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Discussions

The influence of seawater pH on U / Ca ratios in the scleractinian cold-water coral *Lophelia pertusa*

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Abstract

The increasing pCO$_2$ in seawater is a serious threat for marine calcifiers and alters the biogeochemistry of the ocean. Therefore, the reconstruction of past-seawater properties and their impact on marine ecosystems is an important way to investigate the underlying mechanisms and to better constrain the effects of possible changes in the future ocean. Cold-water coral (CWC) ecosystems are biodiversity hotspots. Living close to aragonite-undersaturation, these corals serve as living laboratories as well as archives to reconstruct the boundary conditions of their calcification under the carbonate system of the ocean.

We investigated the reef-building CWC *Lophelia pertusa* as a recorder of intermediate ocean seawater pH. This species-specific field calibration is based on a unique sample set of live in-situ collected *L. pertusa* and corresponding seawater samples. These data demonstrate that uranium speciation and skeletal incorporation for azooxanthellate scleractinian CWCs is pH dependent. However, this also indicates that internal pH up-regulation of the coral does not play a role in uranium incorporation into the majority of the skeleton of *L. pertusa*. This study suggests *L. pertusa* provides a new archive for the reconstruction of intermediate water mass pH and hence may help to constrain tipping points for ecosystem dynamics and evolutionary characteristics in a changing ocean.

1 Introduction

Natural and anthropogenic changes in atmospheric pCO$_2$ strongly influence global climate. The present rise in pCO$_2$ increases the uptake of CO$_2$ by the oceans lowering seawater pH and carbonate ion concentration with severe impacts on marine calcifying organisms (Gattuso et al., 1999). Increasing pCO$_2$ values and decreasing aragonite saturation $\Omega_{arag} < 1 : \Omega_{arag} = [Ca^{2+}][CO_3^{2-}]/K^*_{arag}$, where K^*_{arag} is the stoichiometric solubility product of aragonite) causes the aragonite saturation horizon ($\Omega_{arag} > 1$)

to shoal and probably limits cold-water coral (CWC) growth and survival (Guinotte et al., 2006). In the modern high pCO$_2$ world, CWCs already live at low levels of carbonate saturation (Guinotte et al., 2006; Form et al., 2012; Tanhua et al., 2012). *Lophelia pertusa* (Fig. 1), the most prominent reef-building CWC, is frequently abundant along the European continental margin and mainly occurs in water depths between 200 and 1000 m. In contrast to their tropical counterparts CWCs are filter feeders and have no symbiotic algae enabling them to thrive in the deep dark waters of the oceans. Nevertheless, the modern distribution is limited by temperature and not by depth (Roberts et al., 2006). The tolerated temperature range of *L. pertusa* is 4–14 °C, but pristine reefs thrive between 6 °C on the Norwegian margin and 10 °C on the Irish margin (Roberts et al., 2006). In such environments single polyps can grow as fast as ~ 27 mm yr^{-1} (e.g. Gass and Roberts, 2010), comparable to their tropical counterparts (Dullo et al., 2005). However, recent studies have shown that these unique ecosystems of the North Atlantic have been sensitive to other environmental changes such as bottom currents and nutrient availability (e.g. Frank et al., 2011; Kano et al., 2007; Rüggeberg et al., 2007; Raddatz et al., 2011). Importantly, more than 95 % of living CWC reefs in the modern ocean occur above the aragonite saturation horizon (ASH) indicating that a lower seawater pH jeopardizes their existence (Guinotte et al., 2006). However, some studies indicate scleractinian CWCs are resilient to ocean acidification (e.g. Anagnostou et al., 2012; Form et al., 2011; McCulloch et al., 2012) in conditions with $\Omega_{arag} < 1$. This implies that they may have developed adaptive strategies to not only thrive in cool waters but also to survive under low carbonate saturations states. Biocalcification models suggest that, similar to zooxanthellate tropical corals, scleractinian azooxanthellate CWCs have physiological mechanisms to elevate the aragonite saturation in the extracellular calcifying fluid (ECF, Adkins et al., 2003; McConnaughey, 1989). This potentially complicates seawater pH reconstructions and needs to be explored further with different tracers.

