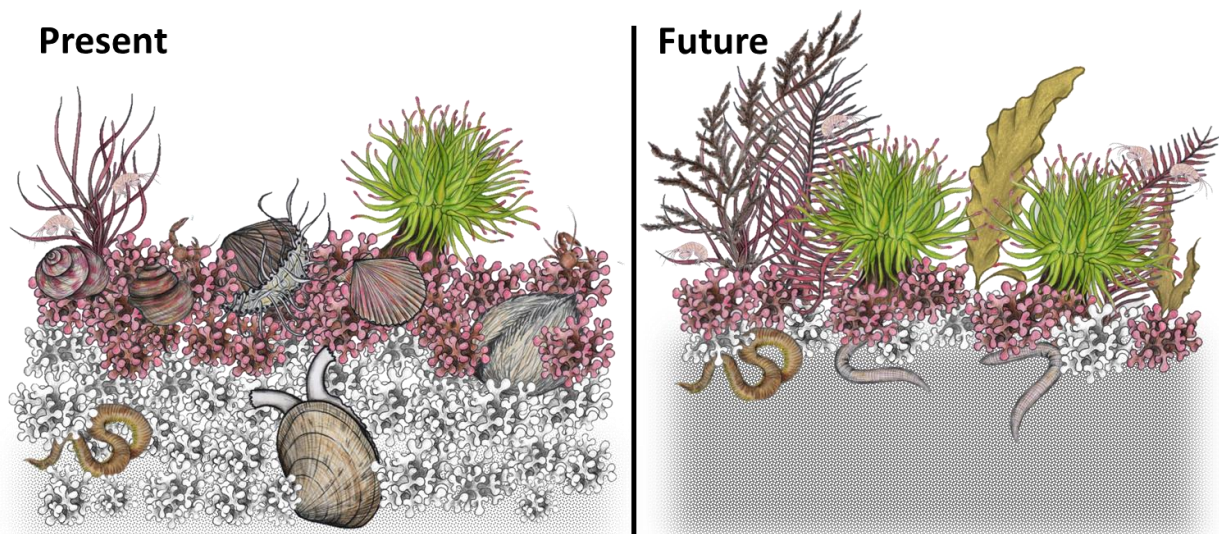
361

362 **4.3 Conclusions**

363 Beds of unattached coralline algae are scarce in waters with naturally low saturation states of
364 carbonate and are likely to decline in the near future as corrosive waters spread due to ocean
365 acidification. This will lead to a degradation of these ecosystems, reducing habitat
366 complexity and their associated biodiversity. Although responses to ocean warming and
367 acidification are variable among species, beds of maerl and rhodoliths are at risk at high
368 latitudes where seawater is becoming corrosive to their high Mg-calcite skeletons. Loss of
369 both live and dead maerl is expected to spread to lower latitudes over the century. Work on
370 the effects of ocean warming and acidification indicates that certain fleshy algae and non-
371 calcified animals may benefit and outcompete corallines and those calcified animals that
372 characterise these habitats (Fig. 7).

373 Given the importance of coralline algae, and the scale of the repercussions if they are
374 adversely impacted by rising CO₂ levels, concerted efforts are required to test whether our
375 concerns are justified. More detailed examinations of the physiology/ecology of corallines
376 need to be undertaken as we have an incomplete understanding of how OA and temperature
377 influence gross calcification, growth, dissolution and competitive interactions between
378 seaweeds. Given that society relies upon coralline algae for ecosystems services, such as
379 providing settlement cues or providing habitat for commercially important species, we
380 recommend that biological monitoring programmes begin as soon as possible since changes
381 may be occurring at a rate that will exceed the environmental niches of numerous coralline
382 alga taxa, testing their capacities for acclimation and genetic adaptation.

