

Tidal downwelling and implications for the carbon biogeochemistry of cold-water corals in relation to future ocean acidification and warming

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Abstract

Cold-water coral (CWC) reefs are recognized as ecologically and biologically significant areas that generate habitats and diversity. The interaction between hydrodynamics and CWCs has been well studied at the Mingulay Reef Complex, a relatively shallow area of reefs found on the continental shelf off Scotland, UK. Within 'Mingulay Area 01' a rapid tidal downwelling of surface waters, brought about as an internal wave, is known to supply warmer, phytoplankton-rich waters to corals growing on the northern flank of an east-west trending seabed ridge. This study shows that this tidal downwelling also causes short-term perturbations in the inorganic carbon (C_T) and nutrient dynamics through the water column and immediately above the reef. Over a 14 h period, corresponding to one semi-diurnal tidal cycle, seawater pH overlying the reef varied by ca. 0.1 pH unit, while pCO_2 shifted by $>60 \mu atm$, a shift equivalent to a ca. 25 year jump into the future, with respect to atmospheric pCO_2 . During the summer stratified period, these downwelling events result in the reef being washed over with surface water that has higher pH, is warmer, nutrient depleted, but rich in phytoplankton-derived particles compared to the deeper waters in which the corals sit. Empirical observations, together with outputs from the European Regional Shelf Sea Ecosystem Model, demonstrate that the variability that the CWC reefs experience changes through the seasons and into the future. Hence, as ocean acidification and warming increase into the future, the downwelling event specific to this site could provide short-term amelioration of corrosive conditions at certain times of the year; however, it could additionally result in enhanced detrimental impacts of warming on CWCs. Natural variability in the C_T and nutrient conditions, as well as local hydrodynamic regimes, must be accounted for in any future predictions concerning the responses of marine ecosystems to climate change.

Keywords: biogeochemistry, climate change, cold-water corals, ecologically and biologically significant Areas (EBSAs), hydrography, ocean acidification, Vulnerable Marine Ecosystems (VMEs)

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Introduction

Cold-water coral (CWC) reefs grow in relatively specific environmental niches with regards to temperature and salinity, but also with respect to other parameters such as water currents (for food supply) and available oxygen (Dullo *et al.*, 2008; Roberts *et al.*, 2008). CWC reefs in the North Atlantic have been reported from depths of >600 m to shallower regions of 100–200 m, for example, on the continental slope, shelf and within fjords (Roberts *et al.*, 2006, 2009), where they provide highly complex habitats supporting rich associated

communities (Henry & Roberts, 2007; Roberts *et al.*, 2008). These reefs cross a variety of environmental gradients but are usually found on sloping topography, such as offshore banks, seamounts, or coral carbonate mounds (Wilson, 1979; Mortensen *et al.*, 2001; Roberts *et al.*, 2006). Interesting hydrodynamic features are often associated with these slope and reef structures; such features are suggested to be important for supplying a sufficient flux of food particles to support the reef and its associated communities (Davies *et al.*, 2009).

The interaction between hydrodynamics and CWCs has been well studied at the Mingulay reef complex (MRC) (Dullo *et al.*, 2008; Duineveld *et al.*, 2012), a relatively shallow CWC reef found on the continental shelf off Scotland, UK (Fig. 1). The Scottish western

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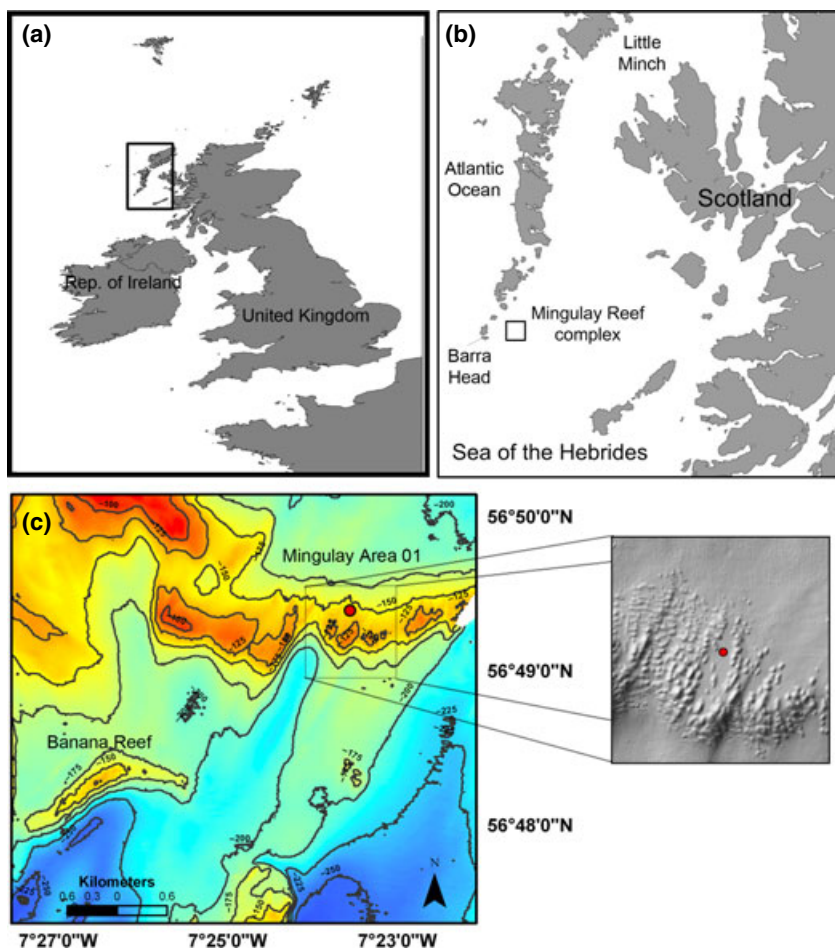


Fig. 1 Maps of study site location: (a) shown in relation to the UK, (b) off the coast of Scotland, and (c) bathymetric map of the Mingulay Reef Complex, showing Mingulay Area 01, Banana Reef and the location of the CTD station (red circle), also showing an enlarged swath image of the reef area nearest to the CTD station.

continental shelf has three main water sources: Atlantic water propagating northward from the west of Ireland, Irish Sea water passing northward through the North Channel, and coastal water created by the high volume of river runoff from the Scottish mainland (Craig, 1959; Ellett, 1979; Ellett & Edwards, 1983). Gillibrand *et al.* (2003) provide evidence of an intrusion of high salinity, high nutrient, Atlantic water into the Sea of the Hebrides, and a study carried out by Hill *et al.* (1997) using drifting buoys revealed a bifurcation of the northward coastal current in the Sea of the Hebrides, with a water mass passing through the Little Minch, recirculating southward current towards Barra Head.