In the past decades CWCs have been tested as archives for paleoceanographic reconstruction (e.g. Case et al., 2010; Cohen et al., 2006; Gagnon et al., 2007; Lutringer

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et al., 2005; Montagna et al., 2006; Smith et al., 2000; Raddatz et al., 2013a; Rollion-Bard et al., 2009; Rüggeberg et al., 2008). To date only a few studies focused on the reconstruction of the carbonate system using CWC skeletons (Anagnostou et al., 2011, 2012; Blamart et al., 2007; McCulloch et al., 2012; Rollion-Bard et al., 2011a, 2011b; Thresher et al., 2011). Coral uranium to calcium (U / Ca) ratios are known to depend on the carbonate system parameters (Anagnostou et al., 2011; Inoue et al., 2011; Min et al., 1995; Shen and Dunbar, 1995; Swart and Hubbard, 1982). Initial studies showed that coral U / Ca ratios are related to seawater temperature (Min et al., 1995; Shen and Dunbar, 1995), but also suggested that seawater pH may also play an important role in the incorporation of uranium into the skeleton of tropical corals. It was recently demonstrated that the U / Ca ratio in cultured warm-water corals mainly depends on seawater pH (Inoue et al., 2011). Additionally, Anagnostou et al. (2011) showed the U / Ca ratio of the solitary growing CWC *Desmophyllum dianthus* is not controlled by temperature but by the carbonate ion concentration $[CO_3^{2-}]$ in seawater. However, so far there has been no direct comparison of CWC U / Ca ratios to in situ measured seawater pH at the coral location. Here, we investigate the influence of seawater pH on U / Ca ratios in the scleractinian CWC *L. pertusa* and evaluate the potential to serve as a pH proxy for intermediate water masses.

2 Material and methods

Living CWC samples of *L. pertusa* were collected from different locations along the European continental margin (Fig. 2, Table 1). Samples were obtained with the manned submersible "JAGO" of GEOMAR (Kiel), the ROV "QUEST" of MARUM (University of Bremen), the ROV "Genesis" of RCMG (University of Ghent), a video-guided grab (TV-G) and a Van-Veen grab during different international cruises (POS325, POS391, M61, POS625, BEL10-17a and b, 64PE284, M70/1, COR2). Analysed samples were processed according to Rüggeberg et al. (2008) by using a dremel tool averaging several growth bands of the theca wall avoiding the centre of calcification (COC). Ad-

ditionally, to quantify the range of intra-skeleton U / Ca variations in *L. pertusa*, one longitudinal mid-plane section (Little Galway Mound, M61/1-218, Table 1) was chosen and seven sub-samples were drilled with a microcmill from the theca wall to the COC. Coral powder was weighed in Teflon beakers together with 2 mL 18.2 MΩ Milli-Q water. Samples were dissolved in 2 % HNO_3 and heated for at least 5 h in closed beakers and then dried at 90 °C. Organic matter was oxidised by adding 200 µL H_2O_2 (30 %) and 200 µL 2N HNO_3 and heated to 90 °C for at least 6 h in closed beakers and evaporated to dryness afterwards. Solutions were analysed for elemental ratios using an Agilent 7500 cs ICP-MS. In a first step, the Ca concentrations were measured and samples were diluted to have ∼ 10 ppm Ca before elemental analysis. Elemental / Ca ratios were calculated from the raw counts using an established method (Rosenthal et al., 1999) and calibrated using standards made from single element solutions. Six aliquots of *Porites* sp. coral powder reference material JCp-1 (Okai et al., 2002) were treated like the *Lophelia* samples and the average U / Ca value obtained during the course of this study ($n = 10$) was $1.21 \pm 0.02\ \mu mol\,mol^{-1}$. This agrees within the uncertainties with the recommended JCp-1 values (Okai et al., 2002; Hathorne et al., 2013b). Based on these results, the reproducibility (2 SD) of the U / Ca analyses was ∼ 0.89 %. Seawater pH data was taken from a study exclusively focusing on the seawater carbonate chemistry in CWCs reefs (Flögel et al., 2013). Briefly, physical and biogeochemical measurements of temperature, salinity, density, pressure, dissolved oxygen, pH, and DIC were conducted at sea and additional parameters sigma-theta (σ_Θ), $\Omega_{aragonite}$, HCO_3^{3-}, CO_3^{2-}, pCO_2, and TA (total alkalinity), were calculated using CO2SYS (http://cdiac.ornl.gov/oceans/co2rprt.html, Lewis and Wallace, 1998). All seawater pH values are reported using the "Total" pH scale and are thus given the standard notation of pH_T. In this study we only used the parameters determined for bottom waters close to coral sites.

