



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

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**Abstract.** The increasing  $p\text{CO}_2$  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 and can be reconstructed with an uncertainty of  $\pm 0.15$ . Our *Lophelia* U/Ca–pH calibration appears to be controlled by the high pH values and thus highlighting the need for future coral and seawater sampling to refine this relationship. However, this study recommends *L. pertusa* as 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  $p\text{CO}_2$  strongly influence global climate. The present rise in  $p\text{CO}_2$  increases the uptake of  $\text{CO}_2$  by the oceans, thus lowering seawater pH and carbonate ion concentration with severe impacts on marine calcifying organisms (Doney et al., 2009; Gattuso et al., 1999). Increasing  $p\text{CO}_2$  values and decreasing aragonite saturation ( $\Omega_{\text{arag}} < 1$ :  $\Omega_{\text{arag}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] / K_{\text{arag}}^*$ , where  $K_{\text{arag}}^*$  is the stoichiometric solubility product of aragonite) causes the aragonite saturation horizon ( $\Omega_{\text{arag}} > 1$ ) to shoal and probably limits cold-water coral (CWC) growth and survival (Guinotte et al., 2006). In the modern high- $p\text{CO}_2$  world, CWCs already live at low levels of carbonate saturation (Guinotte et al., 2006; Form and Riebesell, 2012; Tanhua and Keeling, 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  $\sim 27 \text{ mm year}^{-1}$  (e.g. Gass and Roberts, 2010), comparable to their tropical counterparts (Dullo, 2005). However, recent studies have shown that these



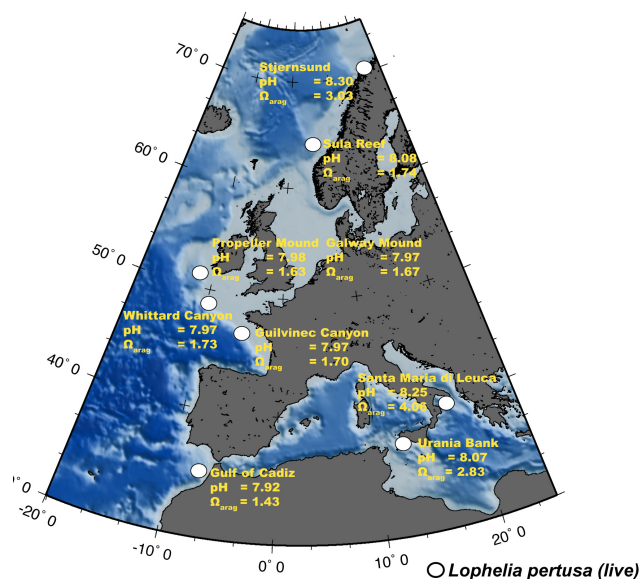
**Fig. 1.** Close-up picture of white *Lophelia pertusa* polyps extending their tentacles (Trondheimsfjord, Norway). Photo courtesy of Solvin Zankl, 2012.

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, 2014). 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 in conditions with  $\Omega_{\text{arag}} < 1$  (e.g. Anagnostou et al., 2012; Form and Riebesell, 2012; Maier et al., 2009; McCulloch et al., 2012). 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; Blamart et al., 2007; 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 palaeoceanographic reconstruction (e.g. Case et al., 2010; Cohen et al., 2006; Gagnon et al., 2007; Lutringer et al., 2005; Montagna et al., 2006; Raddatz et al., 2013; Rollion-Bard et al., 2009; Rüggeberg et al., 2008; Smith et al., 2000). To date only a few studies have 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, b; 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  $[\text{CO}_3^{2-}]$  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.