Within the MRC two tidally controlled food supply mechanisms have been put forward, although their importance seems to vary across the complex: Within 'Mingulay Area 01' (Fig. 1) (Roberts *et al.*, 2005) a rapid downwelling of surface waters brought about as an internal wave impinges on an E-W trending ridge and supplies warmer, phytoplankton-rich waters to corals

growing on the N flank of the ridge. The reefs within Mingulay Area 01 also receive advected bottom waters rich in suspended particulate material (Davies *et al.*, 2009). In contrast, the reefs associated with the slightly deeper 'Banana Reef' (Fig. 1) (Roberts *et al.*, 2009) to the SW of Mingulay Area 01 receive the downwelled water pulse as an ebb tidal advection from the ridge where the Area 01 reefs have developed (Duineveld *et al.*, 2012).

In addition to its role supplying food particles to the reef, the downwelling at Mingulay Area 01 also affects physicochemical gradients through the water column, altering temperature and salinity at the reef top. Thus, it seems likely that carbon and nutrient conditions characteristic of the surface waters will also be drawn down towards the reef. Although these dynamics are expected, there is no data available for the Mingulay site and the distribution and variability in physicochemical parameters are currently unknown. The extent to which the reef itself influences the overlying

water chemistry is also yet to be determined, although tropical reefs have been shown to significantly influence the overlying water carbonate chemistry (Anthony *et al.*, 2011; Kleypas *et al.*, 2011).

Cold-water coral habitats are recognized through the United Nations [U.N. (United Nations), 2007] as Vulnerable Marine Ecosystems (VMEs) and through the Convention on Biological Diversity as Ecologically and Biologically Significant Areas [C.B.D. (Convention on Biological Diversity), 2008], and are therefore considered highly important sites. However, CWC reefs have been of specific concern with regards to ocean acidification (OA) for a number of years (Guinotte *et al.*, 2006; Roberts *et al.*, 2006; Turley *et al.*, 2007). OA, a lowering of pH and an associated shift in the carbonate system, results from an influx of anthropogenic CO₂ into the ocean, and will initially impact surface waters (Caldeira & Wickett, 2003). In addition, projections show that deeper waters will also be affected through the shoaling of the aragonite saturation horizon (ASH) (Orr *et al.*, 2005), as anthropogenic CO₂ penetrates into deeper waters. The ASH is the depth below which seawater becomes undersaturated with respect to aragonite, and therefore mineral dissolution occurs. CWCs are predicted to be particularly vulnerable to future OA primarily because the shoaling of the ASH will result in many of these reefs being exposed to water that is less favourable for skeletal growth (Guinotte *et al.*, 2006; Roberts *et al.*, 2006; Turley *et al.*, 2007). The MRC is located in relatively shallow waters (120–200 m) and therefore is unlikely to be at high risk of corrosion in the near future, resulting from a shoaling of the ASH. However, seasonal uptake of CO₂ into the surface waters, as well as local impacts such as coastal runoff, could potentially influence these more global-level stressors alongside progressively increasing seawater temperatures (see Dodds *et al.*, 2007).

In temperate regions, the seasonal cycle of total dissolved inorganic carbon (C_T) and pH within surface waters is generally such that during the spring and summer months of enhanced primary productivity, there is a drawdown in CO₂ and an increase in pH (e.g. Findlay *et al.*, 2008). Through the water column the carbon concentration increases, while pH decreases, due to enhanced respiration and remineralization of organic matter (Kitidis *et al.*, 2012). Thus, we predict that the downwelling surrounding relatively shallow CWC reef structures, such as the Mingulay reefs, will result in a tidally driven pulse of surface water pH being drawn down onto the reef. This will firstly expose the reef and its associated organisms to a much higher variability in carbonate system parameters than has previously been acknowledged (particularly in laboratory experiments) because of the lack of fine-scale temporal datasets;

while secondly, during the spring–summer this could provide short term alleviation from lower pH conditions of bottom waters. The main aims of this study were therefore to (1) investigate the extant conditions in terms of carbon biogeochemistry around the Mingulay reef as an example of a relatively shallow CWC reef; and (2) consider how tidally driven downwelling might impact the reef, with respect to potential ocean acidification and warming conditions projected for the end of the 21st century.

Materials and methods

Eight CTD and rosette sampling casts were carried out over a tidal cycle at the Mingulay reef site (56.823° N, 7.396° W, Fig. 1) between 21st and 23rd May 2012 (Table S1) during the RRS *James Cook* cruise JC073. A Sea-Bird 911 plus CTD system (9plus underwater unit and Sea-Bird 11plus deck unit) was used, with a Rosette water sampling unit, fitted with 10 L Niskin water bottles. Discrete water samples were taken at numerous depths throughout the water column; the deepest samples were taken ca. 2 m above the reef, using altimeter information on-board the CTD, and are referred hereafter as 'immediately above the reef'.

Pre-cruise laboratory calibrations of the conductivity, temperature and pressure sensors were performed, giving coefficients for a linear fit. A Sea-Bird 43 dissolved oxygen sensor, Chelsea Aquatracka MKIII fluorometer (set to detect Chlorophyll *a*: excitation wavelength of 430 nm and emission wavelength of 685 nm), and Chelsea Aquatracka MKIII Transmissometer, were also attached to the Rosette and used to measure dissolved oxygen, chlorophyll fluorescence, and particle attenuation coefficient (*C_p*; measured at wavelength of 660 nm; e.g. Behrenfeld & Boss, 2003 and references therein) respectively. For the analysis and interpretation of the measurements, the up-cast raw data were used (to match water column state at the time of bottle firing). Further processing of the data was performed using the software SBE Data Processing (V7.21 g) and Ocean Data View (V4.3.7) for visualization. The dissolved oxygen was calibrated against Winkler titrations (Hansen, 1999) made on water samples taken at various depths through the water column. The offset between titrations and sensor measurements was <1%.