3 Results

Our sample set is based on nine *L. pertusa* collected alive and corresponding in situ seawater samples (Fig. 2). The samples cover a wide range of seawater temperatures (6–14 °C), salinities (35.1–38.8 g kg^{-1}), water depths (290–881 m) and pH values (7.92–8.3, Flögel et al., 2013). Overall, the coral U/Ca ratios obtained from the theca wall vary from 1.13 to 1.97 µmol mol^{-1}. U/Ca ratios are not correlated with seawater temperature ($r^2 = 0.1$), carbonate ion concentration ($r^2 = 0.18$) or salinity ($r^2 = 0.01$, Fig. 3). But, the data clearly reveal that U/Ca measured away from the COC is significantly correlated with seawater pH, which can be described by the following equation:

$$U/Ca = -1.72 \pm 0.32 \, pH + 15.43 \pm 2.65 \, (p = 0.007, \ r^2 = 0.80, \text{ Fig. 4}), \qquad (1)$$

The intra coral U/Ca ratios vary from 1.14 to 2.07 µmol mol^{-1}. The highest values are observed within the theca wall and the lowest within the COC (Fig. 5). With respect to Eq. (1) this compositional variability within the coral skeleton would result in intra coral pH values between 7.76 (theca wall) and 8.30 (COC).

Limiting the U/Ca-pH calibration to samples from the North Atlantic this relationship can be described by the following equation:

$$U/Ca = 1.82 \pm 0.32 \, pH + 16.18 \pm 2.56 \, (p = 0.004, \ r^2 = 0.87, \text{ Fig. 4}). \qquad (2)$$

4 Seawater pH influence on uranium speciation and coral uptake

Our observations reveal that seawater pH has a strong influence on the U/Ca ratios measured in the skeleton of the CWC *L. pertusa* (Fig. 4). In particular, coral sites with the most contrasting seawater temperatures Stjernsund (6 °C) and Santa Maria di Leuca (14 °C) have remarkably similar seawater pH values of 8.30 and 8.25, respectively (Flögel et al., 2013). Since these samples have similar U/Ca ratios we can preclude any temperature dependence (Figs. 3 and 4). This is in contrast to the described incorporation of uranium into skeletons of tropical corals, where U/Ca ratios

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show a clear relationship to seawater temperature (Min et al., 1995; Shen and Dunbar, 1995). However, in *L. pertusa* U / Ca ratios decrease by almost 50 % from 2.0 to 1.1 µmol mol^{-1} with increasing pH values from 7.92 to 8.3 (Eq. 1, Fig. 4). In oxygenated aquatic systems, uranium is conservative and exists in the form of different carbonate complexes (Langmuir, 1978). Speciation is controlled by the carbonate ion forming complexes with the uranyl ion UO_2^{2+} (Djogic et al., 1986). Within a typical seawater pH range of > 8 most of the aqueous uranium exists in the form of $UO_2(CO_3)_3^{4-}$ (Reeder et al., 2000). With decreasing pH the aqueous species $UO_2(CO_3)_2^{2-}$ becomes more dominant and the proportion of bicarbonate $UO_2(CO_3)_2^{2-}$ and monocarbonate uranyl complexes ($UO_2CO_3^0$) also increase (Djogic et al., 1986). Our data suggest that a preferential uptake of bicarbonates and monocarbonate uranyl complexes can explain the inverse relationship between coral U / Ca ratios and seawater pH, which makes *L. pertusa* an archive for reconstructions of seawater pH.

In general, seawater pH can be measured with an uncertainty of ±0.01 pH (http://www.epoca-project.eu/index.php/guide-to-best-practices-for-ocean-acidification-research-and-data-reporting.html) and the external reproducibility of our U / Ca measurements is ±0.02 µmol mol^{-1} or 0.89 % (2 SD), hence both can be neglected compared to the error of the calibration slope (Eq. 1). Considering only the standard error of the U / Ca-pH calibration, paleo-pH values can be determined with an uncertainty of ±0.075 pH units, similar to the precision obtained with boron isotopes in CWCs (Anagnostou et al., 2012; McCulloch et al., 2012).