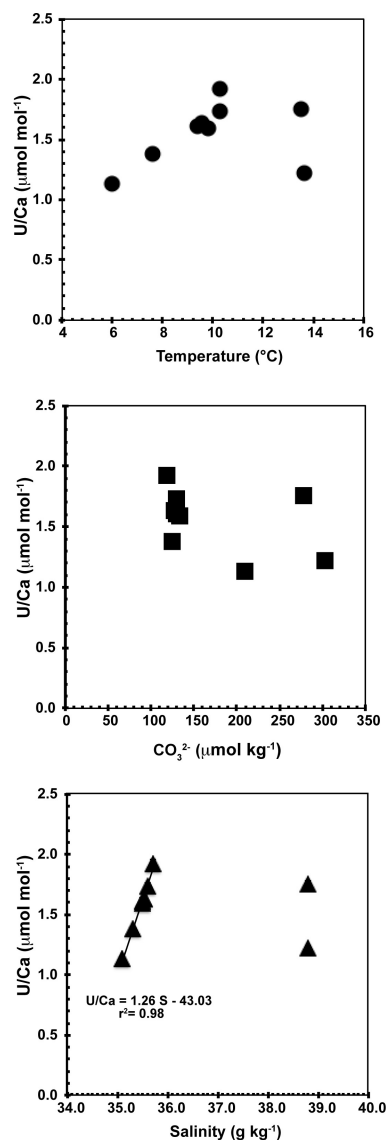
## 2 Material and methods

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 sampler 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). Additionally, to quantify the range of intra-skeleton U/Ca variations in *L. pertusa*, one longitudinal mid-plane section (Little Galway Mound, M61/1-218, temperature = 9 °C, salinity = 35.5 (g kg<sup>-1</sup>), 881 m water depth) was chosen, and seven sub-samples were drilled with a micromill 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<sub>3</sub> and heated for at least 5 h in closed beakers and then dried at 90 °C. Organic matter was oxidized by adding 200 μL H<sub>2</sub>O<sub>2</sub> (30 %) and 200 μL 2N HNO<sub>3</sub> and heated to 90 °C for at least 6 h in closed beakers and



**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  $\Omega_{\text{arag}}$  from 1.63 to 4.09. The GMT map is based on the ETOPO5 digital elevation file (<http://www.ngdc.noaa.gov/>).

evaporated to dryness afterwards. Solutions were analysed for elemental ratios using an Agilent 7500cs ICP-MS. In a first step, the Ca concentrations were measured and samples were diluted to have  $\sim 10$  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  $1.21 \pm 0.02 \mu\text{mol mol}^{-1}$  (2SD). This agrees within the uncertainties with the recommended JCP-1 values (Okai et al., 2002; Hathorne et al., 2013a). Based on these results, the reproducibility (2SD) of the U/Ca analyses was  $\sim 0.89\%$ . Seawater pH data were taken from a study exclusively focusing on the seawater carbonate chemistry in CWCs reefs (Flögel et al., 2014). Briefly, physical and biogeochemical measurements of temperature, salinity, density, pressure, dissolved oxygen, pH, and DIC (Dissolved Inorganic Carbon) were conducted at sea, and additional parameters  $\sigma_{\Theta}$ ,  $\Omega_{\text{aragonite}}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $p\text{CO}_2$ , and TA (total alkalinity) were calculated using CO2SYS (<http://cdiac.ornl.gov/oceans/co2rprt.html>, Lewis and Wallace, 1998). A WTW Multi 350i compact precision handheld meter was used to determine the pH of seawater. The reproducibility was  $< \pm 0.01$  pH. All seawater pH values are reported using the “total” pH scale and are thus given the



**Fig. 3.** Coral U/Ca ratios ( $\mu\text{mol mol}^{-1}$ ) plotted against seawater temperature ( $^{\circ}\text{C}$ ), carbonate ion concentration [ $\text{CO}_3^{2-}$ ] ( $\mu\text{mol kg}^{-1}$ ) and salinity ( $\text{g kg}^{-1}$ ). 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.

standard notation of  $\text{pH}_T$ . In this study we only used the parameters determined for bottom waters close to the coral sites measured by Flögel et al. (2014).

### 3 Results

Our sample set is based on nine *L. pertusa* samples collected alive and corresponding *in situ* seawater samples (Fig. 2). The samples cover a wide range of seawater temperatures (6–14  $^{\circ}\text{C}$ ), salinities (35.1–38.8  $\text{g kg}^{-1}$ ), water depths

**Table 1.** Metadata, in situ seawater characteristics (Flögel et al., 2014) and coral (*Lophelia pertusa*) U/Ca ratios.