Borosilicate glass bottles with ground glass stoppers (50 mL) were used to collect seawater from the Niskin bottles for the C_T and total alkalinity (A_T) analysis. Sample bottles were rinsed and filled according to standard procedures detailed in Dickson *et al.* (2007). Samples were poisoned with 10 µL mercuric chloride for storage and duplicate samples were taken from the same Niskin bottle. Samples were brought into the chemical laboratory onboard the RRS *James Cook*, normalized to room temperature (ca. 24 °C), and analysed for C_T and A_T within 24 h of collection.

Inorganic carbon was measured using a Dissolved Inorganic Carbon Analyser (Model AS-C3; Apollo SciTech, Bogart, GA, USA). The analyser adds a strong acid (10% H₃PO₄ plus 10% NaCl solution), which causes any carbon species within the seawater to be converted to CO₂. The resulting CO₂ gas is

purged from the water sample by the pure nitrogen (N₂) carrier gas. The N₂ gas flow carries the CO₂ from the sample through a drying system that includes a cooling process to reduce water vapour. The concentration of the dried CO₂ gas is then measured with the LICOR LI-7000 CO₂ analyser (a differential, nondispersive, infrared gas analyser). The total amount of CO₂ in the sample was quantified as the integrated area under the concentration–time curve, and converted to C_T using a standard curve created from analysing known concentrations of the Certified Reference Materials (Dickson, Batch 113). A measurement volume of 0.75 mL was used, with up to five measurements made from each sample. Values outside a 0.1% range were excluded from the final result. Duplicate measurements provided an estimate of measurement error = 0.2%. C_T was corrected to the CRM, and for the addition of mercuric chloride.

Total alkalinity was measured using the open-cell potentiometric titration method on 12 mL sample volumes using an automated titrator (Alkalinity Titrator Model AS-ALK2; Apollo SciTech). Calibration was made using Certified Reference Materials (Dickson, Batch 113). The analytical principle is described by Dickson *et al.* (2007). Duplicate measurements were made for each sample, and the estimate of measurement error = 0.4%. A_T was corrected to the CRM, and for the addition of mercuric chloride.

Duplicate samples for nutrients were collected from the CTD Niskin bottles directly after samples were taken for the carbon analysis. Fifty millilitre of collected seawater was filtered (0.45 µm acid-washed Millipore Fluoropore, Millipore, Watford, UK) into acid-cleaned, aged, 60 mL Nalgene bottles. Bottles were stored and shipped back frozen (−20 °C) to land. Analysis was carried out at Plymouth Marine Laboratory (Woodward & Rees, 2001) using a Bran and Luebbe AAIII segmented flow autoanalyser for the colorimetric determination of inorganic nutrients: combined nitrate and nitrite (Brewer & Riley, 1965), nitrite (Grasshoff, 1976), phosphate (Zhang & Chi, 2002) and silicate (Kirkwood, 1989). Nitrate concentrations were calculated by subtracting the nitrite from the combined nitrate+nitrite concentration.

Total alkalinity and C_T, together with depth, temperature, salinity, silicate and phosphate, were used to calculate the remaining carbonate system parameters (pH_T, pCO₂, Ω_{aragonite}) using the programme CO₂sys (Pierrot *et al.*, 2006), with dissociation constants from Mehrbach *et al.* (1973) refit by Dickson & Millero (1987) and KSO₄ using Dickson (1990).

Because of the obvious tidal influence, C_T and A_T were both normalized to a reference salinity (S^{ref} = 35) using standard methods [see Friis *et al.* (2003) for normalization discussion] to elucidate nonsalinity effects and from here on normalized values are denoted nC_T and nA_T respectively; for example, for measured A_T (A_T^{meas}) and measured salinity (S^{meas}):

$$nA_T = \frac{A_T^{\text{meas}}}{S^{\text{meas}}} \cdot S^{\text{ref}} \quad (1)$$

To assess the impact of ocean acidification and climate change on the biogeochemistry, simulated monthly mean values of pH, Ω_{aragonite} and chlorophyll and temperature were extracted from the 3D model POLCOMS-ERSEM (Blackford *et al.*, 2004; Artioli *et al.*, 2012; Wakelin *et al.*, 2012) for the

water column overlying the reef. Two different simulations have been used, one representing present-day (1981–2000) and one representing the end of the century (2080–2099) under the IPCC SRES-A1B scenario (a scenario resulting in global average atmospheric CO₂ concentrations of 700 ppm by year 2100 (Meehl *et al.*, 2007); but see Holt *et al.*, 2012 for more detail).

Results

Temperature & salinity

Water temperature ranged from 9.1 to 9.9 °C through the study period. A clear downwelling signal was observed through the tidal period, with warmer surface waters reaching >100 m depth just after the turn of the tide (Figure S1). Salinity ranged from 34.9 to 35.3 through the water column, with lower salinity at the surface as a result of freshwater inputs from land runoff and rainfall, and the salinity increased with depth. Again, the tidal downwelling is represented in the salinity data as a salinity decrease of 0.21 at 100 m depth at the turn of the tide (Figure S1a). The largest downwelling event occurs during the transition from northward to southward flow about every 12 h.

Fluorescence (chlorophyll), oxygen & particle attenuation coefficient

At the depth of the chlorophyll maximum (depth range 0.5–14 m), the chlorophyll fluorescence ranged from 0.29 to 0.51 µg L^{−1} through the tidal cycle. Directly above the reef the chlorophyll concentration was significantly lower, usually around 0.03–0.04 µg L^{−1}, but with a chlorophyll spike (0.081 µg L^{−1}) at the turn of the tide (Fig. 2). Integrated water column (0–116.5 m) chlorophyll fluorescence was 33.16 mg m^{−2} on 21st May. The chlorophyll maximum occurred at ca. 9 m on 21st May.

Oxygen saturation (%) decreased with depth from supersaturated conditions at the surface to <90% near the reef (Figure S1). Above the reef the oxygen saturation predominantly ranged between 87 and 89%, but increased to >93% at the turn of the tide, also associated with the fluorescence spike. Fluorescence showed an exponential relationship with oxygen, with the highest oxygen occurring where there was highest fluorescence ($r = 0.9618$, $P < 0.0001$, $df = 124$).