Even though the U / Ca-pH relationship covers a wide range of seawater pH this calibration appears to be controlled by the high pH seawater values in Stjernsund (Norwegian Margin) and Santa Maria di Leuca (Mediterranean Sea) as it is lacking coral sites with a seawater pH between 8.1 to 8.2. By limiting the calibration to pH values from 7.9 to 8.1, the r^2 of the resulting relationship is only 0.37. This highlights the need for future coral and seawater sampling to refine this U / Ca-pH relationship in scleractinian CWC. The scatter in the U / Ca data of 0.15 µmol mol^{-1} between a pH of 7.9 and 8 would result

in pH differences of ~ 0.1. Such a scatter could result from the micro-sampling technique and intra coral heterogeneity. Additionally, our calibration may be influenced by other environmental variables. As shown in Fig. 3, the U / Ca-salinity relationship in the Mediterranean Sea is different to that in the North Atlantic. Excluding samples from the Mediterranean Sea the U / Ca-pH relationship has a higher r^2 value of 0.87 (Fig. 4), but does not change in slope or intercept significantly. Clearly more detailed CWC U / Ca and seawater pH measurements are required, especially from different ocean basins, but our unique field calibration dataset suggests U / Ca in *L. pertusa* may compliment δ^{11}B measurements (Anagnostou et al., 2012; McCulloch et al., 2012) to reconstruct seawater pH.

4.1 The effect of coral physiology and symbiotic algae on uranium incorporation

The inverse relationship of U / Ca in the skeletons of *L. pertusa* with seawater pH is up to 8–9 times more sensitive compared to that found on warm-water corals (Inoue et al., 2011). Using a seawater U / Ca ratio of 1.305 μmol mol^{-1} (Chen et al., 1986), the partition coefficient $D = (U / Ca_{skeleton}) / (U / Ca_{seawater})$ varies between 0.9 and 1.6 and is in line with previous studies of U / Ca in CWCs (Anagnostou et al., 2011; Montagna et al., 2005; Sinclair et al., 2006). However, the observed CWC carbonate U / Ca ratios exhibit a two fold greater variability compared to tropical corals (Shen and Dunbar, 1995; Inoue et al., 2011), which cannot be explained by a simple temperature dependency of uranium incorporation as the sensitivity is ~ 0.03–0.05 μmol mol^{-1}/°C (Min et al., 1995; Shen and Dunbar, 1995). In tropical corals symbiotic algae consume CO_2 during photosynthesis and increase the pH of the ambient seawater at the coral surface. This symbiotic pH shift causes a dominance of the $UO_2 (CO_3)_3^{4-}$ species that could result in less U incorporation into the coral aragonite. Therefore, we suggest that symbiotic algae have an effect on the U / Ca ratios incorporated into tropical coral skeletons. Although CWCs have no symbionts, an internal pH up-regulation was demonstrated for both zooxanthellate and azooxanthellate corals (Anagnostou et al., 2012; McCulloch et

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al., 2012; Trotter et al., 2011). However, the $\Delta_{pH}(\Delta_{pH} = pH_{coral} - pH_{seawater})$ for scleractinian azooxanthellate CWCs appears to be higher (McCulloch et al., 2012). In particular, at the same seawater pH, CWCs show Δ_{pH} values up to 0.5 pH units higher than tropical corals inferred from boron isotopes and up to 1 pH unit higher than the ambient seawater pH (McCulloch et al., 2012). The differences in pH-up regulation leads to the conclusion that CO_2 consumption by symbiotic algae affects the internal pH and may suggest that tropical corals have to work less hard at the site of calcification. The higher U/Ca and steeper slope of U/Ca-pH observed for *L. pertusa* relative to tropical corals (Fig. 6) is consistent with this hypothesis. Moreover, this appears to be valid for both aragonite and calcite. A similar offset was also demonstrated for U/Ca ratios in calcitic planktonic foraminifera (Russel et al., 2004) and for $\delta^{11}B$ in *Globigerina bulloides* (no symbionts) and *Orbulina universa* (with symbionts, Hönisch et al., 2003).