383



384

385 **Fig. 7. Predicted changes to a typical maerl bed with rising temperature and CO₂ levels. Present day**
386 **maerl beds with alive (above) and dead (below) unattached coralline are inhabited by a rich diversity of**
387 **calcifying (e.g. gastropods, bivalves, decapods, echinoids) and non-calcifying species. As waters become**
388 **corrosive to carbonate future maerl beds are expected to be degraded, with the loss of habitat complexity**
389 **and biodiversity, although certain fleshy macroalgae and non-calcified fauna (e.g. anemones, polychaetes,**
390 **amphipods) are expected to proliferate (drawing by Sophie Martin).**

391

392 **Credits**

393 IPCC 2013: Summary for Policymakers. In Climate Change 2013: The Physical Science
394 Basis. Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental
395 Panel on Climate Change, Figure SPM.7 (a) and (c); Figure SPM.8 (a) and (d). [Cambridge
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397

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404

405 **Figure legends**

406 **Figure 1.** Equilibrium between the three different species of dissolved inorganic carbon in
407 seawater. Atmospheric CO₂ is absorbed at the surface of the oceans where it combines with
408 the water molecules to form carbonic acid, which dissociates into bicarbonate, carbonate, and
409 hydrogen ions. Different forms of dissolved inorganic carbon (DIC = [CO₂] + [HCO₃⁻] +
410 [CO₃²⁻]) follow thermodynamic equilibria in seawater for the following reactions: CO₂ + H₂O
411 ↔ H₂CO₃ ↔ HCO₃⁻ ↔ H⁺ + CO₃²⁻ + 2H⁺.

412 **Figure 2.** Projected change in global annual mean surface temperature and global mean ocean
413 surface pH, relative to 1986-2005 for Representative Concentration Pathway 2.6 (blue) and
414 RCP8.5 (red) (Source: IPCC 2013).

415 **Figure 3.** Annual mean temperature and pH changes for the scenarios RCP2.6 and RCP8.5 in
416 2081-2100 relative to 1986-2005 (Source: IPCC 2013).

417 **Figure 4.** Summary of the expected impacts of ocean acidification on coralline algae this
418 century (based on studies in Table 1).

419 **Figure 5.** Experimental set-up (a) with replicated aquaria (b) supplied with seawater at
420 ambient or elevated pCO₂ containing alive or dead *Lithothamnion glaciale* maerl that were
421 incubated in Perspex chambers for metabolic fluxes analyses (c,e, dead maerl and d,f, live).
422 Photo S. Martin (Experiments performed at Plymouth Marine Laboratory).

423 **Figure 6.** Sea urchin and coralline algae dominated rocky shore at (a) ambient CO₂
424 (photograph by David Liittschwager, National Geographic) and (b) the loss of coralline algae

425 and proliferation of diatoms and phaeophytes at a CO₂ seep off Ischia, Italy (photograph by
426 Luca Tiberti, Associazione Nemo).

427 **Figure 7.** Predicted changes to a typical maerl bed with rising temperature and CO₂ levels.
428 Present day maerl beds with alive (above) and dead (below) unattached coralline are inhabited
429 by a rich diversity of calcifying (e.g. gastropods, bivalves, heart urchins) and non-calcifying
430 species. As waters become corrosive to carbonate future maerl beds are expected to be
431 degraded, with the loss of habitat complexity and biodiversity, although certain fleshy
432 macroalgae and non-calcified fauna (e.g. anemones, polychaetes) are expected to proliferate
433 (drawing by Sophie Martin).

434

435 **References**

436 Adey, W. H. 1973. Temperature control of reproduction and productivity in a subarctic
437 coralline alga. *Phycologia* 12: 111–118.

438 Agegian, C. R. 1985. The biogeochemical ecology of *Porolithon gardineri* (Foslie). PhD
439 thesis, University of Hawaii, Honolulu.

440 Amado-Filho GM, Moura RL, Bastos AC, Salgado LT, Sumida PY, Guth AZ, Francini-Filho
441 RB, Pereira-Filho GH, Abrantes DP, Brasileiro PS, Bahia RG, Leal RN, Kaufman L, Kleypas
442 JA, Farina M, Thompson FL (2012) Rhodolith beds are major CaCO₃ bio-factories in the
443 tropical South West Atlantic. *Plos One* 7: e35171.