Particle attenuation coefficient was highest at depth, just above the reef, reaching values of 0.5–0.9 m^{−1} (Fig. 2). *C_p* decreased towards middepths of the water column (lowest values ca. 0.2 m^{−1}), and then increased again towards the surface (max values in the surface 0.5 m^{−1}). *C_p* had a strong positive relationship with fluorescence at values >0.05 µg Chl L^{−1} (Figure S2), such

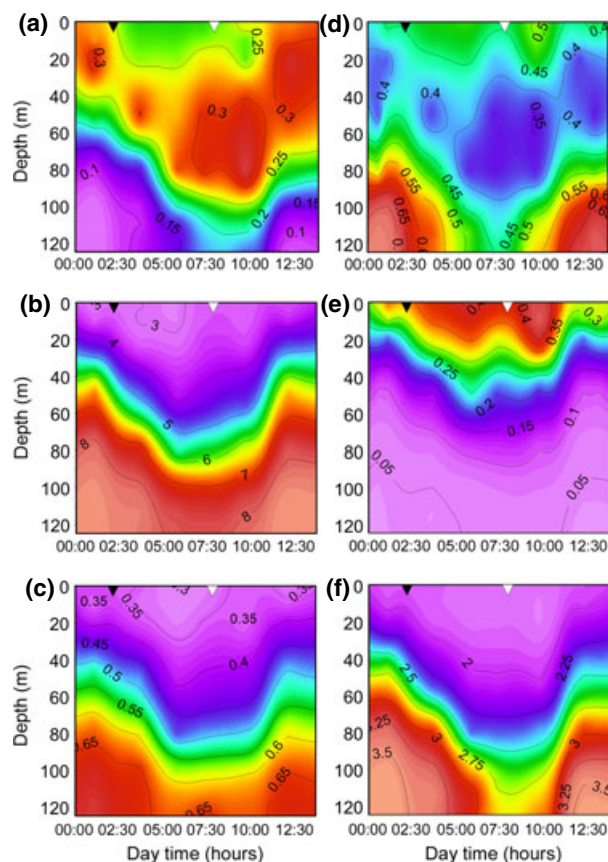


Fig. 2 Water column profile through the tidal cycle of (a) nitrite (μM), (b) nitrate (μM), (c) phosphate (μM), (d) particle attenuation coefficient (C_p), (e) fluorescence ($\mu\text{g Chl L}^{-1}$) and (f) silicate (μM). The black triangle represents the time of the low tide, and the white triangle represents the time of high tide.

that as fluorescence increased C_p increased ($r = 0.9311$, $P < 0.0001$, $df = 58$). Below $0.05 \mu\text{g Chl L}^{-1}$ C_p increased as fluorescence decreased; C_p increased to its highest values just above the reef (Figure S2). These observations illustrate that at least two fractions of particulates were represented here by C_p : first, new production: phytoplankton-derived material, produced in the surface waters; and secondly, older particulate material present at depth around the reef. Above the reef, through the tidal cycle, the C_p concentration remained primarily between 0.75 and 0.85, but decreased to <0.23 at the turn of the tide, associated with the downwelling.

Nutrients

Nitrate, phosphate and silicate all increased with depth (Table 1; Fig. 2). Nitrite concentration was highest in middepths, was slightly reduced in the surface waters corresponding to areas of greatest primary production,

Table 1 Mean ($\pm\text{SD}$) environmental conditions in the surface water (0–20 m, $N = 45$) and in the deep water (100–120 m, $N = 34$) immediately above the Mingulay Reef Complex. Measured values include salinity, temperature, total alkalinity (A_T) and dissolved inorganic carbon (C_T). Also, shown are A_T and DIC normalized to a salinity of 35 (nA_T and nC_T respectively); and calculated values for *in situ* pH (total scale), $p\text{CO}_2$ and saturation states of calcite (Ω_{Calcite}) and aragonite ($\Omega_{\text{Aragonite}}$). These parameters were calculated using CO_2sys (Pierrot *et al.*, 2006) with dissociation constants from Mehrbach *et al.* (1973) refit by Dickson & Millero (1987) and KSO_4 using Dickson (1990)

	Surface (0–20 m)	Deep (100–120 m)
Salinity	34.99 (± 0.02)	35.27 (± 0.03)
Temperature ($^{\circ}\text{C}$)	9.556 (± 0.14)	9.304 (± 0.02)
A_T ($\mu\text{mol kg}^{-1}$)	2303.3 (± 5.26)	2312.9 (± 4.07)
C_T ($\mu\text{mol kg}^{-1}$)	2079.7 (± 8.37)	2117.4 (± 9.27)
nA_T ($S=35$) ($\mu\text{mol kg}^{-1}$)	2303.6 (± 5.2)	2295.1 (± 3.5)
nC_T ($S=35$) ($\mu\text{mol kg}^{-1}$)	2080.0 (± 8.3)	2101.1 (± 8.3)
pH _T (<i>in situ</i>)	8.142 (± 0.018)	8.078 (± 0.020)
$p\text{CO}_2$ (μatm)	308.7 (± 14.1)	362.3 (± 18.4)
Ω_{Calcite}	3.79 (± 0.14)	3.29 (± 0.13)
$\Omega_{\text{Aragonite}}$	2.41 (± 0.09)	2.09 (± 0.08)

but was lowest immediately above the reef (Fig. 2a). Nitrite showed a strong negative correlation with C_p ($r = 0.8839$, $P < 0.0001$, $df = 96$). Nitrate concentration ranged from 2.8 to $4.75 \mu\text{M}$ in the upper 20 m, while above the reef nitrate concentration ranged from 7.88 to $8.91 \mu\text{M}$ (Fig. 2b). Phosphate was always $>0.6 \mu\text{M}$ below 100 m, but was always $<0.4 \mu\text{M}$ in the surface 20 m (Fig. 2c). Silicate concentration reached a maximum of $3.75 \mu\text{M}$ at depth but was reduced to a minimum of $1.5 \mu\text{M}$ in the surface waters (Fig. 2f).

Nitrate had a strong linear correlation with oxygen saturation ($r = 0.9819$, $P < 0.0001$, $df = 96$). Nitrate and phosphate both decreased as chlorophyll fluorescence increased, although this was nonlinear. The N : P ratio was 16.6 : 1, very close to the Redfield ratio (Redfield, 1958).