Geochemical models of coral calcification suggest aragonite is precipitated from modified seawater within the ECF (e.g., Adkins et al., 2003). The carbonate ion concentration within the ECF is actively elevated above ambient seawater concentrations, facilitating crystal nucleation and coral growth (Adkins et al., 2003; Al-Horani et al., 2003; Holcomb et al., 2009). An elevated carbonate ion concentration is accompanied by a pH increase and hence changes the speciation of the uranyl ion. This would result in a lower U/Ca ratio in the COC and is consistent with the measured profile through the *L. pertusa* skeleton (Fig. 5). The observed compositional variability of U/Ca ratios within one single *Lophelia* polyp reveals, that in the COC the Δ_{pH} is > 0.5 compared to the rest of the skeleton (Fig. 5). Accordingly, this suggests that the coral does not manipulate the internal pH for the majority of the skeleton (theca wall) and *L. pertusa* may be susceptible to future ocean acidification. However, U/Ca ratios suggest the early mineralized COC regions have calcified from a solution with an elevated pH compared to the surrounding skeleton. A lower U content in the COC compared to the majority of the skeleton has been observed in other CWCs (Robinson et al., 2006; Sinclair et al., 2006). Some models attempting to explain the trace metal and isotope incorporation into corals suggest that Rayleigh fractionation from a closed system plays a significant

role (e.g Cohen et al., 2006; Gaetani and Cohen, 2006). In such models trace metals are incorporated into the aragonitic lattice from an ECF, which is initially similar to seawater in composition. However, several studies have shown that this cannot be the only controlling mechanism explaining trace metal incorporation during coral biomineraliza-
tion (Case et al., 2010; Gagnon et al., 2007; Hathorne et al., 2013a; Raddatz et al., 2013a). The same transect through this *L. pertusa* (Little Galway Mound, M61/1-218) skeleton reveals higher Mg / Ca and Li / Ca in the COC region (Raddatz et al., 2013a) with lower U / Ca. This opposing behaviour of U / Ca compared to Mg / Ca and Li / Ca has also been observed earlier in CWCs (e.g Case et al., 2010; Gagnon et al., 2007;
Sinclair et al., 2006; Raddatz et al., 2013a). The reason for the differences in the trace metal content of the COC versus the majority of the skeleton requires further study but our U / Ca data point to a potential role of pH up-regulation in CWCs.

5   Conclusions

A unique field calibration dataset reveals U / Ca ratios of the skeleton of *Lophelia pertusa* are inversely correlated with seawater pH. As scleractinian cold-water corals do not harbour symbiotic algae, uranium incorporation appears to be primarily controlled by the carbonate system of seawater and the coral physiology. U / Ca ratios in the majority of the skeleton of *L. pertusa* (avoiding early mineralization zones) reflect variations in seawater pH and may therefore be a promising tool to reveal climatically important pH changes of the intermediate ocean.

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Table 1. Meta data, in situ seawater characteristics (Flögel et al., 2013) and coral (*Lophelia pertusa*) U / Ca ratios.

Province	Latitude	Longitude	T	Salinity	Depth	U / Ca	pH	CO_3^{2-}	Ω_{arag}
			[°C]	[g kg^{-1}]	[m]	[µmol mol^{-1}]		[µmol kg^{-1}]	
Stj	70°16′04″ N	22°27′37″ E	6.0	35.1	365	1.13	8.30	209	3.03
SR	64°05′98″ N	08°05′86″ E	7.6	35.3	290	1.38	8.08	124	1.74
PSB (GM)	51°26′94″ N	11°45′16″ W	9.5	35.5	837	1.63	7.97	127	1.67
PSB (PM)	52°08′89″ N	12°46′31″ W	9.4	35.5	729	1.61	7.98	130	1.63
WC	48°46′79″ N	10°34′20″ W	9.8	35.5	835	1.59	7.97	133	1.73
GC	46°56′20″ N	05°21′60″ W	10.3	35.6	800	1.73	7.97	129	1.70
GoC	34°59′98″ N	07°04′51″ W	10.3	35.7	738	1.92	7.92	119	1.43
UB	36°50′34″ N	13°9′31″ E	13.5	38.8	651	1.75	8.07	278	2.83
SML	39°34′89″ N	18°23′00″ E	13.7	38.8	496	1.22	8.25	303	4.09