Province	Latitude	Longitude	<i>T</i> (°C)	Salinity (g kg <sup>-1</sup> )	Depth (m)	U/Ca (μmol mol <sup>-1</sup> )	pH	CO <sub>3</sub> <sup>2-</sup> (μmol kg <sup>-1</sup> )	Ω <sub>arag</sub>
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 (PM – Propeller Mound, GM – Galway Mound), WC – Whittard Canyon, GC – Guilvinec Canyon, GoC – Gulf of Cadiz, UB – Urania Bank, SML – Santa Maria di Leuca. Additional data of the carbonate system are provided in Flögel et al. (2014).

(290–881 m) and pH values (7.92–8.3, Flögel et al., 2014). Overall, the coral U/Ca ratios obtained from the theca wall vary from 1.13 to 1.97 μmol mol<sup>-1</sup>. 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). We also plot the residuals of the U/Ca–pH relationship of the individual samples against the corresponding temperature, salinity and carbonate ion concentration, but the resulting relationships appear to be negligible with  $r^2 \leq 0.3$ .

The data clearly reveal that U/Ca ratios measured away from the COC are significantly correlated with seawater pH. For example, coral sites with the most contrasting seawater temperatures (Stjernsund (6 °C) and Santa Maria di Leuca (14 °C)) have remarkably similar U/Ca ratios and seawater pH values of 8.30 and 8.25, respectively (Flögel et al., 2014). This dependency can be described by the following equation:

$$U/Ca = -1.72 \pm 0.32 \text{ pH} + 15.43 \pm 2.65$$

$$(p = 0.007, r^2 = 0.8, \text{ Fig. 4a}). \quad (1)$$

The intra-coral U/Ca ratios vary from 1.14 to 2.07 μmol mol<sup>-1</sup>. The highest values are observed within the theca wall and the lowest within the COC. The intra-coral U/Ca variability covers the total measurements range of the nine *L. pertusa* bulk samples. However, with respect to Eq. (1) this compositional variability within the coral skeleton would result in intra-coral pH values between 7.8 (theca wall) and  $8.3 \pm 0.15$  (COC, Fig. 5)

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

$$U/Ca = -1.82 \pm 0.32 \text{ pH} + 16.18 \pm 2.56$$

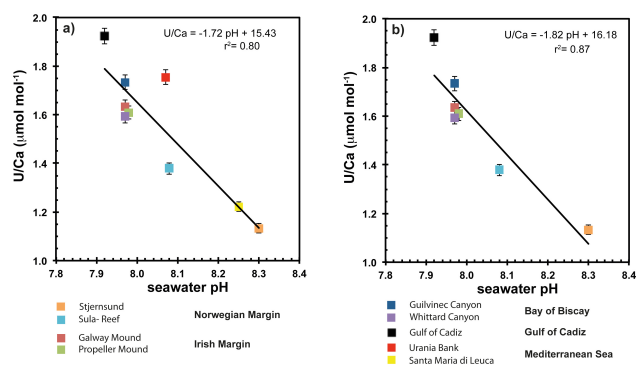
$$(p = 0.004, r^2 = 0.87, \text{ Fig. 4b}). \quad (2)$$

#### 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). This is in contrast to the described incorporation of uranium into skeletons of tropical corals, where U/Ca ratios show a clear relationship to seawater temperature (Min et al., 1995; Shen and Dunbar, 1995). In *L. pertusa* U/Ca ratios decrease by almost 50 % from 2.0 to 1.1 μmol mol<sup>-1</sup> 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<sub>2</sub><sup>2+</sup> (Djogic et al., 1986). Within a typical seawater pH range of > 8, most of the aqueous uranium exists in the form of UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup> (Reeder et al., 2000). With decreasing pH the aqueous species UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> becomes more dominant, and the proportion of bicarbonate UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> and monocarbonate uranyl complexes (UO<sub>2</sub>CO<sub>3</sub><sup>0</sup>) 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.