The downwelling event was evident in all the nutrient parameters, although the signal was weakest in phosphate, with approximately a 21% decrease in bottom water (100–120 m) concentration through the tidal cycle (Fig. 2).

Carbonate system

Inorganic carbon increased with depth, from $2079 \pm 8.37 \mu\text{mol kg}^{-1}$ in the upper 20 m, to $2117 \pm 9.27 \mu\text{mol kg}^{-1}$ above the reef (Table 1). A_T was relatively uniformly distributed throughout the water column, with A_T concentration approximately $10 \mu\text{mol kg}^{-1}$ greater at the surface (Table 1).

Normalized alkalinity (nA_T) remained relatively uniformly distributed throughout the water column, although there was a small reduction in nA_T at depth compared to the surface (Fig. 3); there was only a slight change through the tidal cycle. nC_T still showed a similar distribution through the water column to C_T , with lower carbon present in the surface waters compared to depth (Fig. 3). The downwelling event resulted in surface water, containing lower C_T concentrations, being drawn down to >100 m at the turn of the tide.

Surface water (0–20 m) C_T was negatively correlated with C_p ($r = 0.5125$, $P < 0.0001$, $df = 57$) and fluorescence ($r = 0.4655$, $P = 0.0002$, $df = 57$). The bottom waters (100–120 m) showed a reverse relationship, such that C_T was positively correlated with C_p ($r = 0.3874$, $P = 0.0024$, $df = 64$). The C : N ratio was 5.99 : 1, showing slightly lower C : N ratio than expected from the Redfield ratio (Redfield, 1958). The nA_T : nC_T ratio was –4.54 : 1 (Figure S3).

pH was highest in the surface waters (>8.13), and decreased with depth. When the downwelling was not occurring, pH near the reef was <8.04. In contrast, during the downwelling event, the drawdown of low C_T surface water to the reef resulted in the pH increasing to ca. 8.12 (Fig. 3c). Aragonite saturation state ($\Omega_{\text{aragonite}}$) showed a similar pattern to pH, such that in the surface waters $\Omega_{\text{aragonite}}$ was >2.35. Near the reef surface, during periods when downwelling was not

occurring $\Omega_{\text{aragonite}}$ was <2.1, which increased to 2.27 during the downwelling event (Fig. 3d). Undersaturation of $\Omega_{\text{aragonite}}$ (i.e., $\Omega_{\text{aragonite}} < 1$) was never observed at any point.

The lower C_T concentrations in the surface water resulted in a low pCO_2 (309 μatm), which then increased with depth (Table 1). Seawater pCO_2 did not exceed atmospheric pCO_2 during the period of observations (average global atmospheric CO_2 concentration for May was ca. 394 ppm, Dlugokenck & Tans, 2012), implying this region, at this time of year, is a potential sink for atmospheric CO_2 . pCO_2 varied by ca. 60 μatm during the tidal cycle immediately above the reef.

Discussion

This study investigated the short-term carbon and nutrient dynamics surrounding a CWC reef and the associated hydrodynamics. We provide empirical observations showing that a tidally induced internal wave (Davies *et al.*, 2009) can not only alter the physical environment above the reef (temperature, salinity) but also the biogeochemical environment experienced by the corals themselves.

Water column dynamics

Seasonal stratification normally occurs over the spring and summer months, resulting in an upper mixed layer with characteristically high primary production in the spring, a drawdown of C_T and nutrients progressing into summer, which eventually become limiting for primary producers. As a result of the tidally induced downwelling characteristic of Mingulay Area 01, the mixed layer extends deeper in the water column as a periodic pulse. The pycnocline rapidly shoals again after the initial downwelling event, thereby preventing continued mixing between the upper and lower water masses.

An uptake of carbon and nutrients from the surface waters by primary producers was observed, and is represented by the negative relationships found between C_T , nitrate and silicate against chlorophyll fluorescence. Chlorophyll fluorescence was relatively low during our sampling period, whilst nutrient concentrations were still relatively high and therefore had not yet become fully limiting. Similar chlorophyll fluorescence levels above the MRC have been observed previously (Davies *et al.*, 2009; Duineveld *et al.*, 2012). Davies *et al.* (2009) report fluorescence above the reef in 2006 that averaged around 0.04 $\mu\text{g L}^{-1}$ with downwelling 'spikes' of 0.08 $\mu\text{g L}^{-1}$ or greater, similar results were reported in Duineveld *et al.* (2012) for July 2007. However, Davies *et al.* (2009) report part of a 3 month dataset for 2007,

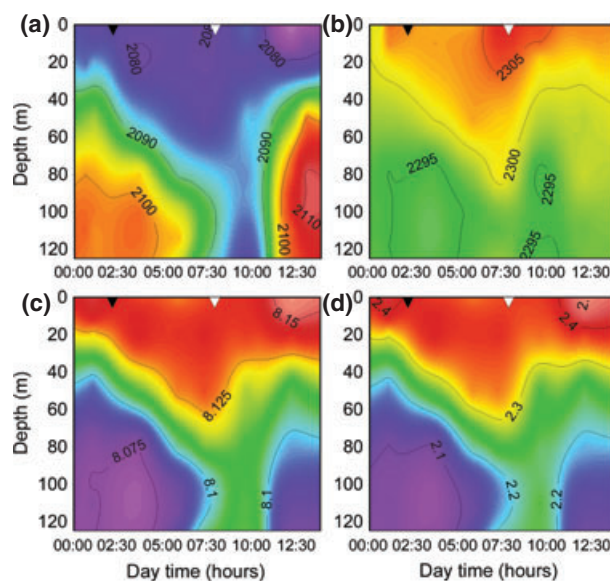


Fig. 3 Water column profile through the tidal cycle of (a) normalized dissolved inorganic carbon (nC_T , $\mu\text{mol kg}^{-1}$), (b) normalized total alkalinity (nA_T , $\mu\text{mol kg}^{-1}$), (c) pH (total scale) and (d) aragonite saturation state ($\Omega_{\text{aragonite}}$). The black triangle represents the time of the low tide, and the white triangle represents the time of high tide.

which shows the chlorophyll fluorescence above the reef can reach $>0.185 \mu\text{g L}^{-1}$ in August, suggesting that the values we observed were relatively low for the summer productive season, and were probably measured slightly before the peak conditions.