444 Andersson AJ, MacKenzie FT, Lerman A (2005) Coastal ocean carbonate ecosystems in the
445 high CO₂ world of the Anthropocene. *American Journal of Sciences*, 305: 875–918.

446 Anthony KRN, Kline DI, Diaz-Pulido G, Dove S, Hoegh-Guldberg O (2008) Ocean
447 acidification causes bleaching and productivity loss in coral reef builders. *Proceedings of the*
448 *National Academy of Sciences of the United States of America* 105: 17442-17446.

449 Anthony KRN, Kleypas JA, Gattuso J-P (2011) Coral reefs modify their seawater carbon
450 chemistry – implications for impacts of ocean acidification. *Global Change Biology* 17: 3655-
451 3666.

452 Arnold T, Mealey C, Leahey H et al. (2012) Ocean acidification and the loss of protective
453 phenolics in seagrasses. *PLoS ONE* 7(4): e35107.

454 Blake C, Maggs CA (2003) Comparative growth rates and internal banding periodicity of
455 maerl species (Corallinales, Rhodophyta) from northern Europe. *Phycologia* 42: 606-612.

456 Borowitzka MA (1981) Photosynthesis and calcification in the articulated coralline red algae
457 *Amphiroa anceps* and *Amphiroa foliacea*. *Marine Biology* 62: 17-23.

458 Borowitzka MA (1987) Calcification in algae: mechanism and the role of metabolism. *Critical*
459 *Reviews in Plant Sciences* 6: 1-45.

460 Bradassi F, Cumani F, Bressan G, Dupont S (2013) Early reproductive stages in the crustose
461 coralline alga *Phymatolithon lenormandii* are strongly affected by mild ocean acidification.
462 *Marine Biology* 160: 2261-2269.

- 463 Büdenbender J, Riebesell U, Form A (2011) Calcification of the Arctic coralline red algae
464 *Lithothamnion glaciale* in response to elevated CO₂. Marine Ecology-Progress Series 441: 79-
465 87.
- 466 Calosi P, Rastrick SPS, Graziano M, Thomas SC, Baggini C, Carter HA, Hall-Spencer JM,
467 Milazzo M, Spicer JI (2013) Distribution of sea urchins living near shallow water CO₂ vents
468 is dependent upon species acid–base and ion-regulatory abilities. Marine Pollution Bulletin
469 73: 470-484.
- 470 Canadell JG, Le Quéré C, Raupach MR, Field CB, Buitenhuis ET, Ciais P, Conway TJ,
471 Gillett NP, Houghton RA, Marland G (2007) Contributions to accelerating atmospheric CO₂
472 growth from economic activity, carbon intensity, and efficiency of natural sinks. Proceedings
473 of the National Academy of Sciences of the United States of America 104: 18866–18870.
- 474 Cigliano M, Gambi MC, Rodolfo Metalpa R, Patti FP, Hall-Spencer JM (2010) Effects of
475 ocean acidification on invertebrate settlement at volcanic CO₂ vents. Marine Biology 157:
476 2489–2502.
- 477 Comeau S, Carpenter RC, Edmunds PJ (2012) Coral reef calcifiers buffer their response to
478 ocean acidification using both bicarbonate and carbonate. Proc R Soc B 280: 20122374.
- 479 Comeau S, Edmunds PJ, Spindel NB, Carpenter RC (2013) The responses of eight coral reef
480 calcifiers to increasing partial pressure of CO₂ do not exhibit a tipping point. Limnology and
481 Oceanography 58: 388-398.
- 482 Connell, S. D. & Russell, B. D. 2010. The direct effects of increasing CO₂ and temperature on
483 non-calcifying organisms: increasing the potential for phase shifts in kelp forests. Proceedings
484 of the Royal Society of London B Biological Sciences 277: 1409–15.
- 485 Cornwall CE, Hepburn CD, Pritchard D, Currie KI, McGraw CM, Hunter KA, Hurd CL
486 (2012) Carbon-use strategies in macroalgae: differential responses to lowered pH and
487 implications for ocean acidification. Journal of Phycology 48: 137-144.
- 488 Cornwall CE, Hepburn CD, McGraw CM, Currie KI, Pilditch CA, Hunter KA, Boyd PW,
489 Hurd CL (2013a) Diurnal fluctuations in seawater pH influence the response of a calcifying
490 macroalga to ocean acidification. Proceedings of the Royal Society B 280: 20122201.
- 491 Cornwall CE, Hepburn CD, Pilditch CA, Hurd CL (2013b) Concentration boundary layers
492 around complex assemblages of macroalgae: Implications for the effects of ocean
493 acidification on understory coralline algae. Limnology and Oceanography 58: 121-130
- 494 De Beer D, Larkum AWD (2001) Photosynthesis and calcification in the calcifying algae
495 *Halimeda discoidea* studied with microsensors. Plant Cell and Environment 24: 1209-1217.
- 496 Diaz-Pulido G, Gouzezo M, Tilbrook B, Dove S, Anthony K (2011) High CO₂ enhances the
497 competitive strength of seaweeds over corals. Ecology Letters 14: 156-162.
- 498 Diaz-Pulido G, Anthony KRN, Kline DI, Dove S, Hoegh-Guldberg O (2012) Interactions
499 between ocean acidification and warming on the mortality and dissolution of coralline algae.
500 Journal of Phycology 48: 32-39