Even though the U/Ca–pH relationship covers a wide range of seawater pH, our 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 and 8.2. By limiting the calibration to pH values from 7.9 to 8.1, the correlation coefficient of the resulting relationship is low ( $r^2 = 0.37$ ). 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 0.3 μmol mol<sup>-1</sup> between a pH of 7.9 and 8 would result in pH uncertainties of about ±0.15. Such a scatter could result





**Fig. 4.** In situ seawater pH values are plotted against U/Ca ratios in *Lophelia pertusa* of (a) the entire samples set and (b) restricted to the North Atlantic samples. 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.

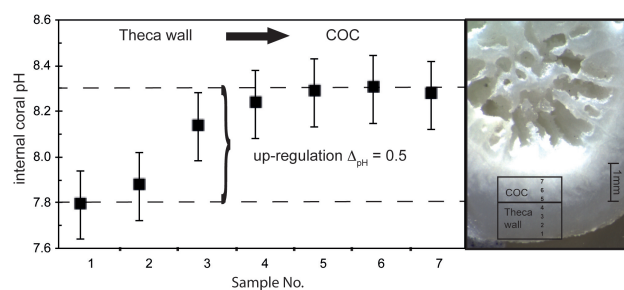
from the micro-sampling technique and intra-coral heterogeneity. Excluding samples from the Mediterranean Sea, the U/Ca–pH relationship has a higher  $r^2$  value of 0.87 (Fig. 4), but does not significantly ( $p = 0.004$ ) change in slope or intercept.

In general, seawater pH can be measured with an uncertainty of  $\pm 0.01$  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  $\pm 0.02 \mu\text{mol mol}^{-1}$  or 0.89% (2SD). Hence, both can be neglected compared to the error of the calibration slope (Eq. 1). However, considering the scatter in the U/Ca–pH calibration palaeo-pH values can be determined with an uncertainty of  $\pm 0.15$ .

Clearly more detailed CWC U/Ca and seawater pH measurements are required, especially from different ocean basins and cultivation experiments, but our unique field calibration data set suggests U/Ca in *L. pertusa* may complement  $\delta^{11}\text{B}$  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  $1.305 \mu\text{mol mol}^{-1}$  (Chen et al., 1986), the partition coefficient  $D_{\text{U}} = (\text{U/Ca})_{\text{skeleton}} / (\text{U/Ca})_{\text{seawater}}$  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.,



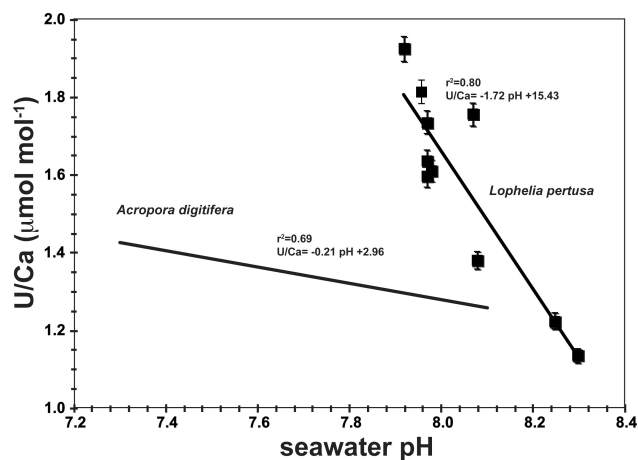
**Fig. 5.** Compositional variability of intra-coral pH variations calculated from U/Ca ratios in *Lophelia pertusa* (Little Galway Mound, M61/1-218) using Eq. (1). The centre of calcification (COC) reveals high intra-coral pH indicating coral pH up-regulation ( $\Delta\text{pH} = 0.5$ ). Error bars correspond to pH of  $\pm 0.15$ . Note: seawater carbonate chemistry data (pH 7.97) can be taken from the nearby Galway Mound (Table 1).