The calculated pCO_2 in the surface water was lower than the atmospheric pCO_2 ($>390 \mu\text{atm}$) at this time and therefore the surface water here is a potential sink for CO_2 . The downwelling event additionally acts as a daily pump of low C_T surface water to the reef (Fig. 3). During the ebb of the tide, C_T builds up below the thermocline, due to respiration processes within the reef, and the remineralization of organic matter. Advection of carbon along the reef will also result in additional carbon storage, potentially enhancing the seasonal pump described by Thomas *et al.* (2004).

Near-reef dynamics

In contrast to the surface waters, there were higher C_T and lower oxygen levels in the deeper waters overlying the reef, as would be expected in a heterotrophic system, where the reef and its associated community are remineralizing organic matter. Interestingly, the higher C_p immediately above the reef suggests that there was a high concentration of particles that had accumulated around the reef and were swept up from the reef into the water column. Indeed, the C_p dynamics observed here clearly match the current interpretation of food supply to the reef based on lander data: firstly, the internal wave supplies higher quality surface material during the downwelling period, and secondly tidal advection supplies bottom water rich in particles of poorer quality (Davies *et al.*, 2009). However, studies at the MRC to date indicate that the corals feed on the downwelling material (Duineveld *et al.*, 2012) augmented by predating on locally available zooplankton (Dodds *et al.*, 2009).

There was only a small increase in chlorophyll with the tidal pulse above the reef. The chlorophyll signal was smaller than that reported by Davies *et al.* (2009), primarily because of lower concentrations of chlorophyll present in the surface waters at the time of this study. This, together with the C_p data suggests that through an annual cycle, the CWC reef organisms are unlikely to rely solely on new production for their food, with the resuspension of organic material within the bottom waters driven by internal waves providing additional fluxes of nutrient supply to the corals and other reef epifauna (Thiem *et al.*, 2006; van Oevelen *et al.*, 2009).

The small decrease in nA_T near the reef, compared to surface waters, was in line with a small removal of alkalinity by calcification; although the dominant

processes that appear to influence the carbonate dynamics are photosynthesis and respiration (see below). As the reef was not currently situated in undersaturated water, dissolution of the calcium carbonate material that forms the large reef mounds underlying the living corals would not be expected. This prediction matches the observations of nA_T , as well as experimental observations of carbon mineralization and carbonate precipitation within the sediments associated with other CWC reefs found off the Norwegian shelf (Wehrmann *et al.*, 2009). Therefore, there was no indication of a large shift in the carbonate system in the overlying water column of this large carbonate reef structure, as has been found on tropical reefs (e.g. Anthony *et al.*, 2011). However, there was a greater influence on the carbonate system due to respiration at the reef itself, which corresponds with observations of high respiration rates on CWC reefs on the Norwegian Shelf (White *et al.*, 2012). Future measurements of the carbonate system upstream and downstream of the reef would be needed to determine the specific contribution of the reef to alkalinity generation and/or consumption. The C_T and A_T observations here are at the lower end, if not outside, of the range for suitable CWC habitat predicted using ecological-niche factor analysis (Davies *et al.*, 2008). However, $\Omega_{\text{aragonite}}$ is above the mean range (c.f. Table 3 in Davies *et al.*, 2008). It therefore seems that at this stage there are still not enough data to constrain the niche for CWCs with respect to C_T and nutrient conditions; especially regarding which carbonate parameters (e.g. $\Omega_{\text{aragonite}}$, CO_2 , pH and/or CO_3^{2-}) are most important for coral growth.

Over a 14 h period, corresponding to just over one tidal cycle, the pH in the water column overlying the reef (110–120 m) varied by ca. 0.1 pH unit (Fig. 3 and Figure S4). To the authors' knowledge, there are no other comparable pH data sets for CWC reefs on this short time-scale. Recently, Lunden *et al.* (2013) investigated carbonate dynamics across several CWC reef patches in the Gulf of Mexico showing pH to vary spatially by ca. 0.18 pH unit, although this is across a large depth range (>2000 – 300 m) and provides no indication of variability through time. In comparison with tropical shallow-water zooxanthellate reefs, which have been shown to experience diel fluctuations in pH up to 0.5 pH unit (Silverman *et al.*, 2007; Santos *et al.*, 2011; Gray *et al.*, 2012), the pH diel fluctuation for the MRC is therefore still comparatively small.

While we do not have longer term records for the carbon and nutrient dynamics, Davies *et al.* (2009) showed an excerpt from a 3 month record illustrating that the presence of the downwelling at the turn of the tide (four times daily) caused an increase in temperature and fluorescence close to the reef (measured ca. 2.5 m

above the sea floor). We would expect the tidal pulse to be present throughout the year, being correspondingly stronger/weaker through the spring/neap cycle respectively. The seasonal baseline projection for pH and saturation state can however be described using models (e.g. POLCOMS-ERSEM). Winter-time mixing causes the surface- and deep-water conditions to be similar and, therefore, a tidal downwelling during the well-mixed season would not add to the daily variability experienced at the reef. As stratification increases in spring and summer, phytoplankton in the upper water column will consume carbon dioxide and therefore increase pH. In contrast to these relatively large effects at the surface, seasonal changes from temperature or

remineralization of organic matter in bottom waters will only produce small changes in pH (Artoli *et al.*, 2012; Kitidis *et al.*, 2012). As the surface and bottom water conditions diverge, there will be increased variability associated with the downwelling pulse that occurs over the tidal cycle (Fig. 4). We therefore predict the highest variability will occur during the summer months, when there is a stratified water column.