- 501 Digby, P. 1977. Photosynthesis and respiration in the coralline algae, *Clathromorphum*
502 *circumscriptum* and *Corallina officinalis* and the metabolic basis of calcification. Journal of
503 the Marine Biological Association UK 57: 1111–1124.
- 504 Doropoulos C, Ward S, Diaz-Pulido G, Hoegh-Guldberg O, Mumby PJ (2012) Ocean
505 acidification reduces coral recruitment by disrupting intimate larval-algal settlement
506 interactions. Ecology Letters 15: 338-346.
- 507 Doropoulos C, Diaz-Pulido G (2013) High CO₂ reduces the settlement of a spawning coral on
508 three common species of crustose coralline algae. Marine Ecology Progress Series 475: 93-
509 99.
- 510 Egilisdottir H, Noisette F, Noel LMLJ, Olafsson J, Martin S (2013) Effects of pCO₂ on
511 physiology and skeletal mineralogy in a tidal pool coralline alga *Corallina elongata*. Marine
512 Biology 160: 2103-2112.
- 513 Fabricius KE, Langdon C, Uthicke S, Humphrey C, Noonan S, De'ath G, Okazaki R,
514 Muehllehner N, Glas MS, Lough JM (2011) Losers and winners in coral reefs acclimatized to
515 elevated carbon dioxide concentrations. Nature Climate Change 1: 165-169.
- 516 Foster MS (2001) Rhodoliths: Between rocks and soft places. Journal of Phycology 37: 659-
517 667
- 518 Gao K, Aruga Y, Asada K, Ishihara T, Akano T, Kiyohara M (1993) Calcification on the
519 articulated coralline alga *Corallina pilulifera*, with special reference to the effect of elevated
520 CO₂ concentration. Marine Biology 117: 129-132
- 521 Gao KS, Zheng YQ (2010) Combined effects of ocean acidification and solar UV radiation on
522 photosynthesis, growth, pigmentation and calcification of the coralline alga *Corallina sessilis*
523 (Rhodophyta). Global Change Biology 16: 2388-2398.
- 524 Hale R, Calosi P, McNeill L, Mieszkowska N, Widdicombe S (2011) Predicted levels of
525 future ocean acidification and temperature rise could alter community structure and
526 biodiversity in marine benthic communities. Oikos 120: 661-674.
- 527 Hall-Spencer JM, Rodolfo-Metalpa R, Martin S, Ransome E, Fine M, Turner SM, Rowley SJ,
528 Tedesco D, Buia MC (2008) Volcanic carbon dioxide vents show ecosystem effects of ocean
529 acidification. Nature 454: 96-99.
- 530 Hall-Spencer JM, Kelly J & Maggs CA (2010) Background document for maerl beds. OSPAR
531 Commission, London. Publication 491/2010 36pp. ISBN 978-1-907390-32-6.
- 532 Harley CDG, Anderson KM, Demes KW, Jorve JP, Kordas RL, Coyle TA, Graham MH
533 (2012) Effects of climate change on global seaweed communities. Journal of Phycology 48:
534 1064-1078.
- 535 Hoegh-Guldberg O, Mumby PJ, Hooten AJ, Steneck RS, Greenfield P, Gomez E, Harvell
536 CD, Sale PF, Edwards AJ, Caldeira K, Knowlton N, Eakin CM, Iglesias-Prieto R, Muthiga N,
537 Bradbury RH, Dubi A, Hatziolos ME (2007) Coral reefs under rapid climate change and
538 ocean acidification. Science 318: 1737-1742.