Stj = Stjernsund; SR = Sula Reef; PSB = Porcupine Seabight; GM = Galway Mound; PM = Propeller Mound; WC = Whittard Canyon
GC = Guilvenic Canyon; GoC = Gulf of Cadiz; UB = Urania Bank; SML = Santa Maria di Leuca.
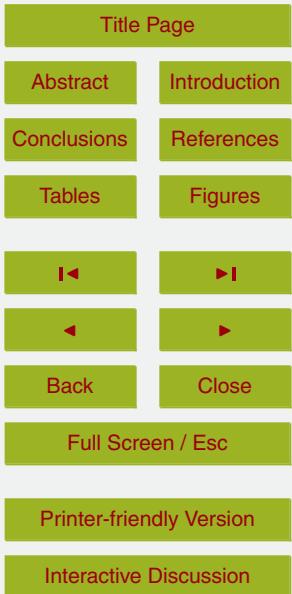
Fig. 1. Close up-picture of white *Lophelia pertusa* polyps extending their tentacles (Trondheims-fjord, Norway).
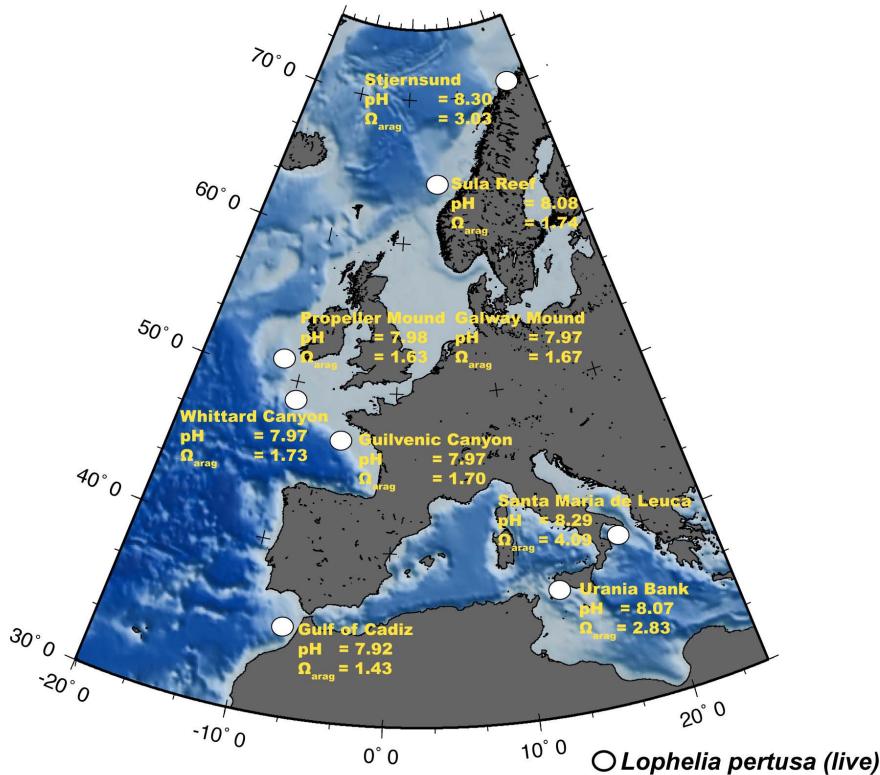
Fig. 2. Map showing sample location of live *Lophelia pertusa* samples and corresponding ambient seawater characteristics. The Propeller Mound and Galway Mound are both located in the Porcupine Seabight (PSB). The sample set covers a large range of seawater pH from 7.92 to 8.3 and seawater Ω_{arag} from 1.63 to 4.09. The GMT map is based on the ETOPO5 digital elevation file (http://www.ngdc.noaa.gov/).
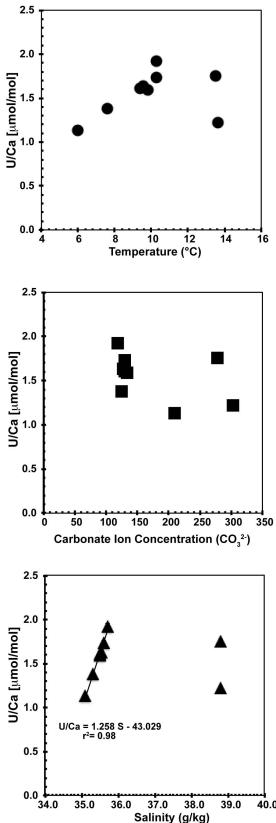
Fig. 3. Coral U / Ca ratios plotted against seawater temperature (°C), carbonate ion (CO_3^2) and salinity (g kg^{-1}). Only considering the Atlantic samples the U / Ca ratios reveal a significant relationship to salinity. However, this can be explained by a covariance between salinity and seawater pH. Error bars are smaller than the dots.
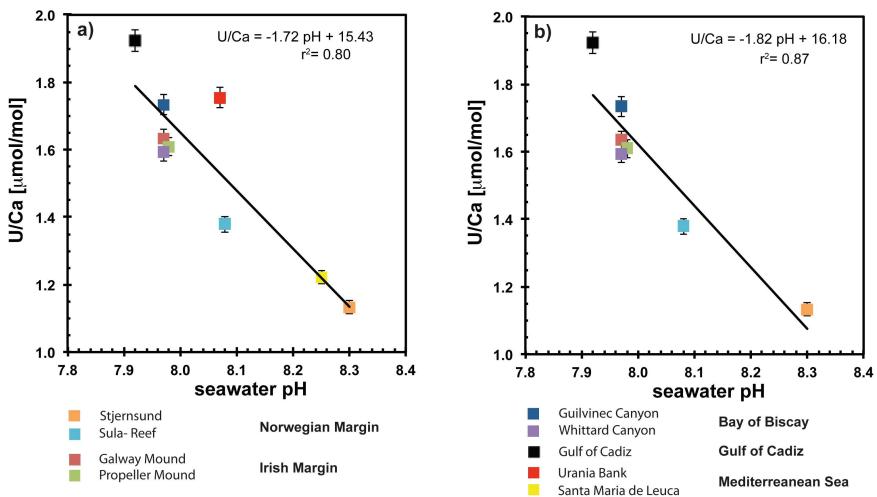
Fig. 4. In situ seawater pH values are plotted against U / Ca ratios in *Lophelia pertusa* of the entire samples set **(a)** and restricted to the North Atlantic samples **(b)**. All relationships show a significant correlation between U / Ca and pH, whereas only considering the North Atlantic samples, this relationship tends to have a smaller scatter.