2011), which cannot be explained by a simple temperature dependency of uranium incorporation (Min et al., 1995; Shen and Dunbar, 1995; Wei et al., 2000). For example taking the equation (Min et al., 1995)  $T$  ( $^{\circ}\text{C}$ ) =  $48.0 - 21.5 \cdot \text{U/Ca}$  ( $\mu\text{mol mol}^{-1}$ ), a value of our data set of  $1.13 \mu\text{mol mol}^{-1}$ ,  $6.0^{\circ}\text{C}$  Stjernsund) would result in temperatures too warm for a CWC site ( $23.7^{\circ}\text{C}$ ). In tropical corals symbiotic algae consume  $\text{CO}_2$  during photosynthesis and increase the pH of the ambient seawater at the coral surface. This symbiotic pH shift causes a dominance of the  $\text{UO}_2(\text{CO}_3)_3^{4-}$  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 (e.g. Anagnostou et al., 2012; McCulloch et al., 2012; Trotter et al., 2011). However, the  $\Delta\text{pH}$  ( $\Delta\text{pH} = \text{pH}_{\text{coral}} - \text{pH}_{\text{seawater}}$ ) for scleractinian azooxanthellate CWCs appears to be higher (McCulloch et al., 2012). In particular, at the same seawater pH, CWCs show  $\Delta\text{pH}$  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 leads to the conclusion that  $\text{CO}_2$  consumption by symbiotic algae affects the internal pH and may suggest that tropical corals have to up-regulate their internal pH less 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  $\delta^{11}\text{B}$  in *Globigerina bulloides* (no symbionts) and *Orbulina universa* (with symbionts; Hönisch et al., 2003).

#### 4.2 Compositional variability of U/Ca ratios in *Lophelia pertusa*

Some geochemical models of coral calcification suggest aragonite is precipitated from modified seawater within the ECF (e.g. Adkins et al., 2003; McConnaughey, 1989). The carbonate ion concentration within the ECF is actively elevated above ambient seawater concentrations, facilitating crystal nucleation and coral growth (e.g. Adkins et al., 2003; Al-Horani et al., 2003; Allison and Finch, 2010; Blamart et al., 2007; Holcomb et al., 2009; Rollion-Bard et al., 2003, 2011b). 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). Speculating that pH is the only parameter controlling the internal coral U/Ca, we have applied our pH–U/Ca calibration. The observed compositional variability of U/Ca ratios within one single *Lophelia* polyp reveals that in the COC the  $\Delta_{\text{pH}}$  is  $>0.5 \pm 0.15$  compared to the rest of the skeleton (Fig. 5). This is in contrast to earlier findings of Blamart et al. (2007) and Rollion-Bard et al. (2011a, b). They showed that internal coral pH variations inferred from boron isotopes are implausible to be explained by environmental parameters and/or biomineralization and hence questioned the accuracy of which B isotopic composition can be determined. Nevertheless, COCs reveal lower  $\delta^{11}\text{B}$  values compared to the fibres indicating that the internal corals pH values are lower in the COC compared to the rest of skeleton (Blamart et al., 2007; Rollion-Bard et al., 2011a, b). If boron isotopes and U/Ca ratios are proxies both dominantly controlled by pH, then they should reveal similar patterns. One of the major assumptions for the applications of boron isotopes systematics as a pH proxy is that only borate ions,  $\text{B}(\text{OH})_4^-$ , are incorporated into the carbonate (e.g. Pagani et al., 2005). However, results of Rollion-Bard et al. (2011a, b) show that  $\text{B}(\text{OH})_3$  is also incorporated into the coral carbonate depending on the coral microstructure. This complicates the use of  $\delta^{11}\text{B}$  as a pH proxy. Subsequently, recent studies only measured  $\delta^{11}\text{B}$  in bulk samples or apart from the COC to minimize potential complications (Anagnostou et al., 2012; McCulloch et al., 2012).