- 539 Hepburn CD, Pritchard DW, Cornwall CE, McLeod RJ, Beardall J, Raven JA, Hurd CL
540 (2011) Diversity of Carbon use strategies in a kelp forest community: implications for a high
541 CO₂ ocean. *Global Change Biology* 17: 2488-2497.
- 542 Hofmann LC, Straub S, Bischof K (2012a) Competition between calcifying and noncalcifying
543 temperate marine macroalgae under elevated CO₂ levels. *Marine Ecology Progress Series*
544 464: 89-105.
- 545 Hofmann LC, Yildiz G, Hanelt D, Bischof K (2012b) Physiological responses of the
546 calcifying rhodophyte, *Corallina officinalis* (L.), to future CO₂ levels. *Marine Biology* 159:
547 783-792.
- 548 Hurd CL, Cornwall CE, Currie KI, Hepburn CD, McGraw CM, Hunter KA, Boyd P (2011)
549 Metabolically-induced pH fluctuations by some coastal calcifiers exceed projected 22nd
550 century ocean acidification: a mechanism for differential susceptibility? *Global Change*
551 *Biology* 17: 3254-3262.
- 552 Ichiki S, Mizuta H, Yasui H, Yamamoto H (2001) Effects of irradiance and water temperature
553 on the photosynthesis and growth of the crustose coralline alga *Lithophyllum yessoense* Foslie
554 (Corallinales, Rhodophyceae). *Bulletin of Fisheries Sciences, Hokkaido University* 52: 103–
555 109.
- 556 Inoue S, Kayanne H, Yamamoto S, and Kurihara K (2013) Spatial community shift from hard
557 to soft corals in acidified water. *Nature Climate Change* 3: 683-687.
- 558 IPCC (2013) Summary for Policymakers. In *Climate Change 2013: The Physical Science*
559 *Basis. Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental*
560 *Panel on Climate Change. Cambridge University Press (in press).*
- 561 Jokiel PL, Rodgers KS, Kuffner IB, Andersson AJ, Cox EF, Mackenzie FT (2008) Ocean
562 acidification and calcifying reef organisms: a mesocosm investigation. *Coral Reefs* 27: 473-
563 483.
- 564 Johnson MD, Carpenter RC (2012) Ocean acidification and warming decrease calcification in
565 the crustose coralline alga *Hydrolithon onkodes* and increase susceptibility to grazing. *Journal*
566 *of Experimental Marine Biology and Ecology* 434-435: 94-101.
- 567 Johnson VR, Russell BD, Fabricius KE, Brownlee C, Hall-Spencer JM (2012) Temperate and
568 tropical brown macroalgae thrive, despite decalcification, along natural CO₂ gradients. *Global*
569 *Change Biology* 18: 2792-2803.
- 570 Johnson VR, Brownlee C, Rickaby REM, Graziano M, Milazzo M, Hall-Spencer JM (2013)
571 Responses of marine benthic microalgae to elevated CO₂. *Marine Biology* 160: 1813-1824.
- 572 Kamenos NA, Burdett HL, Aloisio E, Findlay HS, Martin S, Longbone C, Dunn J,
573 Widdicombe S, Calosi P (2013) Coralline algal structure is more sensitive to rate, rather than
574 the magnitude, of ocean acidification. *Global Change Biology* 19: 3621–3628.
- 575 Kamenos NA, Moore PG, Hall-Spencer JM (2004a) Small-scale distribution of juvenile
576 gadoids in shallow inshore waters; what role does maerl play? *ICES Journal of Marine*
577 *Science* 61: 422-429.