Fig. 5. Compositional variability of intra-coral pH variations calculated from U / Ca ratios in *Lophelia pertusa* (Little Galway Mound M61/1-218) using Eq. (1). The centre of calcification (COC) reveals high intra-coral pH indicating coral pH up-regulation ($\Delta_{pH} = 0.5$). Error bars correspond to pH of ± 0.075.
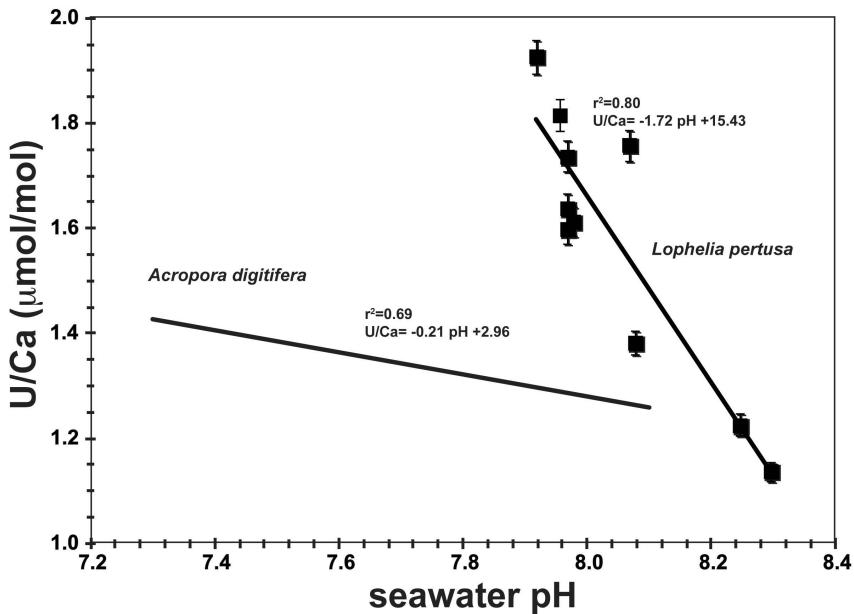
Fig. 6. In situ seawater pH and coral U / Ca ratios of the scleractinian azooxanthellate cold-water coral *Lophelia pertusa* avoiding the centre of calcification (COC). The *Lophelia*-U / Ca ratios show a significant relationship with seawater pH, Eq. (1). Also plotted is the U / Ca-pH relationship in the tropical coral *Acropora digitifera* (Inoue et al., 2011).