Implications for future warming and ocean acidification

Our data show that CWC reefs, especially those found in relatively shallow settings, may experience a more variable biogeochemical environment than previously

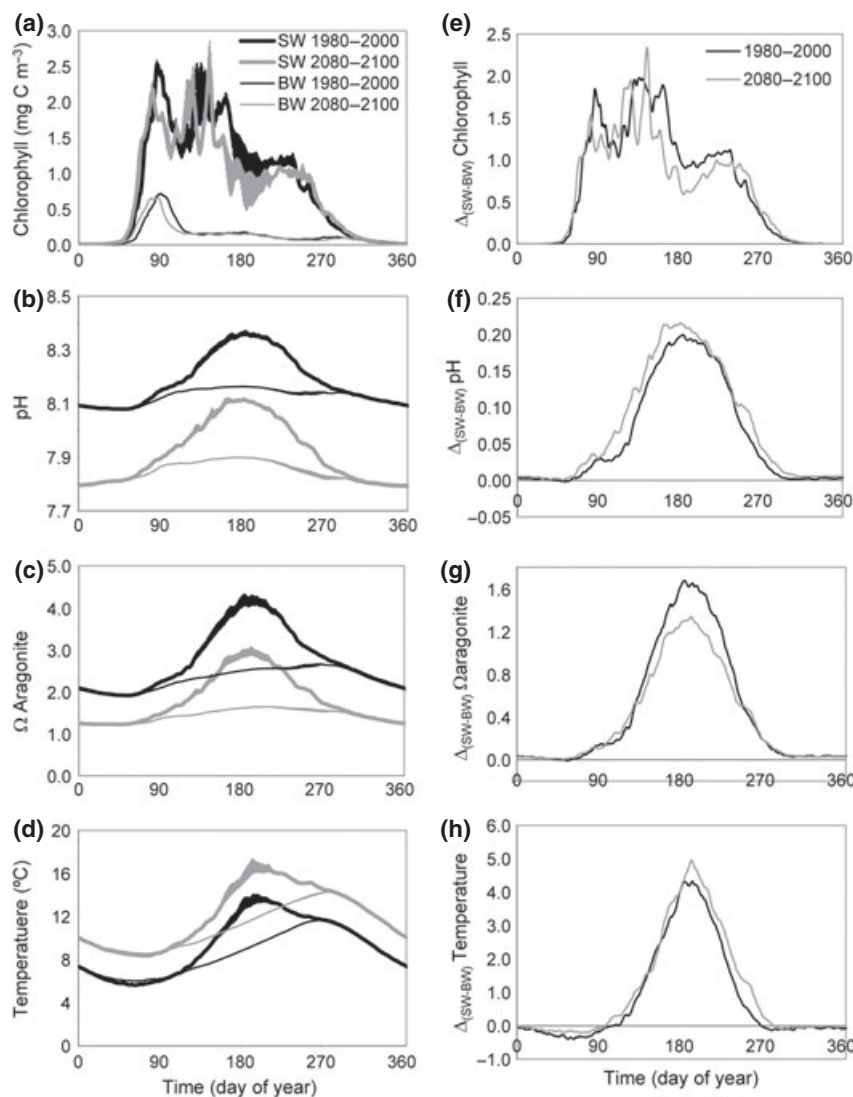


Fig. 4 POLCOMS-ERSEM output (for location of Mingulay Reef Complex, latitude 56.82° N, longitude 7.40° W) of (a–d) current (1980–2000 average) and future (2080–2100 average) seasonal cycles (daily values) of pH (SWS scale), aragonite saturation state, chlorophyll (mg m^{-3}) and temperature ($^{\circ}\text{C}$) in the surface waters (SW; 0–20 m average) and bottom water (BW; 100–120 m average). Difference between SW and BW conditions each day, for pH, aragonite saturation state, chlorophyll and temperature are shown (e–h).

thought (Turley *et al.*, 2007). This is especially important for making predictions about future conditions with respect to ocean acidification. Although there is likely to be a relatively small seasonal cycle in the carbonate system at the depths where many of these reefs are located, the daily tidal pulse of surface water at the MRC imposes additional variability onto the reef system. In the summer, when stratification normally prevents mixing, the variability should be greatest, with daily fluctuations in pH >0.2, depending on surface water primary production. While still not as large a range as experienced in some other coastal regions (e.g. Gray *et al.*, 2012), it is more than double the expected variation for the bottom waters, if there were no tidally induced downwelling; and is nearly 4× greater than the seasonal variation predicted by models (Fig. 4). Thus, this variability needs to be taken into account when assessing the potential vulnerability of CWC, and their associated fauna, to ocean acidification processes.

Guinotte *et al.* (2006) predicted that 70% of CWC locations would be in undersaturated waters, with respect to aragonite, by the year 2100. Thus, in the future, the overlying water will experience a reduction in saturation state, approaching saturation point. For example, the minimum $\Omega_{\text{aragonite}}$ in the 2080–2100 POLCOMS-ERSEM projections is ca. 1.20, which is 0.71 lower than 1980–2000 model minimum. Experimental studies on CWCs to date have shown that in short-term experiments corals have decreased respiration (Hennige *et al.*, in review), and generally have reduced net calcification and growth as the saturation state decreases (Form & Riebesell, 2012). However, over longer term studies in stable pH conditions, CWCs were shown to acclimate and maintain stable growth rates, with the implication that there may be an energetic trade-off to maintaining a calcified structure in lower saturation conditions (Form & Riebesell, 2012; Hennige *et al.*, in review) or that these organisms are already well-adapted to lower saturation state conditions (Form & Riebesell, 2012). Given that our study has demonstrated corals could be subjected to pCO₂ shifts >60 μatm during a 6 h period it is worth considering the value of short-term variable pCO₂ manipulation experiments over days to weeks in understanding CWC response to the natural pCO₂ (and pH) environment. Furthermore, as it is believed that the corals feed on downwelled material (Duineveld *et al.*, 2012), they may be most metabolically active during this low CO₂, high pH downwelling period, although the relative contributions and diurnal supply of downwelled algal material and zooplankton (Dodds *et al.*, 2009) to CWC nutrition are currently unknown.

Laboratory experiments should be interpreted carefully, especially with slow-growing organisms such as

CWCs as they may not respond on these short timeframes, as exemplified by the high levels of inconsistency observed in laboratory experiments to date. However, longer term experiments (Form & Riebesell, 2012) also have yet to account for possible energetic trade-offs within corals, and do not establish mechanistic responses to changes in CO₂; thus, again it is difficult to extrapolate these results to a naturally variable environment. Whether corals are able to respond to, and make use of, rapid shifts in conditions, as demonstrated in this study, is yet to be determined in experiments, although more *in situ* observations of coral response to variability are becoming available (e.g. Price *et al.*, 2012; Shaw *et al.*, 2012). If CWCs are able to take advantage of these transient conditions (e.g. Dodds *et al.*, 2007; Davies *et al.*, 2009) they may also, in the future, benefit from downwelled pulses of higher pH surface water conditions. One important consideration that is not accounted for here is that food supply (i.e. primary productivity) may also change in the future, through increased SST, shifts in nutrient conditions or ocean acidification (Lowe *et al.*, 2009); although the POLCOMS-ERSEM projections do not show significant shifts in chlorophyll concentration in the future (Fig. 4). Exactly how primary production will change into the future is still under debate; however, altered food supply will likely impact the reef's ability to cope with chronic shifts in environmental conditions (Dodds *et al.*, 2007).