- 578 Kamenos NA, Moore PG, Hall-Spencer JM (2004b) Nursery-area function of maerl grounds
579 for juvenile queen scallops *Aequipecten opercularis* and other invertebrates. Marine
580 Ecology Progress Series 274: 183-9.
- 581 Kato A, Hikami M, Kumagai NH, Suzuki A, Nojiri Y, Saka K (2013) Negative effects of
582 ocean acidification on two crustose coralline species using genetically homogeneous samples.
583 Marine Environmental Research (in press) doi: 10.1016/j.marenvres.2013.10.010.
- 584 King RJ, Schramm W (1982) Calcification in the Maerl Coralline Alga *Phymatolithon*
585 *calcareum*: effects of salinity and temperature. Marine Biology 70:197-204.
- 586 Koch M, Bowes G, Ross C, Zhang XH (2012) Climate change and ocean acidification effects
587 on seagrasses and marine macroalgae. Global Change Biology 19: 103-132.
- 588 Kroeker KJ, Micheli F, Gambi MC (2013) Ocean acidification causes ecosystem shifts via
589 altered competitive interactions. Nature Climate Change 3:156-159.
- 590 Kübler JE, Davison IR, Yarish C (1991) Photosynthetic adaptation to temperature in the red
591 algae *Lomentaria baileyana* and *Lomentaria orcadensis*. British Phycological Journal 26: 9–
592 19.
- 593 Kuffner IB, Andersson AJ, Jokiel PL, Rodgers KS, Mackenzie FT (2008) Decreased
594 abundance of crustose coralline algae due to ocean acidification. Nature Geoscience 1: 114-
595 117.
- 596 Lüning, K. 1990. Seaweeds. Their Environment, Biogeography, and Ecophysiology. Wiley
597 Interscience, London. 527 pp.
- 598 McGraw CM, Cornwall CE, Reid MR, Currie KI, Hepburn CD, Boyd P, Hurd CL, Hunter
599 KA (2010) An automated pH-controlled culture system for laboratory-based ocean
600 acidification experiments. Limnology and Oceanography: Methods 8: 686-694.
- 601 Martin S, Clavier J, Guarini J-M, Chauvaud L, Hily C, Grall J, Thouzeau G, Jean F, Richard J
602 (2005) Comparison of *Zostera marina* and maerl community metabolism. Aquatic Botany 83
603 (3), 161-174.
- 604 Martin S, Castets MD, Clavier J (2006) Primary production, respiration and calcification of
605 the temperate free-living coralline alga *Lithothamnion corallioides*. Aquatic Botany 85: 121-
606 128.
- 607 Martin S, Clavier J, Chauvaud L, Thouzeau G (2007) Community metabolism in temperate
608 maerl beds. I. Carbon and carbonate fluxes. Marine Ecology-Progress Series 335: 19-29.
- 609 Martin S, Cohu S, Vignot C, Zimmerman G, Gattuso J-P (2013) One-year experiment on the
610 physiological response of the Mediterranean crustose coralline alga, *Lithophyllum cabiochae*,
611 to elevated pCO₂ and temperature. Ecology and Evolution 3(3), 676-693.
- 612 Martin S, Gattuso JP (2009) Response of Mediterranean coralline algae to ocean acidification
613 and elevated temperature. Global Change Biology 15: 2089-2100.

614 Martin S, Rodolfo-Metalpa R, Ransome E, Rowley S, Buia MC, Gattuso JP, Hall-Spencer J
615 (2008) Effects of naturally acidified seawater on seagrass calcareous epibionts. *Biology*
616 *Letters* 4: 689-692.