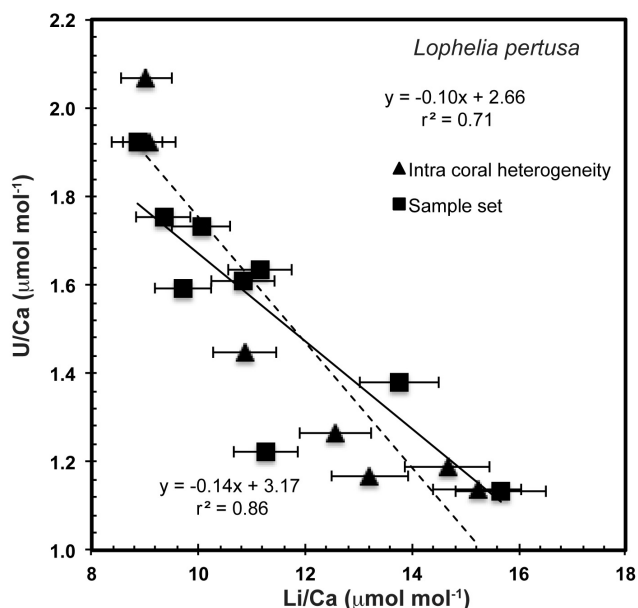
Uranium to calcium ratios are probably not solely controlled by the uranium speciation of seawater. Also growth rates, adsorption and desorption as well as ligand exchange reaction may affect the incorporation of uranium into the coral skeleton. Besides the uranium speciation, the effect of growth rates on coral U/Ca ratios has been investigated and discussed more thoroughly (e.g. Anagnostou et al., 2011; Inoue et al., 2011; Min et al., 1995; Sinclair et al., 2006). The latter study suggested that two different aragonitic end-members may cause the different element composition. In a juvenile stage *Lophelia* rapidly builds a new calyx, which mainly consists of COC and thickens afterwards significantly at a slower rate (e.g. Freiwald et al., 2004; Gass and Roberts,



**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).

2010). This is supported by the fact that the COC contains smaller granular crystal, which is indicative of rapid growth (Cohen et al., 2001). Several studies demonstrated that higher calcification rates might be triggered by an increased carbonate ion concentration and/or higher pH (e.g. Maier et al., 2009; Form and Riebesell, 2012; Marubini et al., 2008), which in turn may explain the obtained U/Ca pattern.

Furthermore, 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 biomineralization (Allison et al., 2010; Brahmi et al., 2012; Case et al., 2010; Gagnon et al., 2007; Hathorne et al., 2013b; Raddatz et al., 2013; Rollion-Bard et al., 2009; Gagnon et al., 2012). The same transect through the *L. pertusa* (Little Galway Mound, M61/1-218) skeleton reveals higher Mg/Ca and Li/Ca ratios in the COC region (Raddatz et al., 2013) associated with lower U/Ca content (Fig. 7). Previous studies that analysed Mg/Ca ratios in *L. pertusa* show comparable absolute values in the theca wall as well as in the COC (compare Cohen et al., 2006; Sinclair et al., 2006). These studies could clearly identify the COC by scanning electron microscope pictures. In particular, the study of Raddatz et al. (2013) shows intra-coral Mg/Ca ratios from min. 2.5 (theca wall) to max.  $3.9 \text{ mmol mol}^{-1}$



**Fig. 7.** Intra-coral and sample set U/Ca ratios plotted against Li/Ca from Raddatz et al. (2013). Note: both elemental ratios were measured on the same samples. Error bars correspond to 0.89 % (2SD) for U/Ca ratios and 5.4 % (2SD) for the Li/Ca ratios (Raddatz et al., 2013) Both relationships display a significant inverse correlation with  $r^2 = 0.71$  for the entire sample set and  $r^2 = 0.86$  for the mid-plan section.

(COC) similar to 2.6 to 4.2 mmol mol<sup>-1</sup> (Cohen et al., 2006) and 2.0 to 3.4 mmol mol<sup>-1</sup> (Sinclair et al., 2006; excluding the interior values as this part was not measured by Raddatz et al., 2013). However, 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; Raddatz et al., 2013; Sinclair et al., 2006). 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 data set reveals that 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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