Models predict that the whole range of pH and aragonite saturation state found through the water column could decrease into the future (Fig. 4). Overlying this climate signal, the seasonal cycle will continue to be an influence. Tidal downwelling seems set to be maintained, or perhaps even increase in intensity in the future if stratification becomes stronger with global warming (Lowe *et al.*, 2009), therefore the diurnal pulse of surface water to the reef will also continue, if not intensify. In the spring and summer months, this tidal downwelling could thereby alleviate corrosive conditions on the reef itself, and provide positive benefits for the CWCs. However, the model demonstrates that this variability could also potentially change into the future (Fig. 4), and especially during the winter, when the water is well-mixed, corrosive conditions are still likely to be an impact on these reefs.

It is important to remember that ocean acidification is not occurring in isolation, and that climate change is also increasing sea temperature, particularly in surface waters, as well as altering other environmental parameters such as salinity, by changing freshwater input and river run-off (Lowe *et al.*, 2009). The tidal downwelling at this site in the future may well provide a brief respite with respect to ocean acidification; however, this will

come with an associated increase in temperature, which may actually be of greater concern for these CWC. Sea surface temperatures (SST) are predicted to increase by 2–4 °C in shelf locations, such as the MRC, with summer periods experiencing temperatures >15 °C (Lowe *et al.*, 2009). Indeed, at the location of the MRC, the POLCOMS-ERSEM projections show July and August SST to be >16 °C with a maximum of 17.25 °C (Fig. 4). Therefore, during the downwelling periods, temperatures will move towards the high end, if not outside, these corals' thermal range (suggested to be 4–12 °C; Freiwald, 2002; Freiwald *et al.*, 2004). Moreover, future projections suggest that temperature could reach ca. 14 °C in the bottom water in the late summer (Fig. 4). Further investigation is required, as laboratory studies have shown that some CWCs can tolerate higher temperatures (i.e. Mediterranean *Desmophyllum dianthus* tolerates up to 17.5 °C, Naumann *et al.*, 2013), although both experimental and *in situ* data for *Lophelia pertusa* suggests that this species has an upper lethal temperature limit near 15 °C (Brooke *et al.*, 2013).

Habitat niche modelling has provided some indication of suitable locations for CWC reefs in the future (e.g. Tittensor *et al.*, 2010), with the suggestion that shelves and seamounts may provide refuge for CWCs from ocean acidification in the future. As it is known that many CWC reefs are located in highly dynamic environments, our analysis shows that the implications of these physical conditions must be taken into account when assessing habitat suitability as they alter the flux of carbon and nutrients to and from the reef, thereby shifting the biogeochemistry of the water column, as well as potentially affecting how the organisms themselves respond to shifting environmental conditions. Furthermore, at the MRC, the local topography and hydrodynamics result in a downwelling of low carbon water to the reef, but this may not be the same situation at all CWC sites. The influence of the local downwelling varies on very small scales across the MRC (Duineveld *et al.*, 2012), hence CWC reefs located at deeper sites that may be influenced by internal waves or other physical dynamics, could instead receive periodic upwelling of high C_T waters which would potentially exacerbate impacts of future ocean acidification (e.g. Feely *et al.*, 2008). While it is difficult to know how widespread the downwelling mechanism may be, given that CWCs, and *Lophelia* in particular, are found where hydrodynamic conditions promote efficient transfer of food particles from the surface to the seabed, we suggest that it seems highly likely that other CWC habitats will experience carbonate chemistry conditions akin to those we report for Mingulay Area 01, which reflect the distinctive properties of near-surface waters.

The rate of change in these environmental conditions justifies experiments on organisms over a variety of time-scales supported by continuous *in situ* recording of physicochemical conditions in the field. Understanding short-term vs. long-term responses to ocean acidification, for example, needs to be carried out in synchrony, and in addition to studies investigating variability and extreme conditions. Temperature shifts will also affect coral metabolism and functioning, and experiments have yet to assess how these two stressors might interact to impact on CWC. Furthermore, these organisms rely on pulsed inputs of food, with evidence of >30% carbon source coming from phytodetritus (van Oevelen *et al.*, 2009), and the level of starvation will also have an impact on how corals respond to additional stressors such as ocean acidification and warming (Dodds *et al.*, 2007). Further work is needed to calculate accurate carbon- and energy-budgets for these important deep-sea ecosystem engineers as without this it is impossible to make realistic inferences of their capacity to adapt to future global change. In turn, this understanding will inform the ecologically relevant future management of CWC habitats already recognized through the UN as VMEs and through the CBD as Ecologically and Biologically Significant Areas.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Figure S1. Salinity, temperature (°C), oxygen saturation (%) and fluorescence ($\mu\text{g Chl L}^{-1}$) profiles with depth, taken through the tidal period, colour bar represents the time of day (00:00 to 14:00) with the low tide and high tide indicated by the triangles.

Figure S2. Particle attenuation coefficient (C_p) and fluorescence ($\text{Chl } \mu\text{g L}^{-1}$) relationship using all data in the study period. The colour bar represents the depth of the water column (m).

Figure S3. Normalized dissolved inorganic carbon (nC_T , $\mu\text{mol kg}^{-1}$) and normalized total alkalinity (nA_T , $\mu\text{mol kg}^{-1}$) relationship using all data in the study period. The colour bar represents the depth of the water column (m).

Figure S4. Average (mean \pm SD) (a) pH (total scale) and (b) aragonite saturation state at each sample time during the tidal cycle at the surface (0–20 m, grey diamonds) and above the reef (100–120 m, black squares).

Table S1. Summary of CTD casts and samples taken during sampling period at Mingulay Reef Complex.