617 Milazzo M, Rodolfo-Metalpa R, Chan VBS, Fine F, Alessi C, Thiyagarajan V, Hall-Spencer,
618 JM, Chemello R (2014) Ocean acidification impairs vermetid reef recruitment. *Scientific*
619 *Reports* 4: 4189

620 Nash MC, Opdyke BN, Troitzsch U, Russell BD, Adey WH, Kato A, Diaz-Pulido G, Brent C,
621 Gardner M, Prichard J, Kline DI (2013) Dolomite-rich coralline algae in reefs resist
622 dissolution in acidified conditions. *Nature Climate Change* 3: 268-272.

623 Nash MC, Troitzsch U, Opdyke BN, Trafford JM, Russell BD, Kline DI (2011) First
624 discovery of dolomite and magnesite in living coralline algae and its geobiological
625 implications. *Biogeosciences* 8: 3331-3340

626 Noisette F, Egilsdottir H, Davoult D, Martin S (2013a) Physiological responses of three
627 temperate coralline algae from contrasting habitats to near-future ocean acidification. *Journal*
628 *of Experimental Marine Biology and Ecology* 448: 179-187

629 Noisette F, Duong G, Six C, Davoult D, Martin S (2013b) Effects of elevated pCO₂ on the
630 metabolism of a temperate rhodolith *Lithothamnion corallioides* grown under different
631 temperatures. *Journal of Phycology* 49: 746-757

632 Olabarria C, Arenas F, Viejo RM, Gestoso I, Vaz-Pinto F, Incera M, Rubal M, Cacabelos E,
633 Veiga P, Sobrino C (2013) Response of macroalgal assemblages from rockpools to climate
634 change: effects of persistent increase in temperature and CO₂. *Oikos* 122: 1065-1079

635 Olischläger M, Bartsch I, Gutow L, Wiencke C (2012) Effects of ocean acidification on
636 different life-cycle stages of the kelp *Laminaria hyperborea* (Phaeophyceae). *Botanica*
637 *Marina* 55: 511-525

638 Pena V, Barbara I, Grall J., Maggs CA, Hall-Spencer JM (2014) The diversity of seaweeds on
639 maerl in the NE Atlantic. *Marine Biodiversity*: DOI: 10.1007/s12526-014-0214-7

640 Porzio L, Buia MC, Hall-Spencer JM (2011) Effects of ocean acidification on macroalgal
641 communities. *Journal of Experimental Marine Biology and Ecology* 400: 278-287

642 Porzio L, Garrard SL, Buia MC (2013) The effects of ocean acidification on early algal
643 colonization stages at natural CO₂ vents. *Marine Biology* 160: 2247-2259

644 Ragazzola F, Foster LC, Form AU, Anderson PSL, Hansteen TH, Fietzke J (2012) Ocean
645 acidification weakens the structural integrity of coralline algae. *Global Change Biology* 18:
646 2804-2812

647 Ragazzola F, Foster LC, Form AU, Büscher J, Hansteen TH, Fietzke J (2013) Phenotypic
648 plasticity of coralline algae in a high CO₂ world. *Ecology and Evolution* 3(10): 3436-3446

649 Raven JA, Beardall J (2003) Carbon acquisition mechanisms of algae: carbon dioxide
650 diffusion and carbon dioxide concentrating mechanisms. *Photosynthesis in algae*. Springer, pp
651 225-244.

- 652 Raven JA, Johnston AM, Kübler JE, Korb RE, McInroy SG, Handley LL, Scrimgeour CM,
653 Walker DI, Beardall J, Vanderkluft MA, Fredriksen S, Dunton KH (2002) Mechanistic
654 interpretation of carbon isotope discrimination by marine macroalgae and seagrasses.
655 *Functional Plant Biology* 29: 355-378.
- 656 Raven JA, Giordano M, Beardall J, Maberly SC (2012) Algal evolution in relation to
657 atmospheric CO₂: carboxylases, carbon-concentrating mechanisms and carbon oxidation.
658 *Philosophical Transactions of the Royal Society B* 367: 493-507.
- 659 Ries JB, Cohen AL, McCorkle DC (2009) Marine calcifiers exhibit mixed responses to CO₂-
660 induced ocean acidification. *Geology* 37: 1131-1134
- 661 Rodolfo-Metalpa R, Houlbreque F, Tambutte E, Boisson F, Baggini C, Patti FP, Jeffree R,
662 Fine M, Foggo A, Gattuso JP, Hall-Spencer JM (2011) Coral and mollusc resistance to ocean
663 acidification adversely affected by warming. *Nature Climate Change* 1: 308-312.
- 664 Roleda, M. Y., Boyd, P. W. & Hurd, C. L. 2012. Before ocean acidification: calcifier
665 chemistry lessons. *Journal of Phycology* 48: 840–3.
- 666 Russell BD, Thompson JA, Falkenberg LJ, Connell SD (2009) Synergistic effects of climate
667 change and local stressors: CO₂ and nutrient-driven change in subtidal rocky habitats. *Global
668 Change Biology* 15: 2153-2162.
- 669 Russell BD, Passarelli CA, Connell SD (2011) Forecasted CO₂ modifies the influence of light
670 in shaping subtidal habitat. *Journal of Phycology* 47: 744–752.
- 671 Russell BD, Connell SD, Uthicke S, Muehllehner N, Fabricius KE, Hall-Spencer JM (2013)
672 Future seagrass beds: increased productivity leading to carbon storage? *Marine Pollution
673 Bulletin* 73: 463-469.
- 674 Semesi IS, Kangwe J, Bjork M (2009) Alterations in seawater pH and CO₂ affect calcification
675 and photosynthesis in the tropical coralline alga, *Hydrolithon* sp. (Rhodophyta). *Estuarine
676 Coastal and Shelf Science* 84: 337-341.
- 677 Smith AD, Roth AA (1979) Effect of carbon dioxide concentration on calcification in the red
678 coralline alga *Bossiella orbigniana*. *Marine Biology* 52: 217–225.
- 679 Steller DL, Hernandez-Ayon JM, Riosmena-Rodriguez R, Cabello-Pasini A (2007) Effect of
680 temperature on photosynthesis, growth and calcification rates of the free-living coralline alga
681 *Lithophyllum margaritae*. *Ciencias Marinas* 33: 441-456.
- 682 Suggett DJ, Hall-Spencer JM, Rodolfo-Metalpa R, Boatman TG, Payton R, Pettay DT,
683 Johnson VR, Warner ME, Lawson T (2012) Sea anemones may thrive in a high CO₂ world.
684 *Global Change Biology* 10: 3015-3025.
- 685 Ware JR, Smith SV, Reaka-Kudla ML (1992). Coral reefs: Sources or sinks of atmospheric
686 CO₂? *Coral Reefs* 11: 127–130.
- 687 Wernberg T, Russell BD, Thomsen MS, Gurgel CFD, Bradshaw CJA, Poloczanska ES,
688 Connell SD (2011) Seaweed communities in retreat from ocean warming. *Current Biology* 21:
689 1828–1832.

- 690 Wiencke C & Bischof K (2012) Seaweed biology: Novel insights into ecophysiology, ecology
691 and utilization. Ecological Studies, 219. Springer-Verlag: Berlin, Heidelberg.
- 692 Wilson S, Blake C, Berges JA, Maggs CA (2004) Environmental tolerances of free-living
693 coralline algae (maerl): implications for European marine conservation. Biological
694 Conservation 120: 283-293
- 695 Wood R (1999) Reef evolution. Oxford University Press 414pp.
- 696 Wootton JT, Pfister CA, Forester JD (2008) Dynamic patterns and ecological impacts of
697 declining ocean pH in a high-resolution multi-year dataset. Proceedings of the National
698 Academy of Sciences USA 105: 18848-18853.